Multiscale Modeling of Multiphase Flow in Porous Media Using the Thermodynamically Constrained Averaging Theory Approach

Amber Bess Sallerson Jackson

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Approved by:

Advisor: Cass T. Miller

Reader: David Adalsteinsson

Reader: M. Gregory Forest

Reader: William G. Gray

Reader: Laura A. Miller

Reader: Peter J. Mucha

ABSTRACT

AMBER JACKSON: Multiscale Modeling of Multiphase Flow in Porous Media Using
the Thermodynamically Constrained Averaging Theory Approach
(Under the direction of Cass T. Miller)

Traditional approaches to multiscale modeling of multiphase flow and transport are
riddled with deficiencies and inconsistencies across scales. The thermodynamically con-
strained averaging theory (TCAT) approach for modeling flow and transport phenomena
in multiscale porous medium systems addresses many of the shortcomings of traditional
models. The TCAT approach is used here, in conjunction with primary restrictions to the
system of interest, to formulate two distinct hierarchies of models: macroscale two-fluid-
phase flow of continuous fluids and two-fluid-phase flow and transport in a transition
region between a multiphase porous medium system and a free flow system. Applica-
tion of the TCAT approach produces a constrained entropy inequality for each system
and secondary restrictions and approximations allow for simplified entropy inequalities
to be determined in each case. The simplified entropy inequality is formulated relying
upon approximations of terms involving geometric variables and recently derived evo-
lution equations for specific entity measures that include interfacial areas and common
curve lengths. The general model formulation and entropy inequality are then used to
close a series of successively less complex models. The formulated models are compared
to existing models when available. The advantages of the models produced using the
TCAT approach are highlighted and the remaining open issues are discussed.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AEI   augmented entropy inequality

CEI   constrained entropy inequality

CIT   classical irreversible thermodynamics

EI   entropy inequality

EOS   equations of state

NAPL   non-aqueous phase liquid

NWP   non-wetting phase

REV   representative elementary volume

RHS   right-hand side

SEI   simplified entropy inequality

TCAT   thermodynamically constrained averaging theory

Roman Symbols

$\hat{A}$ constitutive coefficient for interface velocity

$\hat{B}$ constitutive coefficient for common curve velocity

b entropy source density

b_T total entropy source density

$\mathbf{C}$ Greens' deformation tensor

$\hat{c}^s$ solid phase compressibility parameter

$\hat{c}^\iota$ surface wetting parameter for ι a common curve

$\hat{\mathbf{D}}$ second-rank dispersion tensor

$\mathbf{d}$	rate of strain tensor
$\mathbf{d}^{\backslash}$	rate of strain tensor restricted to the transition region, $\mathbf{d}^{\backslash} = \frac{1}{2}\left[\nabla^{\backslash}\mathbf{v} + \left(\nabla^{\backslash}\mathbf{v}\right)^{\mathrm{T}}\right]$
d	transition region thickness
E	internal energy density
E_T	total energy density
$\mathcal{E}$	the set of entities in the model
$\mathcal{E}_{\mathrm{C}}$	the set of common curve entities
$\mathcal{E}_{\mathrm{c}}$	connected set of entities
$\mathcal{E}_{\mathrm{I}}$	the set of interface entities
$\mathcal{E}_{\mathrm{P}}$	the set of phase entities
$\mathcal{E}$	conservation of energy equation
$\mathbf{e}$	unit normal vector directed outward from the boundary of the REV
$e_{i\iota}$	microscale intra-entity internal energy transfer rate from all other species in entity ι to the i species per unit measure of the ι entity
$e_T^{i\iota}$	total macroscale energy transfered intra-entity from all other species in entity ι to the i species per unit measure of the ι entity
$\mathbf{f}$	general vector function
$\mathbf{f}_\iota{}'$	microscale vector tangent to the ι interface
$\mathbf{f}_\iota{}''$	microscale vector tangent to the ι common curve
f	general microscale property
$\mathbf{G}$	Geometric tensor
$\mathbf{g}$	acceleration vector due to an external force, such as gravity
$\mathbf{g}_T$	total body force
h	heat source density

h_T	total heat source density
$\mathbf{I}$	identity tensor
$\mathbf{I'}$	microscale surface identity tensor, $\mathbf{I'} = \mathbf{I} - \mathbf{n}_\alpha \mathbf{n}_\alpha$
$\mathbf{I}^\backprime$	macroscale surface identity tensor, $\mathbf{I}^\backprime = \mathbf{I} - \mathbf{NN}$
$\mathfrak{I}$	index set of entities
$\mathfrak{I}_C$	index set of common curves
$\mathfrak{I}_c$	index set of connected entities
$\mathfrak{I}_f$	index set of fluid-phase entities
$\mathfrak{I}_I$	index set of interfaces
$\mathfrak{I}_P$	index set of phase entities
$\mathfrak{I}_{Pt}$	index set of common points
$\mathfrak{I}_s$	index set of species
J_ι	microscale surface curvature defined as the surface divergence of the outward normal from entity ι
J_ι^κ	macroscale surface curvature defined as the average over the surface divergence of the outward normal from the ι entity
$J_\iota^{\overline{\overline{\kappa}}}$	macroscale surface curvature defined as the average over the surface divergence of the outward normal from the ι entity holding the interfacial tension constant
j_s	solid-phase Jacobian
$\hat{\mathbf{K}}^\iota$	hydraulic conductivity tensor
$\hat{\mathbf{K}}_q^\iota$	second-rank heat conduction tensor
$K_E^{\overline{\overline{i\iota}}}$	macroscale kinetic energy per unit mass of species i in entity ι due to microscale velocity fluctuations
$K_E^{\overline{\overline{\iota}}}$	macroscale kinetic energy per unit mass of entity ι due to microscale velocity fluctuations
$\hat{K}_M$	mass transfer coefficient

$\hat{K}^{\kappa}_{\iota,Q}$	inter-entity heat transfer parameter
$\hat{K}^{\kappa}_{\iota,W}$	coefficient for work of expansion of entity ι
$\hat{\mathbf{k}}$	second-rank permeability tensor
$\hat{k}^{\iota}_1$	generation rate coefficient for fluid-fluid interfacial area of interface ι
$\hat{k}^{\iota}$	function of system variables for fluid-fluid interface ι including surface curvature, interfacial tension, pressure, and $\hat{k}^{\iota}_1$
$\hat{k}^{\iota s}$	wetting rate parameter, $\iota \in \mathcal{I}_{\mathrm{f}}$
$\hat{k}^{\iota}$	generation rate coefficient common curve ι
$\hat{k}_{i\iota,M}$	mass transfer coefficient at the REV boundary
$\hat{k}_{\iota,q}$	heat transfer parameter at the REV boundary
$\mathbf{l}_{\iota}$	unit vector tangent to the ι common curve
$\hat{l}$	no-negative heat transfer coefficient for transfer normal to the REV boundary
M	general constant
$\mathcal{M}$	conservation of mass equation
$\overset{\kappa \to \iota}{M}$	transfer of mass from the κ to the ι entity
$\overset{i\kappa \to i\iota}{M}$	transfer of mass of species i in the κ entity to the i species in the ι entity
$\overset{\kappa \to \iota}{M_E}$	transfer of energy from the κ to the ι entity resulting from mass transfer
$\overset{i\kappa \to i\iota}{M_E}$	transfer of energy from the κ entity to the ι entity due to inter-entity mass transfer
$\overset{i\kappa \to i\iota}{M_{E_i}}$	transfer of energy from the κ entity to the ι entity due to inter-entity mass transfer of species i
$\overset{\kappa \to \iota}{\mathbf{M}_v}$	exchange of momentum from the κ to the ι entity resulting from mass transfer
$\overset{i\kappa \to i\iota}{\mathbf{M}_v}$	transfer of momentum from the κ entity to the ι entity due to inter-entity mass transfer

$\underset{\mathbf{M}_{v_i}}{^{i\kappa\to i\iota}}$ transfer of momentum from the κ entity to the ι entity due to inter-entity mass transfer of species i

$\underset{M_\eta}{^{i\kappa\to i\iota}}$ transfer of entropy from the κ entity to the ι entity due to inter-entity mass transfer

$\underset{M_{\eta_i}}{^{i\kappa\to i\iota}}$ transfer of entropy from the κ entity to the ι entity due to inter-entity mass transfer of species i

$\mathbf{N}$ unit vector tangent to the axis corresponding to the megascopic dimension of the REV

$\mathbf{n}_\alpha$ unit outward normal from the α phase and normal to Ω_ι where $\alpha \in \mathcal{I}_{c\iota}$.

$\mathbf{n}_\iota$ unit outward normal vector from entity ι on its boundary when $\iota \in \mathcal{I}_P$, tangent vector to the surface and outward normal from the bounding common curve when $\iota \in \mathcal{I}_I$, and tangent to the common curve at ends of common curve and pointing outward from the curve such that $\mathbf{n}_\iota \cdot \mathbf{l}_\iota = \pm 1$ when $\iota \in \mathcal{I}_C$

$\mathcal{P}$ conservation of momentum equation

$\mathcal{P}_i$ general microscale property

$\mathbf{p}_{i\iota}$ microscale intra-entity momentum transfer rate from all other species in entity ι to the i species per unit measure of the entity

$\mathbf{p}^{\overline{\overline{i\iota}}}$ macroscale intra-entity momentum transfer rate from all other species in entity ι to the i species per unit measure of the entity

p fluid pressure

p^c capillary pressure

$\underset{Q}{^{\kappa\to\iota}}$ transfer of energy from the κ to the ι entity resulting from heat transfer and deviation from mean processes

$\underset{Q}{^{j\kappa\to i\iota}}$ transfer of energy from species in the κ entity to the i species in the ι entity resulting from heat transfer and deviation from mean processes

$\mathbf{q}$ non-advective heat flux density vector

$\hat{\mathbf{R}}$ second-rank resistance tenor

$\hat{\mathbf{r}}$ second-rank resistance tensor for viscous stress normal to the REV boundary

$r_{i\iota}$	microscale intra-entity reaction rate resulting in the production of species i in entity ι from all other species per unit measure of the entity
$r^{i\iota}$	macroscale intra-entity reaction rate resulting in the production of species i in entity ι from all other species per unit measure of the entity
$\mathcal{S}$	entropy balance equation
s	saturation
$\mathcal{T}$	CIT-based thermodynamic equation for material derivative of internal energy
$\overset{\kappa\to\iota}{\mathbf{T}}$	transfer of momentum from the κ to the ι entity resulting from interfacial stress
$\overset{j\kappa\to i\iota}{\mathbf{T}}$	transfer of momentum from species in the κ entity to the i species in the ι entity due to stress and deviation from mean processes
$\overset{\kappa\to\iota}{T_v}$	transfer of energy from the κ to the ι entity resulting from interfacial stress
$\overset{j\kappa\to i\iota}{T_{v_i}}$	transfer of energy from species in the κ entity to the i species in the ι entity due to work and deviation from mean processes
$\mathbf{t}$	stress tensor
t	time
$\mathbf{u}$	dispersion velocity
$\mathbf{V}$	constant reference velocity
$\overline{V}$	partial mass volume
$\mathbf{v}$	velocity
$\mathbf{v}_{\text{ext}}$	velocity vector of the boundary of the REV
$\mathbf{v}^{\overline{\iota},\overline{\kappa}}$	macroscale mass-averaged velocity of the ι entity relative to the mass-averaged velocity of the κ entity, $\mathbf{v}^{\overline{\iota},\overline{\kappa}} = \mathbf{v}^{\overline{\iota}} - \mathbf{v}^{\overline{\kappa}}$
W	weighting function in averaging operator
$\mathbf{w}$	average velocity normal to entity
$\mathbf{X}$	material coordinate position vector

$\mathbf{x}$	position vector in the solid phase
x	mole fraction of a species within an entity
$\underset{j\kappa\to i\iota}{z_Q}$	fraction of heat energy transferred from species in the κ entity to the ι entity that impacts the i species in the ι entity
$\underset{j\kappa\to i\iota}{z_T}$	fraction of stress transferred from species in the κ entity to the ι entity that impacts the i species in the ι entity
$\underset{j\kappa\to i\iota}{z_\Phi}$	fraction of entropy transferred from species in the κ entity to the ι entity that impacts the i species in the ι entity

Greek Symbols

$\hat{\alpha}^{\mathrm{b}}$	bulk compressibility or bulk modulus
$\hat{\beta}^{\iota}$	compressibility of the ι phase
Γ	boundary of domain of interest
Γ_m	boundary of the REV in the macroscale directions
Γ_M	boundary of the REV in the megascale direction
γ	interfacial tension for interfaces and curvilinear tension for common curves
δ_C	Dirac delta function
ϵ	porosity
ϵ^{ι}	specific entity measure of the ι entity
η	entropy density
θ	temperature
κ	intrinsic permeability
$\kappa^{r\iota}$	relative permeability
κ_G	geodesic curvature

κ_N	normal curvature
Λ	entropy production density
$\boldsymbol{\lambda}$	vector of Lagrange multipliers
λ	Lagrange multiplier
μ	chemical potential
ρ	mass density
$\boldsymbol{\sigma}$	solid-phase Lagrangian stress tensor
$\boldsymbol{\tau}$	viscous stress tensor
$\hat{\tau}_A$	coefficient in linearized force-flux relation for capillary pressure dynamics
$\overset{\kappa\to\iota}{\Phi}$	transfer of entropy from the κ entity to the ι entity
$\overset{j\kappa\to i\iota}{\Phi}$	transfer of entropy from species j in the κ entity to species i in the ι entity
$\boldsymbol{\varphi}$	non-advective entropy flux vector
φ	contact angle
χ_ι	indicator function for entity ι
χ_ι^{ss}	fraction of the solid surface in contact with the ι entity
ψ	body force potential
Ω	spatial domain
$\bar{\Omega}$	closure of spatial domain
ω	mass fraction of a species within an entity

Subscripts and Superscripts

$\backslash$	a superscript indicating the operator or property is restricted to the surface
α	entity qualifier
β	entity qualifier

bot	qualifier of the bottom of the transition region
C	common curve set qualifier
$\mathcal{E}$	energy equation qualifier
eq	subscript indicating the property is at equilibrium
γ	entity qualifier
g	gas-phase qualifier
gs	qualifier for interface formed by the intersection of the gas and solid phases
I	interface set qualifier
ι	entity qualifier
i	interior of domain qualifier
i	species qualifier
j	general index
κ	entity qualifier
k	general index
$\mathcal{M}$	mass equation qualifier
M	index that indicates megascale direction
m	index that indicates macroscale direction
n	non-wetting-phase qualifier
ns	qualifier for interface formed by the intersection of the non-wetting and solid phases
$\mathcal{P}$	momentum equation qualifier
P	phase set qualifier
r	residual portion of specified equation
s	solid-phase qualifier

ss solid surface qualifier

$\mathcal{T}$ thermodynamic equation qualifier

top qualifier of the top of the transition region

w wetting-phase qualifier

wg qualifier for interface formed by the intersection of wetting and non-wetting gas phases

wn qualifier for interface formed by the intersection of wetting and non-wetting phases

wgs qualifier for common curve formed by the intersection of the wetting, non-wetting gas, and solid phases

wns qualifier for common curve formed by the intersection of the wetting, non-wetting, and solid phases

ws qualifier for interface formed by the intersection of wetting and solid phases

Mathematical Operator Symbols

$\langle \, \rangle$ averaging operator

$\mathrm{D}^{\bar{\iota}}/\mathrm{D}t$ material derivative of entity ι

$\mathrm{D}^{\prime\bar{\iota}}/\mathrm{D}t$ material derivative of a point moving along interface ι

$\mathrm{D}^{\prime\prime\bar{\iota}}/\mathrm{D}t$ material derivative of a point moving along common curve ι

$\mathrm{D}^{\overline{i\iota}}/\mathrm{D}t$ material derivative of species i in entity ι

$\mathrm{D}^{\prime\overline{i\iota}}/\mathrm{D}t$ material derivative of species i moving along interface ι

$\mathrm{D}^{\prime\prime\overline{i\iota}}/\mathrm{D}t$ material derivative of species i moving along common curve ι

$\partial^{\backslash}/\partial t$ partial time derivative restricted to a point on the moving macroscale interface

$\partial^{\prime}/\partial t$ partial time derivative restricted to a point on the moving microscale interface

$\partial^{\prime\prime}/\partial t$ partial time derivative restricted to a point on the moving microscale common curve

$\nabla^\backslash$ macroscale surficial del operator

∇' microscale surficial del operator

∇'' microscale curvilinear del operator

$\nabla_X \mathbf{x}$ derivative of a microscale location on the solid phase with respect to its initial location

CHAPTER 1

Introduction

1.1. Porous Medium Systems

A porous medium is a solid material permeated by an interconnected three-dimensional network of capillary channels of nonuniform sizes and shapes, commonly referred to as pore or, less accurately, void spaces [20]. The pore structure in a porous medium can be characterized by its morphology and topology. The morphology of a porous medium is the characterization of the distribution of sizes of the pore space; the way in which these pore spaces are then connected is the topology of the pore space [65]. Porous medium systems occur routinely in nature and industry with a wide range of applications including oil recovery, carbon sequestration, seismic phenomena, and water protection and restoration [37, 53, 72, 122, 145].

Shallow subsurface systems are an application of flow through a porous medium system that is of critical importance for a number of reasons including: reliance on groundwater as a source of supply, the routine practice of subsurface waste disposal, and protection and restoration of water quality [135]. In fact, the domestic water use of nearly half the population of the United States relies upon groundwater [71, 167]; however, widespread sources of soil and groundwater contamination by hazardous chemicals is threatening this valuable resource. Depending on the phenomena of interest, a subsurface porous medium system can be described by single-phase flow, single-phase flow and

transport, multiphase flow, or multiphase flow and transport models. The issues involved in modeling subsurface porous media can vary greatly, and this variance as well as interest in the many other application areas, provides a clear motivation for general frameworks for formulating mathematical models.

For our purposes, single fluid phase flow, which we will refer to as single-phase flow, refers to the characterization of a single fluid phase moving through a porous media. Examples of systems for which single-phase flow is applicable would be flow of water through rock fractures with applications to underground excavations [109] and the flow of groundwater in shallow subsurface systems with applications to groundwater supply and management [135].

Single-phase flow and transport systems are those in which there is interest in not only the flow of the fluid through the porous medium, but also the behavior of the individual components present within the fluid or solid phases. They can be used to describe such phenomena as the sorption of chemicals from a fluid onto the solid phase [17, 119, 139], desorption of components through mass transfer from the solid phase into a fluid phase [33, 41, 49, 94], and reaction of chemical components leading to such processes as ion exchange or biodegradation [29, 30]. An example of single-phase flow and transport can arise in subsurface systems when contaminants enter a groundwater supply. This can occur through a variety of sources: improperly stored or transported hazardous wastes, leaking landfills, fertilizer, road salt runoff, and dissolution of contaminants from near surface sources [36]. In these cases, the individual components in the fluid may play an important role in the system dynamics, making it necessary to determine not only the overall flow of the fluid through the porous medium, but also the behavior of the individual chemical components.

Multiphase flow in porous medium systems involves systems in which the pore space is filled with at least two distinct immiscible fluid phases that can be in the form of liquids or gases. Multiphase systems require that the dynamics of not only solid-fluid interactions, but also fluid-fluid interactions be resolved. Examples of applications requiring an understanding of multiphase flow in porous media include oil recovery [37] and flow in the unsaturated zone above the water table [138].

Multiphase flow and transport systems are those in which there is interest in not only the flow of the fluids through the porous medium, but also the behavior of the individual components present within the phases. Such systems include all of the issues involved with species transport such as sorption, desorption, ion exchange, and biodegradation, but with the added complication of multiple fluid phases from which the transport may arise. Examples of importance in subsurface porous medium are the dissolution and movement of chemical contaminants in a groundwater supply [34, 36, 57, 118].

The last two decades have seen tremendous efforts devoted to investigating the complex processes governing each of these categories and in pursuing effective remediation strategies for applications involving contamination of the subsurface [36, 108, 153]. To date standard remediation technologies still remain expensive and unpredictable in their success when applied at the field-scale [105, 135, 151, 174]; making evident the importance of finding more effective and cost efficient methods for characterizing the complex processes governing porous medium systems. Mathematical models play an important role in this pursuit.

1.2. Modeling Multiphase Systems

Understanding and predicting the processes involved in multiphase flow in porous media requires three different components; experimentation, theory, and simulation. For naturally occurring subsurface systems, information can be obtained by extensive field-scale characterization, but this method is both expensive and time-consuming. As such, mathematically based numerical modeling that combines both theory and simulation provides an indispensable tool, reducing the amount of field-scale investigations and often making those that must be performed, for purposes of parameter estimation, more cost efficient [134].

The purpose of formulating models for multiphase flow in shallow subsurface systems include (1) to better understand and predict the movement of fluids through a porous media, (2) to develop strategies for remediation of contaminated groundwater sources, and (3) to use the information gained to optimize strategies for sustainability and management of groundwater resources [135].

There exist standard approaches for formulating models to describe multiphase flow in porous media. The models are typically associated with the scale being considered, with the most common models being formulated at the microscale and macroscale.

The microscale, also referred to as the pore scale, is the scale at which there is complete resolution of the pore morphology and topology. In this case, the length scale of the fluid system is much larger than that of a single molecule or its mean free path, and hence fluids are considered continuous at this scale [4]. The concept of a point is essential to the treatment of fluids as a continuum. A microscale point is considered to be an ensemble of many molecules contained in a small volume. A porous medium

system at the microscale is said to consist of points over which the individual phases can be assigned definite dynamic and kinematic properties.

The macroscale, which is often referred to as the lab scale or porous medium continuum scale, is the scale at which instruments and techniques for experimentally determining characteristics of porous media exist. At the macroscale a point is considered to encompass tens to hundreds of pore diameters [75] and the different phases in the porous medium system are described as overlapping continua, each occupying a fraction of space [82].

Regardless of scale, there are two main components for models of multiphase flow in porous media, conservation equations and closure relations [134]. Closure relations are typically a combination of equations of state (EOS) and constitutive relations that can be used in conjunction with the conservation equations to form a closed system of equations, i.e. an equivalent number of equations and unknowns.

1.2.1. Microscale Modeling. With detailed information available at the microscale, pore-scale modeling allows for the study of essential phenomena in multiphase fluid flow [28, 148]. Pore-scale modeling presents an important tool for developing constitutive relations deemed difficult or even impossible to obtain by lab experiments and it provides a significant means to investigating the role of relatively new variables such as interfacial area and common curve length for use in system closure [58, 103, 181].

Pore-scale modeling through simulation allows for a greater variety of quantitative data to be collected; it affords more versatility in choosing parameters; and provides an easier means for design of numerical experiments. Over the last decade, the availability of relatively inexpensive high-performance computers coupled with advances in

micro-modeling experiments and high-resolution imaging has caused a surge of interest in pore-scale modeling. This surge continues to help advance not only computational aspects of pore-scale modeling, but also the theoretical basis upon which the numerical models are built. Still, applications are limited to relatively small domains and simplified problems [148]. With ever increasing computational power and continued interest in multiphase flow, it is foreseeable that pore-scale simulations will soon be capable of simulating microscopic flows and parameters that include larger scale heterogeneities.

1.2.2. Macroscale Modeling. The majority of porous medium flow simulators are based on continuum theory. Typical macroscale models consist of the governing conservation equations, which are closed using equations of state and constitutive relations. Performing experiments to derive constitutive relationships can be difficult and expensive; however, constitutive relations play a crucial role in the accuracy of such subsurface models. Traditional approaches to formulating models for multiphase flow in porous media exist and have been used widely [43, 121, 123, 159]. Despite the routine use of the standard approaches, there are aspects of the resulting models that limit both their effectiveness and predictability. Even in cases where the numerical solution is considered precise and the model parameters are specified, errors may still occur; the two fundamanetal reasons for which are that the representation of the physics is inadequate or that the parameters that appear are not clearly defined and not easily measurable [84].

1.3. Continuum Modeling

Over the past two decades a wide array of research to build improved models for multiphase flow in porous media has been undertaken [38, 53, 59, 72, 75, 80, 96, 127, 144, 158, 180]. The traditional approach to formulating models for multiphase flow in porous medium systems, the limitations of traditional approaches, the advances that have been made in an effort to produce more theoretically reasonable models, and the desired properties of new approaches are discussed in turn.

1.3.1. Traditional Approach. While macroscale continuum modeling of multiphase flow in porous medium systems has recently received a lot of attention in the research community (e.g. [13, 37, 84, 128, 135, 137]), traditional approaches are still commonly implemented by researchers (e.g. [43, 66, 156, 159]). A traditional model for multiphase flow at the macroscale typically involves

(i) applying simplifying assumptions

(ii) specifying the minimum set of mass conservation equations necessary to describe the behavior of interest;

(iii) using a multiphase form of Darcy's law to approximate conservation of momentum equations;

(iv) defining equations of state; and

(v) specifying constitutive relations among fluid pressures, saturations, and permeabilities.

Several simplifying assumptions are commonly made including asserting that the solid phase is inert, that the solid can be modeled without including its conservation equations explicitly in the formulation, and that the system is isothermal.

1.3.1.1. *Conservation Equations.* A general conservation of mass equation can be written as:

$$\frac{\partial(\epsilon^{\iota}\rho^{\iota})}{\partial t} + \nabla \cdot (\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\iota}) = 0 \tag{1.1}$$

where ι is a phase qualifier, ϵ^{ι} is the volume fraction of the pore space filled by phase ι; ρ^{ι} is the density of the phase; and $\mathbf{v}^{\iota}$ is the velocity of the phase. The volume fraction, ϵ^{ι}, can be written as ϵs^{ι} where ϵ is the porosity of the porous medium system and s^{ι} is the saturation of the ι phase. Given this relationship, a continuity statement is used

$$\sum_{\iota} s^{\iota} = 1, \tag{1.2}$$

which states that the pore space is jointly filled by the fluid phases present in the system.

Formal momentum balance equations are not traditionally included in the standard approach for continuum formulations of multiphase flow. Instead, it is traditional in the environmental literature to substitute a multiphase extension of Darcy's law. Darcy's law, which actually represents single-fluid-phase flow for a control volume in cases of low Reynolds number, is extended in order to define the Darcy velocity, $\epsilon^{\iota}\mathbf{v}^{\iota}$. This extension assumes that the pressure gradient of the individual phases is a driving force for that specific phase [62, 177]. This extension can be written for an isotropic porous medium

system as:

$$(1.3) \qquad \epsilon^\iota \mathbf{v}^\iota = \frac{-\kappa \kappa^{r\iota}}{\nu^\iota} \left(\nabla p^\iota - \rho^\iota \mathbf{g} \right)$$

where κ is the intrinsic permeability; $\kappa^{r\iota}$ is the relative permeability relation defining the reduction of κ due to the incomplete saturation of fluid phase ι; ν^ι is the dynamic viscosity of fluid ι; p^ι denotes the pressure in phase ι; and $\mathbf{g}$ is the gravitational acceleration. Substituting Eqn. 1.3 into Eqn. 1.1 yields:

$$(1.4) \qquad \frac{\partial (\epsilon \rho^\iota)}{\partial t} + \nabla \cdot \left[\rho^\iota \frac{\kappa \kappa^{r\iota}}{\nu^\iota} \left(\nabla p^\iota - \rho^\iota \mathbf{g} \right) \right] = 0$$

for each phase, ι, of interest in the multiphase porous medium system.

Since most multiphase environmental model formulations assume an isothermal system, they do not consider an energy balance equation, although there are some notable exceptions [68, 69, 86, 149].

1.3.1.2. *Closure Relations.* Closure of the set of balance equations requires a sufficient number of additional equations such that the number of unknowns and the number of equations are equal. This can be accomplished by stipulating EOS and constitutive relations. Typical EOS express the equilibrium relationships based on thermodynamic models that are empirical in origin [157]. For example, in standard formulations of multiphase flow in porous media in which conservation of energy is omitted by argument of an isothermal system and compositional effects are not being considered, an EOS

relating fluid pressure and density is posited as

$$(1.5) \qquad\qquad\qquad \rho^{\iota} = \rho^{\iota}\left(p^{\iota}\right)$$

A constitutive relation for linking the saturation of the phases and the capillary pressure, p^{c}, which is typically interpreted as the differences in pressure between the fluid phases, can be written as:

$$(1.6) \qquad\qquad\qquad p^{c} = p^{c}(s^{\iota})$$

and for relative permeabilities, which are commonly written as functions of phase saturation,

$$(1.7) \qquad\qquad\qquad \kappa^{r\iota} = \kappa^{r\iota}\left(s^{\iota}\right)$$

Constitutive relationships are approximate, often uncertain, and typically empirically based [134]. There are many specific forms that exist, many of which are hysteretic in nature and difficult to measure.

1.3.2. Deficiencies of Traditional Models. Deficiencies in traditional approaches for formulating macroscale models for multiphase flow in porous media are widely acknowledged [78, 79, 101, 102, 134], and efforts to develop a sound theoretical basis upon which new models can be constructed have been undertaken [77, 84, 93, 98, 116, 129, 164, 175, 178].

The traditional approach to modeling multiphase flow in porous media leads to multiple issues of concern. These issues include, but are not limited to, a lack of rigorous connection with the pore scale physics, inadequate definition of variables, implicit approximations concerning system behavior, as well as lack of a structured framework for model refinement, extension, and simplification [84].

The classical approach to modeling multiphase flow in porous media lacks a rigorous connection with pore-scale physics by proposing conservation equations and closure relations directly at the macroscale. When microscale physics is not a part of the macroscale formulation procedure, correspondence of physical descriptions between scales is not attained [84].

The lack of a rigorous connection between the microscale and the macroscale thus has two serious consequences. First, macroscale equations are written in terms of macroscale quantities, the definitions of which can be too vague or ill-defined for direct measurability. For example, at the microscale notions such as temperature and pressure are well understood; however, a rigorous connection of these quantities to the macroscale formulation is lacking [84]. As a result, issues may arise such as in the case of a varying microscale pressure within a macroscale region under conditions of no flow. In this situation the choice of a representative macroscale pressure to describe the thermodynamic state of that region is not obvious and it is unclear as to which property's gradient is balanced by the gravitational effects [83]. Second, processes observable and studied at the microscale that are known to influence system behavior are not incorporated into the model. An example of this situation is fluid wettability as measured by the contact angle, which is the angle formed between fluid-fluid interface and the solid phase at the pore scale. Wettability is well known to dramatically influence behavior of multiphase flow at the

macroscale, but does not appear in traditional models of flow at that scale [84]. In addition, microscopic thermodynamic notions are often used to discuss macroscopic systems in which they are no longer meaningful [134].

Standard modeling approaches include implicit approximations resulting from the use of closure relations. While such approaches may provide useful models in some cases, the implicit nature of the assumptions causes difficulty in assessing model errors and in proposing corrective actions [84]. An example of an implicit approximation for standard multiphase flow models is the use of a modified form of Darcy's law instead of a formal conservation of momentum equation. This approximation can potentially obscure important physical phenomena—such as viscous coupling between different fluids and the transient nature among relations involving fluid pressures and saturations—which are understood as important for some systems [14, 160].

1.3.3. Evolving Approaches. To advance macroscale models, the deficiencies of traditional models must be addressed. Clearly macroscale modeling is in fact a multi-scale problem based on the physics of multiphase flow. Many researchers have attempted to develop rigorous macroscale models that are consistent with smaller-scale representations [16, 21, 25, 55, 77, 80, 98, 99, 129, 136, 143, 178]. They use the notion of averaging or upscaling as a means to connect the microscale physics to a macroscale model [38, 145]. Formulating models in this way affords the ability to produce models that are consistent across scales, have well-defined macroscale variables that relate to properties at the microscale, and can include microscale phenomena.

Along the lines of including microscale phenomena comes advancements in the understanding of the pore-scale physics. The impact of pore-scale properties, such as interfacial areas, on larger scales is one such area that has received notable attention [46, 47, 53, 75, 80, 142, 152]. In particular, the role of interfaces as observed through viscous and capillary coupling has led the field toward including interfacial effects at the macroscale. An example of a mechanism employed to accomplish this, is the inclusion of interfaces as jump conditions or discontinuities between phases [13]. Another approach is to include balance equations for not only phases, but interfaces and common curves in the model formulation [80, 85, 110, 136, 137, 144].

Including the transient behavior associated with the approach to a capillary pressure equilibrium state is yet another evolving approach to advance macroscale models. It is commonly accepted that the relationship between capillary pressure and saturation demonstrates memory effects in the form of hysteresis; and capillary pressure-saturation relationships that include both hysteretic and dynamic effects are an active area of research [23, 96, 97, 163]. However, advances in pore-scale modeling suggest that the hysteretic behavior can in fact be reduced or eliminated by the inclusion of additional variables of dependence such as interfacial areas, common curve lengths, and interfacial curvatures [80, 103, 113].

1.3.4. Desired Approach Properties. The development of a complete and consistent theory for macroscale modeling of multiphase flow in porous media requires mathematical tools that allow the equations and thermodynamics to be formulated consistently and in such a way that the variables have physical, measurable meaning [84]. An acceptable approach must establish a clear connection between pore-scale physics and larger scale

behavior; obey the second law of thermodynamics [80]; and include only well-defined variables and measurable parameters. The approach should be consistent across scales and have a flexible framework for guiding the formulation of models for describing multiphase flow in porous media [84]. Ideally this framework should allow for model refinement, extension, and simplification.

Even with the desired approach properties in mind and recent advances to the field, such as those listed in §1.3.3, open issues remain [84, 110, 134, 135, 144]. The clear statement and understanding of the open issues is fundamental to resolving current difficiencies in model formulations.

1.4. Open Issues

The inherent heterogeneity in subsurface porous media together with the complexity involved in the physics of such systems [48, 56, 73], often over multiple scales [54], results in a significant challenge to the development of fundamental theories crucial to the design of approaches for modeling multiphase flow in porous medium systems.

1.4.1. Consistency Across Scales. A more satisfying approach than that taken by traditional models is based on formal averaging to produce mass, momentum, and energy conservation equations that are formulated about volumes, interfacial areas between each pair of phases, and common curves for all unique three-phase intersections [78, 102]. Supplementing these averaged equations with constitutive relations resulting from constraining an averaged entropy inequality, the second law of thermodynamics, and certain other equilibrium thermodynamic relations [50, 99] allows for all macroscale variables to

14

be defined in terms of microscale counterparts. Unfortunately, while helping to resolve many inconsistency issues, formal averaging approaches along these lines result in large systems of equations, with an even larger number of unknowns, which must be substantially simplified in order to be tractable with currently available computational resources [134]. In addition to creating a larger set of equations, formal averaging introduces considerable complexity to the system. However, formal averaging methods have been able to provide some enlightening information when applied to specific systems of interest [2, 85, 87, 110], and hold promise for providing improved understanding of other complex systems. Nonetheless, it is important to note formal averaging requires the existence of a representative elementary volume (REV), a region of porous medium large enough to include all phases and of a sufficient size that the values of averages that characterize a phase are independent of that size [84], yet most natural systems are stochastic in nature and the strict assumption of an REV and clearly separable length scales may not be met for many such systems (i.e. [155]).

1.4.2. General Constitutive Relation Formulation. The problem of formulating comprehensive constitutive theory has resulted in several approaches. Mapping microscale quantities to macroscale quantities such that a differential equation arises whose solution completes the closure problem [178] is an approach that has most often been applied for a rigid solid matrix. This approach has the drawback of not including interface dynamics and macroscale thermodynamics. An entropy inequality formulation with equations for interfaces was developed by Kalaydjian [115], however it omits common curves and makes significant assumptions. Mixture theory can be used for multiphase flow [8], but closure conditions are incomplete because interface effects are neglected.

Use of the entropy inequality in obtaining porous medium flow equations have been formulated to include interfaces [25, 27, 78] with the postulation of the thermodynamic dependence of internal energy improved by making the postulations in terms of extensive variables and the closure conditions clarified by stating the need for dynamics of geometric variables [75]. The closure conditions developed were based on approximations to averaging theorems and neglected to account for the average orientation of the interfaces within the averaging volume, limiting their applicability [93].

To overcome the shortcomings of the above approaches, consistency across scales as discussed in §1.4.1, is necessary as well as the inclusion of dynamics for interfaces and common curves. However, the result of including averaged balance equations for interfaces and common curves increases the discrepancy that already existed in traditional approaches between the number of equations and the number of unknown variables. These new variables must be approximated using additional constitutive relations and evolution equations. Closure relations consistent with the second law of thermodynamics [26, 78, 80, 99] present the most conceptually satisfying approach in that they can include interface and common curve dynamics. A particularly challenging part of this approach however is formulating the second law constraint at a scale consistent with the scale of the governing equations. While an averaged entropy inequality has been derived, statement of the functional dependence of macroscale entropy on macroscale properties in a manner consistent with microscale thermodynamics has only been accomplished in relatively few instances [85, 87, 110].

Closure of the conservation equations has two main elements, evolution equations for the geometric densities that arise, such as volume fractions and interfacial area densities, and proper formulation of the thermodynamics. The geometric densities are not

subject to conservation equations, rather they must be considered from a mathematical perspective, for which unique relations among the geometric densities do not exist [84]. Equations indicating how these densities evolve are desired, but are not generally available [133]. Currently, approximate relations are employed [75, 93], but finding better relations is an open issue in the field.

The other important element to closure, the proper formulation of the thermodynamics at the macroscale, is complicated as a result of dealing with dynamic systems. Classical thermodynamics relates to the study of systems at equilibrium, thus researchers are forced to deal with extensions of thermodynamics for systems which vary in space and time. Several theoretical approaches to the general field of thermodynamics exist and have been successfully applied at the microscale [114, 130]. However, a consistent macroscale representation requires averaging the thermodynamics from the microscale to the macroscale [84]. The choice of an optimal thermodynamic theory for use at the macroscale has yet to be determined, and comparisons of competing theories should be investigated for a range of models and systems.

1.4.3. pSk **Relations.** Pressure, saturation, and permeability constitutive relations, commonly referred to as pSk relations, are of central importance for modeling of multiphase systems. The modeling of these relations can be broken into several categories, including pressure-saturation (pS) relations, saturation-permeability (Sk) relations, and hysteresis models.

Frequently used pS relations, which describe capillarity, include the Brooks-Corey (BC) model [40], the van Genuchten (VG) model [173], and the Parker *et al.* model [150]. These models were experimentally determined and relate the capillary pressure to

the saturation; they are relations that depend on the porous media and fluid properties, and have parameters which vary according to the porous medium system of interest.

Similarly Sk empirical relations exist [52]. The two most commonly used are the Mualem [141] and Parker *et al.* [150] statistical models. While Sk relations were developed as a means to include the physical properties of the porous medium, measuring these relations for more than two fluid phases is of significant difficulty [134].

Hysteresis in pS and Sk relations arise due to pore-scale effects associated with contact angle hysteresis, because of non-wetting fluid entrapment during saturation path reversals [125], and because the effect of interfacial area is commonly neglected. Nonetheless, non-hysteretic pS and Sk relations are often used because they require far less data and computational resources[134]. pSk relations tend to be minimally calibrated, but even if they were measured extensively, several issues still require attention, namely the treatment of non-wetting phase entrapment, the effects of interfacial spreading, mixed wettability, and dynamics.

1.4.3.1. *Non-wetting phase entrapment.* Non-wetting phase (NWP) entrapment is an issue of central importance to multiphase environmental systems. When the non-wetting phase appears in the subsurface as a source of contaminant and becomes trapped in a residual form in a water wet system, the accurate modeling of its formation and mobilization become vital steps for realistic assessment, analysis, and remediation. A macroscopic NWP-entrapment model that captures the displacement history to correctly predict the initial-residual NWP saturation [117, 172] has been referred to as the residual-initial NWP relation and is used as a sub-model in hysteretic pSk relations. Understanding and predicting NWP entrapment as well as understanding and predicting the behavior

of the NWP once it is entrapped, i.e. appearing as a disconnected phase, are both areas of open research. Recent efforts have been made to study NWP entrapment [5, 19, 154, 179] and the importance of such characterizations is widely acknowledged.

1.4.3.2. *Interfacial spreading and mixed wettability.* Interfacial tensions must be balanced between gas-aqueous, non-aqueous phase liquids (NAPL)-aqueous, and gas-NAPL interfaces [3], which may lead to spreading of a NAPL on a gas-aqueous interface. It has been found that spreading can greatly influence both the advancement of imbibition fronts and lateral migration at the water table [9, 131]. The additional driving force resulting from the spreading of NAPLs remains an issue for further investigation. In addition, other interfacial phenomena such as solid phase wettability, which is important in mixed-wettability porous medium systems, are still not well characterized. These interfacial effects are believed to play a crucial role in formulating improved pSk constitutive relations and some work has been done to characterize these effects [35, 63, 106, 113, 174].

1.4.3.3. *Dynamics.* The mass and momentum balance equations are inherently dynamic however, they are often closed using constitutive equations, such as pSk relations that are empirical in nature and usually collected at pseudo-static equilibrium [134]. For these closure relations to actually be independent of dynamic effects, their relations must not be affected by the rate at which steady state is reached or by the number of intermediate points used to form the relation. Evidence for dynamic effects has been found experimentally [24, 60, 64, 166, 168–170], the extent of dynamic effects is not fully understood and deserves further study.

1.5. Dissertation Overview

The overall goal of this work is to improve macroscale models of multiphase flow in porous media for the case of two-fluid-phases. The primary hypotheses of this work are that (1) traditional and currently used models for multiphase flow suffer from inadequately defined variables, a lack of connection between scales, and inflexible frameworks; (2) pore scale analysis can be used to elucidate the deficiencies in standard models and to test proposed constitutive relations and their consistency across scales; and (3) new approaches can provide consistent, well-defined, flexible models for two-phase flow in porous medium systems.

Specific research objectives include:

(1) to formulate a hierarchy of improved macroscale models for flow of two continuous fluids in a porous medium system;

(2) to formulate a model for describing the transition region between two distinct mediums with differing entity sets for the case where one of the mediums includes two-fluid-phase flow and transport in a porous medium system; and

(3) to compare the derived models with those commonly applied in the literature.

The modeling approach for accomplishing the goals of this work is the thermodynamically constrained averaging theory (TCAT) approach. The TCAT approach [84] provides a more comprehensive and logical theoretical basis for modeling multiphase flow than the traditional approach, while also making efforts towards not only connecting the microscale to the desired scale through averaging of the conservation and balance equations, but also presenting a consistent and methodical process of upscaling which

allows for model revision, extension, and simplification. TCAT differs from previous averaging theory work in this area in that it involves averaging of the thermodynamics and equilibrium conditions in addition to the conservation and balance equations; it includes equations for all microscale entities present in a system thus including evolution equations for entities such as interfacial areas; it uses the averaged conservation equations and thermodynamics to constrain an entropy inequality using a force-flux pair approach to develop closure relations; and it provides well defined variables, clearly separates between exact forms and approximations, and provides a detailed set of assumptions.

Transformation of conservation equations from the microscale to macroscale is made possible with the use of averaging theorems [10, 15, 81, 165, 176], which convert averages of derivatives of microscale quantities into derivatives of macroscale averages. Analogous in form and function to the transport and divergence theorems, they change the order of integration and differentiation, and are useful for dealing with phases that occupy a portion of a three-dimensional space. For TCAT-based models, several classes of desirable transformations of integrals over a domain (phases, interfaces, or common curves) arise routinely. These transformations have been developed and published as theorems using generalized functions [81]. Miller and Gray [136], in a publication on the foundational components necessary to utilize the TCAT approach, also present a set of multiscale deviation theorems that are a necessary addition to the transformations referenced above.

Averaged equations contain quantities that must be approximated by constitutive relations in order to close the system of equations. An averaged entropy inequality, constrained by the averaged conservation equations and averaged thermodynamics, can be used in order to guide the formulation of the constitutive relations.

Several theoretical approaches to the general field of thermodynamics exist and the choice of one such theory when developing a TCAT model requires some consideration. Gray and Miller [83] present a summary of various classes of thermodynamic theories and a more thorough discussions of the theories can be found in [114] and [130]. A consistent macroscale formulation has been developed for multiphase flow along the lines of Classical Irreversible Thermodynamics (CIT) [76], which is a theory that includes irreversible processes and is built upon the local equilibrium assumption. This formulation results from averaging the microscale CIT theory to the macroscale, which creates additional terms in the thermodynamic expressions that must be accounted for.

The TCAT approach is meant to be used as a systematic methodology for formulating porous medium models using rigorous averaging of continuum conservation principles and microscale thermodynamics and is intended as a framework for generating consistent, closed models, over a range of scales from micro to mega scales. The scale of each equation is transformed systematically eliminating any ambiguity in the meaning of variables at larger scales and providing consistency between the definitions of variables across scales. The steps to the TCAT approach can be written as:

(1) an entropy inequality (EI) expression for the entire system of concern is generated by averaging from the microscale to the scale of interest;

(2) an appropriate set of mass, momentum, and energy conservation equations are formulated by averaging from the microscale to the scale of interest for all relevant entities (phases, interfaces, etc.);

(3) an appropriate microscale thermodynamic theory is averaged up to the desired scale, and differential forms of internal energy dependence for spatial and temporal derivatives are generated;

(4) equilibrium conditions are formulated;

(5) the EI is augmented using the product of Lagrange multipliers with conservation equations and differential, consistent-scale thermodynamic equations;

(6) the set of Lagrange multipliers is determined to select the combination of conservation equations that describes the physics of interest and to eliminate time derivatives in an effort to write entropy generation in terms of products of dissipative fluxes and forces transforming the augmented EI (AEI) into the constrained EI (CEI);

(7) geometric identities and approximations are applied to the CEI to eliminate additional remaining time derivatives as needed to produce the simplified EI (SEI);

(8) the resultant SEI is used to guide the formulation of general forms of closure approximations consistent with the second law of thermodynamics; and

(9) microscale and macroscale modeling and experimentation are used to advance appropriate forms of closure relations.

Aside from the choice of thermodynamic theories, the TCAT approach can be considered "exact" until the formation of the SEI (step 7), and hence any improvements in approximations that may be found or deemed necessary would not require starting a new formulation from the beginning, but rather revisiting this step.

The dissertation consists of two focused model developments, and a summary and conclusions chapter. Chapter 2, was published in *Advances in Water Resources* in 2009. Detailed in this work are the elements of the TCAT approach necessary to construct a model for two-fluid-phase flow in porous media for the case of two continuous fluids. Chapter 3 will be submitted to *Advances in Water Resources*. Detailed in this work are

the elements of the TCAT approach necessary to construct a model for two-fliud-phase flow and transport within a transition region. Assumptions and restrictions placed on the systems are outlined in detail. Resulting formulations are compared to traditional models when available and notable advantages are discussed. All models presented include closure relations that are in functional form, and determining expressions for these relationships is necessary for application of the models. The Summary and Discussion chapter, Chapter 4, includes possible extensions to the work presented here and additional areas of research in need of attention to further advance the overall goals of this work.

CHAPTER 2

Thermodynamically Constrained Averaging Theory Approach for Modeling Flow and Transport Phenomena in Porous Medium Systems: 6. Two-Fluid-Phase Flow

2.1. Introduction

This paper is the sixth in a series of efforts to produce complete, rigorous closed models that describe flow and transport phenomena in multiscale porous medium systems using the thermodynamically constrained averaging theory (TCAT) approach. Work to date has provided an overview of the general TCAT approach [84], introduced mathematical fundamentals and theorems necessary to generate macroscale equations [136], illustrated the application of the method for single-fluid-phase, single-species flow [85], developed fundamental components of the theory for multispecies models [137], and described the application of the method for single-fluid-phase, multi-species flow [87]. The present study is focused on two-fluid-phase flow in porous media in which the fluid phases are continuous.

A traditional model for multiphase flow in an isothermal system void of compositional effects at the macroscale is typically derived [e.g., 1, 23, 51, 59, 134] by (1) writing equations for mass conservation of each phase; (2) using a modified Darcy's law as an approximate momentum equation for each phase; (3) writing the system of equations in terms of fluid pressures and saturations; (4) specifying an equation of state relating fluid pressures to their densities; (5) assuming an incompressible solid phase and immiscible fluid phases; and (6) specifying constitutive relationships for fluid saturations and relative permeabilities as functions of fluid pressures.

The traditional model for two-fluid-phase flow is established firmly and used routinely for applications in soil science [e.g., 43, 104], contaminant hydrology [e.g., 36, 121], petroleum engineering [e.g., 37, 70], and many other fields. While the traditional model is commonly used it is not without flaws [78, 79, 84, 101, 102, 134]. These flaws include the lack of a rigorous connection between microscale physics and macroscale models, assumed dependence of fluid saturations on fluid pressures alone—leading to hysteresis, dynamics in the relationship between fluid pressures and saturations that is typically ignored, and the lack of explicit account for the physics associated with interfaces and common curves. The TCAT approach can be used to construct models that resolve many of the common shortcomings associated with traditional multiphase flow models and also reveal the assumptions that are inherent in traditional models.

The overall goal of this work is to develop a hierarchy of models to describe continuous two-fluid-phase flow in porous medium systems. The specific objectives of this work are: (1) to formulate a constrained entropy inequality that connects formally the second law of thermodynamics to quantities appearing in mass, momentum, and energy conservation equations; (2) to produce a simplified entropy inequality that can be used to guide the formulation of closure relations needed to produce well-posed models; (3) to detail the restrictions and approximations needed to produce a hierarchy of two-fluid-phase flow models; (4) to populate the hierarchy of models with formulations that cover a range of sophistication and physical fidelity; and (5) to discuss ways in which the general models developed can be further specified, linked to the microscale, and evaluated.

The basic steps involved with formulating a TCAT model for continuous two-fluid-phase flow are identical to those previously outlined and shown in previous work [84, 85, 87, 136, 137]. Minimal re-discussion of these details is needed, and the focus of this work is on the novel aspects of the present contribution. These novel aspects include the extension of the TCAT approach to multiple fluid-phase systems, the forms of the constrained entropy inequality (CEI) and simplified entropy inequality (SEI), closure approximations, and the hierarchy of models proposed.

2.2. System Definition

Two scales are of interest in this work. The microscale, or pore scale, is a scale at which the details of the extent of all phases, interfaces, and common curves are known. The macroscale, or porous medium continuum scale, is a scale at which all quantities are expressed as averages over a representative elementary volume (REV) [20]. TCAT models are developed at the macroscale, where an appropriate REV is assumed to exist. These models provide a rigorous connection to the microscale by expressing macroscale quantities in terms of clearly defined averages of microscale quantities.

Following the standard TCAT notation, the system of concern in this work consists of the set of domains of entities given by

$$(2.1) \qquad \mathcal{E} = \{\Omega_\iota | \iota \in \mathfrak{I}\} = \{\Omega_w, \Omega_n, \Omega_s, \Omega_{wn}, \Omega_{ws}, \Omega_{ns}, \Omega_{wns}\},$$

where $\mathfrak{I}$, the index set of entity qualifiers, is given by

$$(2.2) \qquad \mathfrak{I} = \{w, n, s, wn, ws, ns, wns\},$$

where Ω represents a domain of interest, the members of the index set specify the wetting phase (w), the non-wetting phase (n), the solid phase (s), the wetting-non-wetting interface (wn), the wetting-solid interface (ws), the non-wetting-solid interface (ns), and the wetting-non-wetting-solid common curve (wns).

The connected entity set defines all the entities in contact with a particular entity Ω_ι (i.e., the interfaces that bound a phase, the two phases and common curve that bound an interface, the three interfaces and the common points that bound a common curve). This set is defined by

$$(2.3) \qquad \mathcal{E}_{c\iota} = \{\Omega_\kappa | (\bar{\Omega}_\iota \cap \bar{\Omega}_\kappa \neq \emptyset) \wedge (\bar{\Omega}_\iota \neq \bar{\Omega}_\kappa), \forall \Omega_\kappa \in \mathcal{E}\},$$

where the closure of the domain of the entities is defined as $\bar{\Omega}_\iota = \Omega_\iota \cup \Gamma_\iota$, Γ_ι is the boundary of Ω_ι, and $\mathfrak{I}_{c\iota}$ is the index set corresponding to $\mathcal{E}_{c\iota}$ so $\mathcal{E}_{c\iota} = \{\Omega_\kappa | \kappa \in \mathfrak{I}_{c\iota}\}$. $\mathcal{E}_{c\iota}$

is the set of entities that form an internal boundary for entity Ω_ι. For example, in the case of the wn interface, $\mathcal{E}_{cwn} = \{\Omega_w, \Omega_n, \Omega_{wns}\}$.

Thus, the systems of concern include a porous medium in which the solid phase is filled by two fluid phases. Specifically excluded is the case in which one of the fluid phases is entrapped. The system of concern applies in many cases, such as drainage of a wetting fluid saturated media or the simultaneous flow of two continuous fluid phases.

2.3. Equilibrium Conditions

In order to exploit the system entropy inequality (EI) to guide the formulation of appropriate closure relations, it is important to arrange the EI into products of independent fluxes and groupings of forces known to vanish at equilibrium. The development of such equilibrium conditions for microscale properties can be accomplished using variational methods [7, 31, 32] and the macroscale equilibrium conditions are obtained as averages of these results [91]. The particular equilibrium conditions needed for the present study have been derived in [137] and the expressions obtained are given here for convenience.

At equilibrium, the mass-averaged macroscale velocity satisfies the condition that it is constant and equal in all entities. This may be expressed as

$$(2.4) \qquad \qquad \mathbf{v}^{\overline{\iota}} - \mathbf{v}^{\overline{s}} = 0 \qquad \forall \iota \in \mathcal{I}$$

with

$$(2.5) \qquad \qquad \mathbf{d}^{\overline{\overline{\iota}}} = 0 \qquad \forall \iota \in \mathcal{I}.$$

where $\mathbf{d}^{\overline{\overline{\iota}}}$ is the rate of strain of entity ι. The macroscale temperatures are also constant and equal for all entities such that

$$(2.6) \qquad \qquad \theta^{\overline{\overline{\iota}}} - \theta^{\overline{\overline{s}}} = 0 \qquad \forall \iota \in \mathcal{I}$$

along with

(2.7)
$$\nabla \theta^{\overline{\overline{\iota}}} = 0 \qquad \forall \iota \in \mathfrak{I}.$$

In the current study, the transport of chemical species between phases is not being considered. Nevertheless, there is a need to account for the formation and dissipation of interfaces between phases and of common curves. These entities are formed as mixtures of the pure phase materials. In this case,

(2.8)
$$M^w = \mu^{\overline{w}} + \psi^{\overline{w}} = \mu^{\overline{w,wn}} + \psi^{\overline{wn}} = \mu^{\overline{w,ws}} + \psi^{\overline{ws}} = \mu^{\overline{w,wns}} + \psi^{\overline{wns}},$$

(2.9)
$$M^n = \mu^{\overline{n}} + \psi^{\overline{n}} = \mu^{\overline{n,wn}} + \psi^{\overline{wn}} = \mu^{\overline{n,ns}} + \psi^{\overline{ns}} = \mu^{\overline{n,wns}} + \psi^{\overline{wns}}$$

and

(2.10)
$$M^s = \mu^{\overline{s}} + \psi^{\overline{s}} + \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{\rho_s j_s} \right\rangle_{\Omega_s,\Omega_s} - \frac{1}{\rho^s} \left\langle \frac{\mathbf{t}_s \colon \mathbf{I}}{3} \right\rangle_{\Omega_s,\Omega_s} = \mu^{\overline{s,ws}} + \psi^{\overline{ws}}$$
$$= \mu^{\overline{s,ns}} + \psi^{\overline{ns}} = \mu^{\overline{s,wns}} + \psi^{\overline{wns}},$$

where M^w, M^n, and M^s are constants, $\mu^{\overline{\iota}}$ and $\psi^{\overline{\iota}}$ are the chemical and gravitational potentials of entity ι, respectively, $\mu^{\overline{\iota,\kappa}}$ is the chemical potential of the material comprising the pure phase ι in interface or common curve entity κ, ρ is density, $\mathbf{I}$ is the identity tensor, $\boldsymbol{\sigma}_s$ is the Lagrangian stress tensor, $\mathbf{C}_s$ is the Greens' deformation tensor, $\mathbf{t}_s = (2/j_s)\boldsymbol{\sigma}_s \colon (\nabla_X \mathbf{x} \nabla_X \mathbf{x})$ is the microscale Cauchy stress tensor, $j_s = |\frac{\partial' \mathbf{x}}{\partial \mathbf{X}}|$ is the solid-phase Jacobian, $\mathbf{x}$ represents the position in the solid phase, $\mathbf{X}$ represents the initial position in the solid phase, $\nabla_X \mathbf{x}$ is the gradient of a spatial location vector relative to its initial location, and the angled bracket notation represents the averaging operator [83]. Since the quantities M^{ι} in Eqns (2.8)–(2.10) are constants, their gradients are zero so that, for example,

(2.11)
$$\nabla \left(\mu^{\overline{\iota}} + \psi^{\overline{\iota}} \right) = \nabla \left(\mu^{\overline{s}} + \psi^{\overline{s}} + \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{\rho_s j_s} \right\rangle_{\Omega_s,\Omega_s} - \frac{1}{\rho^s} \left\langle \frac{\mathbf{t}_s \colon \mathbf{I}}{3} \right\rangle_{\Omega_s,\Omega_s} \right) = 0.$$

The macroscale geometric variables are not evolving with time at equilibrium so that their material derivatives are zero

$$(2.12) \qquad \frac{\mathrm{D}^{\overline{s}}\epsilon^{\iota}}{\mathrm{D}t} = 0 \qquad \forall \iota \in \mathfrak{I},$$

where ϵ^{ι} is the specific measure of entity ι. Within the solid phase the equilibrium condition is

$$(2.13) \qquad \left\langle \rho_s \nabla \left(\frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s} \right) - \nabla{\cdot}\mathbf{t}_s \right\rangle_{\Omega_s,\Omega_s} = 0.$$

This equation, along with the microscale versions of the equilibrium constraints and the Gibbs-Duhem equation, can be used to deduce the equilibrium condition

$$(2.14) \qquad \left\langle \nabla{\cdot}\mathbf{t}_s - \nabla\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s} \right\rangle_{\Omega_s,\Omega_s} = 0.$$

For the system under consideration, various unit vectors can be identified that contribute to the quantitative description of the system. The outward normal from phase ι on its boundary is designated as $\mathbf{n}_{\iota}$ such that $\iota \in \{w, n, s\}$. At the common curve forming the boundary of an interface $\alpha\beta$ between the α and β phases, a unit vector can be identified that is tangent to the interface and also normal to the boundary curve of the interface pointing outward from the interface. This unit vector is denoted $\mathbf{n}_{\alpha\beta}$ where $\alpha\beta \in \{wn, ws, ns\}$. Also, the unit vector tangent to the wns common curve is designated as $\mathbf{l}_{wns}$. In addition, the microscale contact angle between the wn and ws interfaces is designated as $\varphi_{ws,wn}$. From geometric considerations, these quantities can be inter-related at a common curve on a smooth surface and expressed in terms of $\mathbf{n}_s$, $\mathbf{n}_{ws}$, and $\varphi_{ws,wn}$. The following identities apply at the interface

$$(2.15) \qquad \mathbf{n}_{\alpha} = -\mathbf{n}_{\beta} \qquad \text{on } \Omega_{\alpha\beta}.$$

On the common curve at the smooth solid surface with normal $\mathbf{n}_s$

$$(2.16) \qquad \mathbf{n}_{wn} = \cos\varphi_{ws,wn}\mathbf{n}_{ws} - \sin\varphi_{ws,wn}\mathbf{n}_s,$$

(2.17)
$$\mathbf{n}_{ns} = -\mathbf{n}_{ws}.$$

Also along the *wns* common curve the identity exists such that

(2.18)
$$\mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} = \mathbf{l}_{wns} \cdot \nabla \mathbf{l}_{wns} \cdot \mathbf{n}_s \mathbf{n}_s + \mathbf{l}_{wns} \cdot \nabla \mathbf{l}_{wns} \cdot \mathbf{n}_{ws} \mathbf{n}_{ws}.$$

Then the normal curvature, κ_{Nwns}, and the geodesic curvature, κ_{Gwns} are defined, respectively as

(2.19)
$$\kappa_{Nwns} = \mathbf{l}_{wns} \cdot \nabla \mathbf{l}_{wns} \cdot \mathbf{n}_s$$

and

(2.20)
$$\kappa_{Gwns} = \mathbf{l}_{wns} \cdot \nabla \mathbf{l}_{wns} \cdot \mathbf{n}_{ws}$$

so that Eqn (2.18) may be written

(2.21)
$$\mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} = \kappa_{Nwns} \mathbf{n}_s + \kappa_{Gwns} \mathbf{n}_{ws}.$$

The corresponding macroscale normal and geodesic curvatures are defined according to

(2.22)
$$\kappa_N^{\overline{\overline{wns}}} = \langle \kappa_{Nwns} \rangle_{\Omega_{wns},\Omega} \qquad \text{and} \qquad \kappa_G^{\overline{\overline{wns}}} = \langle \kappa_{Gwns} \rangle_{\Omega_{wns},\Omega}.$$

The macroscale contact angle is defined such that

(2.23)
$$\cos \varphi^{\overline{\overline{ws,wn}}} = \frac{\langle \cos \left(\varphi_{ws,wn} \right) \rangle_{\Omega_{wns},\Omega_{wns}}}{[\langle \cos \left(\varphi_{ws,wn} \right) \rangle_{\Omega_{wns},\Omega_{wns}}^2 + \langle \sin \left(\varphi_{ws,wn} \right) \rangle_{\Omega_{wns},\Omega_{wns}}^2]^{1/2}}$$

or, equivalently

(2.24)
$$\sin \varphi^{\overline{\overline{ws,wn}}} = \frac{\langle \sin \left(\varphi_{ws,wn} \right) \rangle_{\Omega_{wns},\Omega_{wns}}}{[\langle \cos \left(\varphi_{ws,wn} \right) \rangle_{\Omega_{wns},\Omega_{wns}}^2 + \langle \sin \left(\varphi_{ws,wn} \right) \rangle_{\Omega_{wns},\Omega_{wns}}^2]^{1/2}}.$$

The macroscale surface curvature, $J_\iota^{\overline{\overline{\kappa}}}$, obtained as the divergence of $\mathbf{n}_\iota$ averaged over the κ interface is defined by

(2.25)
$$J_\iota^{\overline{\overline{\kappa}}} = \langle \nabla' \cdot \mathbf{n}_\iota \rangle_{\Omega_\kappa,\Omega_\kappa,\gamma_\kappa} \approx \langle \nabla' \cdot \mathbf{n}_\iota \rangle_{\Omega_\kappa,\Omega_\kappa} = J_\iota^\kappa, \qquad \kappa \in \mathfrak{I}_\mathrm{I}, \ \iota \in (\mathfrak{I}_\mathrm{P} \cap \mathfrak{I}_{c\kappa}).$$

The macroscale pressure of phase ι averaged over an interface κ is denoted p_ι^κ where

(2.26) $$p_\iota^\kappa = \langle p_\iota \rangle_{\Omega_\kappa, \Omega_\kappa}, \qquad \iota \in \mathcal{I}_f, \text{and } \kappa \in \mathcal{I}_{c\iota}$$

and macroscale interfacial tension of surface ι averaged over the common curve wns is defined by

(2.27) $$\gamma_\iota^{wns} = \langle \gamma_\iota \rangle_{\Omega_{wns}, \Omega_{wns}}, \qquad \iota \in \mathcal{I}_I,$$

where $\mathcal{I}_f$ is the index set of all fluid phases.

Next, define χ_ι for $\iota \in (\mathcal{I}_I \cap \mathcal{I}_{ss})$ as

(2.28) $$\chi_\iota = \begin{cases} 1 & \text{on } \Omega_\iota \\ 0 & \text{elsewhere on } \Omega_{ss}, \end{cases}$$

where ss denotes the entire surface of the solid phase. Then

(2.29) $$\chi_\iota^{ss} = \langle \chi_\iota \rangle_{\Omega_{ss}, \Omega_{ss}}, \qquad \iota \in (\mathcal{I}_I \cap \mathcal{I}_{ss}).$$

Similarly a Dirac delta function, $\delta_C(\mathbf{x}_\kappa)$, can be defined such that

(2.30) $$\langle \delta_C(\mathbf{x}_\kappa) f_\iota \rangle_{\Omega_{ss}, \Omega_{ss}} = \langle f_\iota \rangle_{\Omega_\kappa, \Omega_{ss}} = \frac{\epsilon^\kappa}{\epsilon^{ss}} f_\iota^\kappa, \qquad \iota \in \mathcal{I}, \ \kappa \in (\mathcal{I}_C \cap \mathcal{I}_{css}).$$

These functions allow for averages over interfaces and the common curve to be written as averages over the solid surface. The expression for the equilibrium balance of normal stress at the solid surface is

$$\begin{aligned}
(2.31) \quad & \langle \chi_{ws} \left(p_w + \gamma_{ws} \nabla' \cdot \mathbf{n}_s - \rho_{ws} \mathbf{g}_{ws} \cdot \mathbf{n}_s \right) \rangle_{\Omega_{ss}, \Omega_{ss}} \\
& + \langle \chi_{ns} \left(p_n + \gamma_{ns} \nabla' \cdot \mathbf{n}_s - \rho_{ns} \mathbf{g}_{ns} \cdot \mathbf{n}_s \right) \rangle_{\Omega_{ss}, \Omega_{ss}} + \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}} \\
& + \langle \delta_C(\mathbf{x}_{wns}) \left(\gamma_{wns} \kappa_N{}_{wns} - \gamma_{wn} \sin \varphi_{ws,wn} - \rho_{wns} \mathbf{g}_{wns} \cdot \mathbf{n}_s \right) \rangle_{\Omega_{ss}, \Omega_{ss}} \\
= \; & \chi_{ws}^{ss} \left(p_w^{ws} + \gamma^{ws} J_s^{ws} - \langle \rho_{ws} \mathbf{g}_{ws} \cdot \mathbf{n}_s \rangle_{\Omega_{ws}, \Omega_{ws}} \right) \\
& + \chi_{ns}^{ss} \left(p_n^{ns} + \gamma^{ns} J_s^{ns} - \langle \rho_{ns} \mathbf{g}_{ns} \cdot \mathbf{n}_s \rangle_{\Omega_{ns}, \Omega_{ns}} \right) + \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}}
\end{aligned}$$

$$+\frac{\epsilon^{wns}}{\epsilon^{ss}}\left(\gamma^{wns}\kappa_N^{\overline{wns}} - \gamma_{wn}^{wns}\sin\varphi^{\overline{ws,wn}} - \langle\rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_s\rangle_{\Omega_{wns},\Omega_{wns}}\right) = 0,$$

where $\mathbf{g}_\iota$ is the microscale body force acceleration vector acting on entity ι and integral separability has been assumed. At the wn interface, the macroscale equilibrium condition obtained is

$$(2.32) \quad \langle p_w - p_n - \gamma_{wn}\nabla'\cdot\mathbf{n}_w + \rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w\rangle_{\Omega_{wn},\Omega_{wn}}$$

$$= p_w^{wn} - p_n^{wn} - \gamma^{wn}J_w^{wn} + \langle\rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w\rangle_{\Omega_{wn},\Omega_{wn}} = 0.$$

The vector equilibrium condition in any direction tangent to the solid surface is obtained as

$$(2.33) \quad \langle\delta_C(\mathbf{x}_{wns})\left(\gamma_{wn}\cos\varphi_{ws,wn} + \gamma_{ws} - \gamma_{ns} + \gamma_{wns}\kappa_{Gwns}\right)\mathbf{n}_{ws}\rangle_{\Omega_{ss},\Omega_{ss}}$$

$$-\langle\delta_C(\mathbf{x}_{wns})\rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{ws}\mathbf{n}_{ws} - \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\rangle_{\Omega_{ss},\Omega_{ss}} = 0,$$

where $\mathbf{I}'$ is the surface identity tensor. These equilibrium conditions will play an important role subsequently in work to obtain macroscale closure conditions.

2.4. Augmented Entropy Inequality

A key step in the development of a TCAT-based model is the specification of the augmented entropy inequality (AEI). A properly formed AEI connects the conservation of mass, momentum, and energy equations to an EI for the entire system using appropriate averaged thermodynamic expressions that relate material derivatives of entropy to material derivatives appearing in the conservation equations. Because the components of a continuous two-fluid-phase flow model have already been derived [76, 80, 137], these components may be combined into an AEI given by

$$(2.34) \qquad \sum_{\iota\in\mathcal{I}}\left(\mathcal{S}^\iota + \lambda_\mathcal{M}^\iota\mathcal{M}^\iota + \boldsymbol{\lambda}_\mathcal{P}^\iota\cdot\boldsymbol{\mathcal{P}}^\iota + \lambda_\mathcal{E}^\iota\mathcal{E}^\iota + \lambda_\mathcal{T}^\iota\mathcal{T}^\iota\right) = \Lambda \geq 0,$$

where $\mathcal{S}^{\iota}$ represents an EI, $\mathcal{M}^{\iota}$ is a conservation of mass equation, $\mathcal{P}^{\iota}$ is a conservation of momentum equation, $\mathcal{E}^{\iota}$ is a conservation of total energy equation, $\mathcal{T}^{\iota}$ is a thermodynamic expression for the material derivatives of internal energy, λ's and $\boldsymbol{\lambda}$'s are Lagrange multipliers, the subscripts of which specify the respective equation, while the superscript ι is an entity qualifier, and Λ is the entropy produced by the system. In formulating the AEI, all conservation equations are arranged such that they are equal to zero. Therefore, adding the products of λ's and a conservation equation affect neither the sign nor the magnitude of Λ. The Lagrange multipliers are free parameters and as such may be chosen arbitrarily. Selecting the Lagrange multipliers to eliminate some of the material derivative terms in the AEI allows the formulation to focus on the dissipative processes involved in two-fluid-phase flow. To make clear the distinction between those material derivatives that can be eliminated and the remainder of the terms in the balance and conservation equations, shorthand notation is employed for the remaining terms.

The system EI is

$$(2.35) \qquad \sum_{\iota \in \mathfrak{I}} \mathcal{S}^{\iota} = \sum_{\iota \in \mathfrak{I}} \left(\frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \eta^{\bar{\bar{\iota}}} \mathbf{I} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}} - \nabla \cdot \left(\epsilon^{\iota} \boldsymbol{\varphi}^{\bar{\bar{\iota}}} \right) - \epsilon^{\iota} b^{\iota} \right) = \Lambda \geq 0,$$

where $\eta^{\bar{\bar{\iota}}}$ is the entropy density, t is time, $\boldsymbol{\varphi}^{\bar{\bar{\iota}}}$ is an entropy flux vector, b^{ι} is an entropy source density, and Λ is the entropy production rate density for the system. We can write the shorthand expression for the entropy inequality as

$$(2.36) \qquad \sum_{\iota \in \mathfrak{I}} \mathcal{S}^{\iota} = \sum_{\iota \in \mathfrak{I}} \left(\frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \mathcal{S}_r^{\iota} \right) = \Lambda \geq 0,$$

where $\mathcal{S}_r^{\iota}$ represents the residual terms in the entropy inequality, Eqn (2.35). Residual terms refers to the collection of all terms in the original equation not explicitly listed in the shorthand form.

Similarly each of the conservation equations may be written in shorthand notation. Conservation of mass equations are expressed

$$(2.37) \qquad \mathcal{M}^{\iota} = \frac{D^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\right)}{Dt} + \epsilon^{\iota}\rho^{\iota}\mathbf{I}{:}\mathbf{d}^{\bar{\iota}} - \sum_{\kappa\in\mathfrak{I}_{c\iota}} \overset{\kappa\to\iota}{M} = 0 \quad \text{for } \iota \in \mathfrak{I}$$

with the shorthand form

$$(2.38) \qquad \mathcal{M}^{\iota} = \frac{D^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\right)}{Dt} + \mathcal{M}^{\iota}_{r} = 0 \quad \text{for } \iota \in \mathfrak{I},$$

where ρ^{ι} is the mass density, $\overset{\kappa\to\iota}{M}$ represents mass exchange from the κ to the ι entity, and $\mathcal{M}^{\iota}_{r}$ accounts for the residual terms in Eqn (2.37).

Conservation of momentum equations for the system entities may be written as

$$(2.39) \quad \mathcal{P}^{\iota} = \frac{D^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\right)}{Dt} + \epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}} - \nabla\cdot\left(\epsilon^{\iota}\mathbf{t}^{\bar{\bar{\iota}}}\right) - \epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\bar{\iota}}$$
$$- \sum_{\kappa\in\mathfrak{I}_{c\iota}}\left(\overset{\kappa\to\iota}{\mathbf{M}_{v}} + \overset{\kappa\to\iota}{\mathbf{T}}\right) = 0 \quad \text{for } \iota \in \mathfrak{I}.$$

These have the corresponding shorthand form

$$(2.40) \qquad \mathcal{P}^{\iota} = \frac{D^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\right)}{Dt} + \mathcal{P}^{\iota}_{r} = 0 \quad \text{for } \iota \in \mathfrak{I},$$

where $\mathbf{t}^{\bar{\bar{\iota}}}$ is the stress tensor, $\overset{\kappa\to\iota}{\mathbf{M}_{v}}$ represents momentum exchange from the κ to the ι entity due to mass transfer, $\overset{\kappa\to\iota}{\mathbf{T}}$ represents momentum exchange from the κ to the ι entity due to interfacial stress, and $\mathcal{P}^{\iota}_{r}$ represents the residual terms in Eqn (2.39).

Conservation of total energy equations are written as

$$(2.41) \quad \mathcal{E}^{\iota} = \frac{D^{\bar{\iota}}\left[E^{\bar{\bar{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{1}{2}\mathbf{v}^{\bar{\iota}}{\cdot}\mathbf{v}^{\bar{\iota}} + K^{\bar{\bar{\iota}}}_{E} + \psi^{\bar{\iota}}\right)\right]}{Dt}$$
$$+ \left[E^{\bar{\bar{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{1}{2}\mathbf{v}^{\bar{\iota}}{\cdot}\mathbf{v}^{\bar{\iota}} + K^{\bar{\bar{\iota}}}_{E} + \psi^{\bar{\iota}}\right)\right]\mathbf{I}{:}\mathbf{d}^{\bar{\iota}} - \nabla\cdot\left(\epsilon^{\iota}\mathbf{t}^{\bar{\bar{\iota}}}{\cdot}\mathbf{v}^{\bar{\iota}} + \epsilon^{\iota}\mathbf{q}^{\bar{\bar{\iota}}}\right)$$
$$- \epsilon^{\iota}h^{\bar{\bar{\iota}}} - \left\langle\rho_{\iota}\frac{\partial\psi_{\iota}}{\partial t}\right\rangle_{\Omega_{\iota},\Omega} - \sum_{\kappa\in\mathfrak{I}_{c\iota}}\left(\overset{\kappa\to\iota}{M_{E}} + \overset{\kappa\to\iota}{T_{v}} + \overset{\kappa\to\iota}{Q}\right) = 0 \quad \text{for } \iota \in \mathfrak{I}.$$

Expansion of the material derivative and introduction of shorthand notation yields

$$(2.42) \quad \mathcal{E}^\iota = \frac{D^{\bar\iota} E^{\bar{\bar\iota}}}{Dt} + \mathbf{v}^{\bar\iota}\cdot\frac{D^{\bar\iota}\left(\epsilon^\iota\rho^\iota\mathbf{v}^\iota\right)}{Dt} + \left(K_E^{\bar{\bar\iota}} - \frac{\mathbf{v}^{\bar\iota}\cdot\mathbf{v}^{\bar\iota}}{2} + \psi^{\bar\iota}\right)\frac{D^{\bar\iota}\left(\epsilon^\iota\rho^\iota\right)}{Dt}$$

$$+\mathcal{E}_r^\iota = 0 \quad \text{for } \iota \in \mathfrak{I},$$

where $E^{\bar{\bar\iota}}$ is the internal energy density; $K_E^{\bar{\bar\iota}}$ is the kinetic energy per unit mass due to microscale velocity fluctuations; $\psi^{\bar\iota}$ is the gravitational potential; $\mathbf{q}^{\bar\iota}$ is the heat flux density vector; $h^{\bar\iota}$ is an energy source density, $\overset{\kappa\to\iota}{M_E}$, $\overset{\kappa\to\iota}{T_v}$, and $\overset{\kappa\to\iota}{Q}$ express the transfer of energy from entity κ to entity ι due to mass transfer, interfacial stress, and heat transfer, respectively, and $\mathcal{E}_r^\iota$ represents the residual terms in the conservation of energy equation.

Thermodynamic expressions for the material derivatives of internal energy are based upon averaging classical irreversible thermodynamic (CIT) expressions from the microscale to the macroscale and differentiation of those expressions, which has been detailed in previous work [76, 84, 91, 137]. This procedure yields for the fluid phases

$$(2.43) \quad \mathcal{T}^\iota = \frac{D^{\bar\iota} E^{\bar{\bar\iota}}}{Dt} - \theta^{\bar{\bar\iota}}\frac{D^{\bar\iota}\eta^{\bar{\bar\iota}}}{Dt} - \mu^\iota\frac{D^{\bar\iota}\left(\epsilon^\iota\rho^\iota\right)}{Dt} + p^\iota\frac{D^{\bar\iota}\epsilon^\iota}{Dt}$$

$$+\left\langle \eta_\iota\frac{D^{\bar\iota}\left(\theta_\iota - \theta^{\bar{\bar\iota}}\right)}{Dt} + \rho_\iota\frac{D^{\bar\iota}\left(\mu_\iota - \mu^\iota\right)}{Dt} - \frac{D^{\bar\iota}\left(p_\iota - p^\iota\right)}{Dt}\right\rangle_{\Omega_\iota,\Omega} = 0 \quad \iota \in \mathfrak{I}_\mathrm{f},$$

where $\theta^{\bar{\bar\iota}}$ is the macroscale temperature of entity ι. For the solid phase,

$$(2.44)$$

$$\mathcal{T}^s = \frac{D^{\bar s} E^{\bar{\bar s}}}{Dt} - \theta^{\bar{\bar s}}\frac{D^{\bar s}\eta^{\bar{\bar s}}}{Dt} - \mu^{\bar s}\frac{D^{\bar s}\left(\epsilon^s\rho^s\right)}{Dt} + \left\langle \eta_s\frac{D^{\bar s}\left(\theta_s - \theta^{\bar{\bar s}}\right)}{Dt} + \rho_s\frac{D^{\bar s}\left(\mu_s - \mu^{\bar s}\right)}{Dt}\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\iota\in\mathfrak{I}_{cs}}\left\langle \left(\frac{\mathbf{C}_s}{j_s}{:}\boldsymbol{\sigma}_s\right)(\mathbf{v}_\iota - \mathbf{v}_s)\cdot\mathbf{n}_s\right\rangle_{\Omega_\iota,\Omega} - \left\langle \mathbf{n}_s\cdot\left[\mathbf{t}_s\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar s}\right)\right]\right\rangle_{\Omega_{ss},\Omega}$$

$$+\left\langle \left(\nabla\cdot\mathbf{t}_s - \nabla\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar s}\right)\right\rangle_{\Omega_s,\Omega} + \epsilon^s\boldsymbol{\sigma}^{\bar{\bar s}}\vdots\frac{\mathbf{C}^s}{j^s}\mathbf{I}{:}\mathbf{d}^{\bar{\bar s}} - \langle\mathbf{t}_s\rangle_{\Omega_s,\Omega}{:}\mathbf{d}^{\bar{\bar s}}$$

$$-\nabla\cdot\left\langle\left(\mathbf{t}_s - \boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar s}\right)\right\rangle_{\Omega_s,\Omega} = 0.$$

The material derivative of the thermodynamic expression for the interface internal energy per unit volume yields

$$(2.45) \quad \mathcal{T}^\iota = \frac{D^{\bar\iota} E^{\bar{\bar\iota}}}{Dt} - \theta^{\bar{\bar\iota}} \frac{D^{\bar\iota} \eta^{\bar{\bar\iota}}}{Dt} - \mu^{\bar\iota} \frac{D^{\bar\iota} (\epsilon^\iota \rho^\iota)}{Dt} - \gamma^\iota \frac{D^{\bar\iota} \epsilon^\iota}{Dt}$$

$$+ \left\langle \eta_\iota \frac{D'^{\bar\iota} \left(\theta_\iota - \theta^{\bar{\bar\iota}}\right)}{Dt} + \rho_\iota \frac{D'^{\bar\iota} \left(\mu_\iota - \mu^{\bar\iota}\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \frac{D'^{\bar\iota} \left(\gamma_\iota - \gamma^\iota\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} - \nabla\theta^{\bar{\bar\iota}} \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar\iota} - \mathbf{v}_\iota\right) \eta_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla\mu^{\bar\iota} \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar\iota} - \mathbf{v}_\iota\right) \rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla\gamma^\iota \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar\iota} - \mathbf{v}_\iota\right) \right\rangle_{\Omega_\iota,\Omega}, \quad \iota \in \mathcal{I}_I,$$

where $\mathbf{n}_\kappa$ is the unit normal to the surface ι with $\kappa \in \mathcal{I}_{c\iota} \cap \mathcal{I}_P$, and

$$(2.46) \qquad\qquad \frac{D'^{\bar\iota}}{Dt} = \frac{D^{\bar\iota}}{Dt} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar\iota}\right) \cdot \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \nabla.$$

For the common curve

$$(2.47) \quad \mathcal{T}^\iota = \frac{D^{\bar\iota} E^{\bar{\bar\iota}}}{Dt} - \theta^{\bar{\bar\iota}} \frac{D^{\bar\iota} \eta^{\bar{\bar\iota}}}{Dt} - \mu^{\bar\iota} \frac{D^{\bar\iota} (\epsilon^\iota \rho^\iota)}{Dt} + \gamma^\iota \frac{D^{\bar\iota} \epsilon^\iota}{Dt}$$

$$+ \left\langle \eta_\iota \frac{D''^{\bar\iota} \left(\theta_\iota - \theta^{\bar{\bar\iota}}\right)}{Dt} + \rho_\iota \frac{D''^{\bar\iota} \left(\mu_\iota - \mu^{\bar\iota}\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega}$$

$$- \left\langle \frac{D''^{\bar\iota} \left(\gamma_\iota - \gamma^\iota\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} - \nabla\theta^{\bar{\bar\iota}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\bar\iota} - \mathbf{v}_\iota\right) \eta_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla\mu^{\bar\iota} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\bar\iota} - \mathbf{v}_\iota\right) \rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \nabla\gamma^\iota \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\bar\iota} - \mathbf{v}_\iota\right) \right\rangle_{\Omega_\iota,\Omega}, \quad \iota \in \mathcal{I}_C,$$

where $\mathbf{l}_\iota$ is the unit vector tangent to Ω_ι, and

$$(2.48) \qquad\qquad \frac{D''^{\bar\iota}}{Dt} = \frac{D^{\bar\iota}}{Dt} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar\iota}\right) \cdot (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \nabla.$$

For the interfaces and common curves, the compositional nature of these entities is manifest in an implicit summation of chemical potential terms, which is compressed in the above notation, without loss of generality.

It may be observed that all thermodynamic equations can be written using shorthand notation as

$$(2.49) \qquad \mathcal{T}^\iota = \frac{\mathrm{D}^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \theta^{\bar{\bar{\iota}}} \frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \mu^{\bar{\iota}} \frac{\mathrm{D}^{\bar{\iota}} (\epsilon^\iota \rho^\iota)}{\mathrm{D}t} + \mathcal{T}_r^\iota = 0, \quad \iota \in \mathfrak{I},$$

where $\mathcal{T}_r^\iota$ represents the residual terms not explicitly shown in the shorthand form. It follows that the precise definition of this variable depends upon the type of entity, but the respective definition for each entity type can be easily deduced from the complete forms listed.

2.5. Constrained Entropy Inequality

2.5.1. Lagrange Multiplier Solution. A key step in TCAT model building is constructing a CEI. The CEI is important because it represents a general and exact statement of the second law of thermodynamics that is derived based upon a set of primary restrictions for a given system. Ultimately, the CEI is used, pending some approximations, to guide the formulation of allowable closure relations. Deriving a CEI for a given system requires a substantial amount of manipulation, but once formulated a CEI can be used to derive a hierarchy of models of varying complexity and fidelity. The goal is to match the sophistication of the final model to the level of sophistication necessary to describe a physical system of concern. The steps needed to derive a CEI for a continuous two-fluid-phase flow system are detailed below, while relying upon the literature for certain well-established aspects of the formulation.

Closure relations are sought for dissipative processes. To formulate these relations, the near equilibrium case is examined. To facilitate this focus, material derivative expressions are removed from the EI through judicious selection of the Lagrange multipliers.

38

Substitution of Eqs. (2.38), (2.40), (2.42), and (2.49) into Eqn (2.34) gives a system with 42 explicitly written material derivatives. By considering only these 42 material derivatives, although some additional material derivatives do remain in the residual terms, a unique solution for the λ's can then be accomplished as outlined in [85]. This yields

$$
(2.50) \qquad \left\{ \begin{array}{c} \lambda_{\mathcal{M}}^{\iota} \\ \boldsymbol{\lambda}_{\mathcal{P}}^{\iota} \\ \lambda_{\mathcal{E}}^{\iota} \\ \lambda_{\mathcal{T}}^{\iota} \end{array} \right\} = \frac{1}{\theta^{\iota}} \left\{ \begin{array}{c} K_{E}^{\bar{\bar{\iota}}} + \mu^{\bar{\iota}} + \psi^{\bar{\iota}} - \dfrac{\left(\mathbf{v}^{\bar{\iota}}{\cdot}\mathbf{v}^{\bar{\iota}}\right)}{2} \\ \mathbf{v}^{\bar{\iota}} \\ -1 \\ 1 \end{array} \right\} \qquad \text{for } \iota \in \mathfrak{I}.
$$

Substitution of these results into Eqn (2.34) and using Eqs. (2.38), (2.40), (2.42), and (2.49) yields a CEI of the form

$$
(2.51) \quad \sum_{\iota \in \mathfrak{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left[\theta^{\bar{\bar{\iota}}} \mathcal{S}_{r}^{\iota} + \left(K_{E}^{\bar{\bar{\iota}}} + \mu^{\bar{\iota}} + \psi^{\bar{\iota}} - \frac{\left(\mathbf{v}^{\bar{\iota}}{\cdot}\mathbf{v}^{\bar{\iota}}\right)}{2} \right) \mathcal{M}_{r}^{\iota} + \mathbf{v}^{\bar{\iota}}{\cdot}\boldsymbol{\mathcal{P}}_{r}^{\iota} - \mathcal{E}_{r}^{\iota} + \mathcal{T}_{r}^{\iota} \right]
$$

$$
= \Lambda \geq 0.
$$

2.5.2. Thermodynamics Simplifications. The expressions denoted by $\mathcal{T}_{r}^{\iota}$ result from the averaging of CIT-based expressions relating material derivatives of internal energy to other quantities. Some manipulation of these terms is desirable to facilitate the formulation of the final form of the CEI. These manipulations are detailed in turn for each of the entities of concern.

Beginning with the fluid phases, the material derivatives and velocities are referenced to a common frame, namely the macroscale, mass-averaged solid-phase velocity, $\mathbf{v}^{\bar{s}}$. Note that the solid-phase thermodynamics is already referenced to $\mathbf{v}^{\bar{s}}$. The referencing of the fluid phases is accomplished using the identity:

$$
(2.52) \qquad \frac{\mathrm{D}^{\bar{\iota}}}{\mathrm{D}t} = \frac{\mathrm{D}^{\bar{s}}}{\mathrm{D}t} + \mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\nabla,
$$

where $\mathbf{v}^{\bar{\iota},\bar{s}} = \mathbf{v}^{\bar{\iota}} - \mathbf{v}^{\bar{s}}$ is the macroscale mass-average relative velocity of entity ι with respect to the reference velocity $\mathbf{v}^{\bar{s}}$. The thermodynamic expressions in the CEI then become, for $\iota \in \mathcal{I}_\mathrm{f}$,

$$(2.53) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}^{\bar{s}}\left(\theta_\iota - \theta^{\bar{\iota}}\right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}^{\bar{s}}\left(\mu_\iota - \mu^{\bar{\iota}}\right)}{\mathrm{D}t} - \frac{\mathrm{D}^{\bar{s}}\left(p_\iota - p^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left[\eta_\iota \nabla\left(\theta_\iota - \theta^{\bar{\iota}}\right) + \rho_\iota \nabla\left(\mu_\iota - \mu^{\bar{\iota}}\right) - \nabla\left(p_\iota - p^\iota\right) \right] \right\rangle_{\Omega_\iota,\Omega}$$

$$+ p^\iota \frac{\mathrm{D}^{\bar{s}}\epsilon^\iota}{\mathrm{D}t} + p^\iota \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \nabla\epsilon^\iota.$$

The microscale Gibbs-Duhem equation can be used to deduce

$$(2.54) \qquad \left\langle \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left(\eta_\iota \nabla\theta_\iota + \rho_\iota \nabla\mu_\iota - \nabla p_\iota \right) \right\rangle_{\Omega_\iota,\Omega} = 0, \quad \iota \in \mathcal{I}_\mathrm{f},$$

which may be used to simplify Eqn (2.53) to

$$(2.55) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}^{\bar{s}}\left(\theta_\iota - \theta^{\bar{\iota}}\right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}^{\bar{s}}\left(\mu_\iota - \mu^{\bar{\iota}}\right)}{\mathrm{D}t} - \frac{\mathrm{D}^{\bar{s}}\left(p_\iota - p^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$- \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left[\eta^{\bar{\iota}} \nabla\theta^{\bar{\iota}} + \epsilon^\iota \rho^\iota \nabla\mu^{\bar{\iota}} - \nabla\left(\epsilon^\iota p^\iota\right) \right] + p^\iota \frac{\mathrm{D}^{\bar{s}}\epsilon^\iota}{\mathrm{D}t}.$$

The material derivative term involving the fluid pressure can be simplified by applying Theorem MC[3,(3,0),0] [136] giving

$$\left\langle \frac{\mathrm{D}^{\bar{s}}\left(p_\iota - p^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} = \sum_{\kappa \in \mathcal{I}_{c\iota}} \left\langle \left(p_\iota - p^\iota\right)\left(\mathbf{v}^{\bar{s}} - \mathbf{v}_\kappa\right) \cdot \mathbf{n}_\iota \right\rangle_{\Omega_\kappa,\Omega}$$

$$(2.56) \qquad = \sum_{\kappa \in \mathcal{I}_{c\iota}} \left[\left\langle p_\iota \left(\mathbf{v}^{\bar{s}} - \mathbf{v}_\kappa\right) \cdot \mathbf{n}_\iota \right\rangle_{\Omega_\kappa,\Omega} \right] + p^\iota \frac{\mathrm{D}^{\bar{s}}\epsilon^\iota}{\mathrm{D}t}.$$

Combination of this result with Eqn (2.55) yields

$$(2.57) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}^{\bar{s}}\left(\theta_\iota - \theta^{\bar{\iota}}\right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}^{\bar{s}}\left(\mu_\iota - \mu^{\bar{\iota}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$-\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left[\eta^{\bar{\iota}}\nabla\theta^{\bar{\bar{\iota}}}+\epsilon^{\iota}\rho^{\iota}\nabla\mu^{\bar{\iota}}-\nabla\left(\epsilon^{\iota}p^{\iota}\right)\right]+\sum_{\kappa\in\mathcal{J}_{c\iota}}\left\langle p_{\iota}\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}.$$

Consider the residual term for the solid-phase thermodynamics and note that

(2.58) $\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}=\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{I}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$

$=\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\left(\mathbf{n}_{s}\mathbf{n}_{s}+\mathbf{I}'\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$

$=\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\mathbf{n}_{s}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}+\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{I}'\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}.$

Thus the solid-phase thermodynamics residual can be written as

(2.59) $\mathcal{T}_{r}^{s}=\left\langle\eta_{s}\dfrac{\mathrm{D}^{\bar{s}}\left(\theta_{s}-\theta^{\bar{\bar{s}}}\right)}{\mathrm{D}t}+\rho_{s}\dfrac{\mathrm{D}^{\bar{s}}\left(\mu_{s}-\mu^{\bar{s}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega}$

$-\sum_{\iota\in\mathcal{J}_{cs}}\left\langle\left(\dfrac{\mathbf{C}_{s}}{j_{s}}:\boldsymbol{\sigma}_{s}\right)(\mathbf{v}_{\iota}-\mathbf{v}_{s})\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{\iota},\Omega}-\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\mathbf{n}_{s}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$

$-\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{I}'\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}+\left\langle\left(\nabla\cdot\mathbf{t}_{s}-\nabla\boldsymbol{\sigma}_{s}:\dfrac{\mathbf{C}_{s}}{j_{s}}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{s},\Omega}$

$+\epsilon^{s}\boldsymbol{\sigma}^{\bar{\bar{s}}}\dfrac{\mathbf{C}^{s}}{j^{s}}\mathbf{I}:\mathbf{d}^{\bar{\bar{s}}}-\langle\mathbf{t}_{s}\rangle_{\Omega_{s},\Omega}:\mathbf{d}^{\bar{\bar{s}}}-\nabla\cdot\left\langle\left(\mathbf{t}_{s}-\boldsymbol{\sigma}_{s}:\dfrac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{s},\Omega}=0.$

A similar process can be applied for the case of interfaces. At the microscale, it is necessary to restrict the material derivative to the interface, which is accomplished using the expression

(2.60) $$\dfrac{\mathrm{D}'^{\bar{\iota}}}{\mathrm{D}t}=\dfrac{\partial'}{\partial t}+\mathbf{v}^{\bar{\iota}}\cdot\nabla',$$

where

(2.61) $$\dfrac{\partial'}{\partial t}=\dfrac{\partial}{\partial t}+\mathbf{v}_{\iota}\cdot\mathbf{n}_{\kappa}\mathbf{n}_{\kappa}\cdot\nabla$$

and

(2.62) $$\nabla'=\nabla-\mathbf{n}_{\kappa}\mathbf{n}_{\kappa}\cdot\nabla,$$

where $\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_\mathrm{P})$. Eqn (2.60) may be rearranged to

$$\text{(2.63)} \qquad \frac{\mathrm{D}'^{\bar{\iota}}}{\mathrm{D}t} = \frac{\mathrm{D}'^{\bar{s}}}{\mathrm{D}t} + \mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\nabla'.$$

Combination of this form with Eqn (2.45) gives

$$\text{(2.64)} \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}'^{\bar{s}}\left(\theta_\iota - \theta^{\bar{\iota}}\right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}'^{\bar{s}}\left(\mu_\iota - \mu^{\bar{\iota}}\right)}{\mathrm{D}t} + \frac{\mathrm{D}'^{\bar{s}}\left(\gamma_\iota - \gamma^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$+\left\langle \mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\left[\eta_\iota \nabla'\left(\theta_\iota - \theta^{\bar{\iota}}\right) + \rho_\iota \nabla'\left(\mu_\iota - \mu^{\bar{\iota}}\right) + \nabla'\left(\gamma_\iota - \gamma^\iota\right)\right]\right\rangle_{\Omega_\iota,\Omega}$$

$$-\nabla\theta^{\bar{\iota}}{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}_\iota\right)\eta_\iota \right\rangle_{\Omega_\iota,\Omega} - \nabla\mu^{\bar{\iota}}{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}_\iota\right)\rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$-\nabla\gamma^\iota{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}_\iota\right) \right\rangle_{\Omega_\iota,\Omega} - \gamma^\iota \frac{\mathrm{D}^{\bar{s}}\epsilon^\iota}{\mathrm{D}t} - \gamma^\iota \mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\nabla\epsilon^\iota.$$

The microscale Gibbs-Duhem equation can be applied to show

$$\text{(2.65)} \qquad \left\langle \mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\left(\eta_\iota \nabla'\theta_\iota + \rho_\iota \nabla'\mu_\iota + \nabla'\gamma_\iota\right) \right\rangle_{\Omega_\iota,\Omega} = 0, \qquad \iota \in \mathcal{I}_\mathrm{I},$$

which may be used to simplify Eqn (2.64) to

$$\text{(2.66)} \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}'^{\bar{s}}\left(\theta_\iota - \theta^{\bar{\iota}}\right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}'^{\bar{s}}\left(\mu_\iota - \mu^{\bar{\iota}}\right)}{\mathrm{D}t} + \frac{\mathrm{D}'^{\bar{s}}\left(\gamma_\iota - \gamma^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$-\mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\left\langle \eta_\iota \nabla'\theta^{\bar{\iota}} + \rho_\iota \nabla'\mu^{\bar{\iota}} + \nabla'\gamma^\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$-\nabla\theta^{\bar{\iota}}{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}_\iota\right)\eta_\iota \right\rangle_{\Omega_\iota,\Omega} - \nabla\gamma^\iota{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}_\iota\right) \right\rangle_{\Omega_\iota,\Omega}$$

$$-\nabla\mu^{\bar{\iota}}{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}_\iota\right)\rho_\iota \right\rangle_{\Omega_\iota,\Omega} - \gamma^\iota \frac{\mathrm{D}^{\bar{s}}\epsilon^\iota}{\mathrm{D}t} - \gamma^\iota \mathbf{v}^{\bar{\iota},\bar{s}}{\cdot}\nabla\epsilon^\iota.$$

Theorem MC[2,(3,0),0] [136] may be applied to write the material derivative of interfacial tension term from Eqn (2.66) as

$$\text{(2.67)} \quad \left\langle \frac{\mathrm{D}'^{\bar{s}}\left(\gamma_\iota - \gamma^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} = \nabla{\cdot}\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\left(\gamma_\iota - \gamma^\iota\right) \right\rangle_{\Omega_\iota,\Omega}$$

$$-\left\langle \left(\nabla'{\cdot}\mathbf{n}_\kappa\right)\mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\left(\gamma_\iota - \gamma^\iota\right) \right\rangle_{\Omega_\iota,\Omega} + \left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa \left(\gamma_\iota - \gamma^\iota\right)\right\rangle_{\Omega_\iota,\Omega}{:}\mathbf{d}^{\bar{\bar{s}}}$$

$$- \sum_{j \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{C})} \left\langle \mathbf{n}_{\iota} \cdot \left(\mathbf{v}_{j} - \mathbf{v}^{\overline{s}} \right) \left(\gamma_{\iota} - \gamma^{\iota} \right) \right\rangle_{\Omega_{j},\Omega},$$

where $\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{P})$. Theorems T[2,(3,0),0] and G[2,(3,0),0] [82] may be employed in averaging a constant to obtain

$$(2.68) \quad \gamma^{\iota} \frac{D^{\overline{s}} \epsilon^{\iota}}{Dt} = -\nabla \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \gamma^{\iota} \right\rangle_{\Omega_{\iota},\Omega} + \nabla \gamma^{\iota} \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{\iota},\Omega}$$

$$+ \left\langle \left(\nabla' \cdot \mathbf{n}_{\kappa} \right) \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \gamma^{\iota} \right\rangle_{\Omega_{\iota},\Omega} - \langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \gamma^{\iota} \rangle_{\Omega_{\iota},\Omega} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \sum_{j \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{C})} \left\langle \mathbf{n}_{\iota} \cdot \left(\mathbf{v}_{j} - \mathbf{v}^{\overline{s}} \right) \gamma^{\iota} \right\rangle_{\Omega_{j},\Omega},$$

where $\iota \in \mathcal{I}_{I}$, and $\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{P})$. Combining Eqs. (2.66), (2.67), and (2.68) yields

$$(2.69) \quad \mathcal{T}_{r}^{\iota} = \left\langle \eta_{\iota} \frac{D'^{\overline{s}} \left(\theta_{\iota} - \theta^{\overline{\iota}} \right)}{Dt} + \rho_{\iota} \frac{D'^{\overline{s}} \left(\mu_{\iota} - \mu^{\overline{\iota}} \right)}{Dt} \right\rangle_{\Omega_{\iota},\Omega} - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \gamma^{\iota} \nabla \epsilon^{\iota}$$

$$- \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_{\iota} \nabla' \theta^{\overline{\iota}} + \rho_{\iota} \nabla' \mu^{\overline{\iota}} + \nabla' \gamma^{\iota} \right\rangle_{\Omega_{\iota},\Omega} - \nabla \gamma^{\iota} \cdot \langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \rangle_{\Omega_{\iota},\Omega} \cdot \mathbf{v}^{\overline{\iota},\overline{s}}$$

$$- \nabla \theta^{\overline{\iota}} \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_{\iota} \right) \eta_{\iota} \right\rangle_{\Omega_{\iota},\Omega} - \nabla \mu^{\overline{\iota}} \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_{\iota} \right) \rho_{\iota} \right\rangle_{\Omega_{\iota},\Omega}$$

$$+ \nabla \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{\iota},\Omega} - \left\langle \left(\nabla' \cdot \mathbf{n}_{\kappa} \right) \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{\iota},\Omega}$$

$$+ \langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \gamma_{\iota} \rangle_{\Omega_{\iota},\Omega} : \mathbf{d}^{\overline{\overline{s}}} - \left\langle \mathbf{n}_{\iota} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{wns},\Omega}.$$

Eqn (2.63) and the product rule can be used to show

$$(2.70) \quad - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_{\iota} \nabla' \theta^{\overline{\iota}} + \rho_{\iota} \nabla' \mu^{\overline{\iota}} + \nabla' \gamma^{\iota} \right\rangle_{\Omega_{\iota},\Omega}$$

$$= - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_{\iota} \left(\nabla - \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \nabla \right) \theta^{\overline{\iota}} \right\rangle_{\Omega_{\iota},\Omega} - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \rho_{\iota} \left(\nabla - \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \nabla \right) \mu^{\overline{\iota}} \right\rangle_{\Omega_{\iota},\Omega}$$

$$- \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \langle \left(\nabla - \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \nabla \right) \gamma^{\iota} \rangle_{\Omega_{\iota},\Omega}$$

$$= - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \eta^{\overline{\iota}} \nabla \theta^{\overline{\iota}} + \nabla \theta^{\overline{\iota}} \cdot \left\langle \eta_{\iota} \left(\mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \right) \cdot \mathbf{v}^{\overline{\iota},\overline{s}} \right\rangle_{\Omega_{\iota},\Omega} - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \epsilon^{\iota} \rho^{\iota} \nabla \mu^{\overline{\iota}}$$

$$+ \nabla \mu^{\overline{\iota}} \left\langle \rho_{\iota} \left(\mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \right) \cdot \mathbf{v}^{\overline{\iota},\overline{s}} \right\rangle_{\Omega_{\iota},\Omega} - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \epsilon^{\iota} \nabla \gamma^{\iota} + \nabla \gamma^{\iota} \cdot \langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \rangle_{\Omega_{\iota},\Omega} \cdot \mathbf{v}^{\overline{\iota},\overline{s}}.$$

Eqn (2.70) can be combined with Eqn (2.69) to write a final form of the residual term for interfacial thermodynamics

$$(2.71) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}'^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}'^{\overline{s}} \left(\mu_\iota - \mu^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$- \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left[\eta^{\overline{\overline{\iota}}} \nabla \theta^{\overline{\overline{\iota}}} + \epsilon^\iota \rho^\iota \nabla \mu^{\overline{\iota}} + \nabla \left(\gamma^\iota \epsilon^\iota \right) \right] + \nabla \theta^{\overline{\overline{\iota}}} \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \eta_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \nabla \mu^{\overline{\iota}} \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \right\rangle_{\Omega_\iota,\Omega} + \nabla \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \left\langle \left(\nabla' \cdot \mathbf{n}_\kappa \right) \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega} + \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \gamma_\iota \right\rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}}$$

$$- \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_{wns},\Omega}.$$

Applying a similar approach to that used to simplify the interface thermodynamics to the residual term for a common curve results in

$$(2.72) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}''^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}''^{\overline{s}} \left(\mu_\iota - \mu^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$- \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left[\eta^{\overline{\overline{\iota}}} \nabla \theta^{\overline{\overline{\iota}}} + \epsilon^\iota \rho^\iota \nabla \mu^{\overline{\iota}} - \nabla \left(\epsilon^\iota \gamma^\iota \right) \right] - \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \nabla \theta^{\overline{\overline{\iota}}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \eta_\iota \right\rangle_{\Omega_\iota,\Omega} + \nabla \mu^{\overline{\iota}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega} - \left\langle \left(\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega}.$$

The detailed residual terms of the thermodynamic expressions are in a convenient form. The manipulations performed to derive these expressions are exact and all terms are well-defined averages of microscale quantities. The only remaining material derivatives in these residual terms involve averages of deviations of microscale temperature and chemical potential deviations from their macroscale expressions.

2.5.3. Flux-Force Form. The only remaining material derivatives in the CEI not referenced to $\mathbf{v}^{\overline{s}}$ appear in the $\mathcal{E}_r^\iota$ portion. These can be referenced to $\mathbf{v}^{\overline{s}}$ by making use of

the identity

$$(2.73) \qquad \epsilon^\iota \rho^\iota \frac{D^{\bar\iota}\left(K_E^{\bar{\bar\iota}} + \psi^{\bar\iota}\right)}{Dt} = \epsilon^\iota \rho^\iota \frac{D^{\bar s}\left(K_E^{\bar{\bar\iota}} + \psi^{\bar\iota}\right)}{Dt} + \epsilon^\iota \rho^\iota \mathbf{v}^{\bar\iota, \bar s} \cdot \nabla \left(K_E^{\bar{\bar\iota}} + \psi^{\bar\iota}\right).$$

Two additional terms appearing in $\mathcal{E}_r^\iota$ can be expanded using the product rule. The divergence of the stress tensor term may be written as

$$(2.74) \qquad \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}} \cdot \mathbf{v}^{\bar\iota}\right) = \mathbf{v}^{\bar\iota} \cdot \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}}\right) + \epsilon^\iota \mathbf{t}^{\bar{\bar\iota}} : \mathbf{d}^{\bar{\bar\iota}},$$

making use of the fact that $\mathbf{t}^{\bar\iota}$ is symmetric. The divergence of the heat flux vector may be rearranged to show

$$(2.75) \qquad -\frac{1}{\theta^{\bar\iota}} \nabla \cdot \left(\epsilon^\iota \mathbf{q}^{\bar{\bar\iota}}\right) = -\nabla \cdot \left(\frac{\epsilon^\iota \mathbf{q}^{\bar{\bar\iota}}}{\theta^{\bar\iota}}\right) - \frac{\epsilon^\iota \mathbf{q}^{\bar{\bar\iota}}}{\left(\theta^{\bar\iota}\right)^2} \cdot \nabla \theta^{\bar\iota}.$$

Eqs. (2.73), (2.74), and (2.75) can be used to write the residual portion of the energy equation as

$$(2.76) \quad \mathcal{E}_r^\iota = \epsilon^\iota \rho^\iota \frac{D^{\bar s}\left(K_E^{\bar{\bar\iota}} + \psi^{\bar\iota}\right)}{Dt} + \epsilon^\iota \rho^\iota \mathbf{v}^{\bar\iota, \bar s} \cdot \nabla \left(K_E^{\bar{\bar\iota}} + \psi^{\bar\iota}\right)$$

$$+ \left[E^{\bar{\bar\iota}} + \epsilon^\iota \rho^\iota \left(\frac{1}{2} \mathbf{v}^{\bar\iota} \cdot \mathbf{v}^{\bar\iota} + K_E^{\bar{\bar\iota}} + \psi^{\bar\iota}\right)\right] \mathbf{I} : \mathbf{d}^{\bar{\bar\iota}} - \mathbf{v}^{\bar\iota} \cdot \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}}\right)$$

$$- \epsilon^\iota \mathbf{t}^{\bar{\bar\iota}} : \mathbf{d}^{\bar{\bar\iota}} - \theta^{\bar{\bar\iota}} \nabla \cdot \left(\frac{\epsilon^\iota \mathbf{q}^{\bar{\bar\iota}}}{\theta^{\bar{\bar\iota}}}\right) + \theta^{\bar{\bar\iota}} \frac{\epsilon^\iota \mathbf{q}^{\bar{\bar\iota}}}{\left(\theta^{\bar{\bar\iota}}\right)^2} \cdot \nabla \theta^{\bar{\bar\iota}} - \epsilon^\iota h^{\bar{\bar\iota}}$$

$$- \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) = 0, \quad \text{for } \iota \in \mathcal{I}.$$

The residual terms $\mathcal{S}_r^\iota$, $\mathcal{M}_r^\iota$, $\mathcal{P}_r^\iota$, $\mathcal{E}_r^\iota$, and $\mathcal{T}_r^\iota$ are next substituted back into Eqn (2.51). Cancellation of like terms along with extensive but routing manipulations are then employed. These routine manipulations include applying the product rule, algebraic rearrangements, and regrouping of terms into force-flux pairs consistent with derived equilibrium conditions. The completion of these manipulations provides the final form of the CEI

(2.77)

$$
-\sum_{\iota\in\{\mathfrak{I}_{\mathrm{f}}\cup\mathfrak{I}_{\mathrm{I}}\cup\mathfrak{I}_{\mathrm{C}}\}} \nabla\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\iota}} - \frac{\epsilon^{\iota}\mathbf{q}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\right)
$$

$$
-\nabla\cdot\left\{\epsilon^{s}\boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{s}}}\left[\epsilon^{s}\mathbf{q}^{\overline{\overline{s}}} - \left\langle\left(\mathbf{t}_{s}-\boldsymbol{\sigma}_{s}{:}\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}\right]\right\}
$$

$$
-\sum_{\iota\in\mathfrak{I}_{\mathrm{P}}}\left[\epsilon^{\iota}b^{\iota} - \frac{1}{\theta^{\overline{\overline{\iota}}}}\left(\epsilon^{\iota}h^{\overline{\iota}} + \left\langle\eta_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right)\right.
$$

$$
\left.-\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\rho_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_{E}^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]
$$

$$
-\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\left[\epsilon^{\iota}b^{\iota} - \frac{1}{\theta^{\overline{\overline{\iota}}}}\left(\epsilon^{\iota}h^{\overline{\iota}} + \left\langle\eta_{\iota}\frac{\mathrm{D}'^{\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right)\right.
$$

$$
\left.-\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\rho_{\iota}\frac{\mathrm{D}'^{\overline{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_{E}^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]
$$

$$
-\epsilon^{wns}b^{wns} + \frac{1}{\theta^{\overline{\overline{wns}}}}\left(\epsilon^{wns}h^{\overline{\overline{wns}}} + \left\langle\eta_{wns}\frac{\mathrm{D}''^{\overline{s}}\left(\theta_{wns}-\theta^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\right)
$$

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\rho_{wns}\frac{\mathrm{D}''^{\overline{s}}\left(\mu_{wns}+\psi_{wns}-\mu^{\overline{wns}}-\psi^{\overline{wns}}-K_{E}^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}
$$

$$
+\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{\epsilon^{\iota}}{\theta^{\overline{\iota}}}\left(\mathbf{t}^{\overline{\iota}}+p^{\iota}\mathbf{I}\right){:}\mathbf{d}^{\overline{\iota}} + \frac{\epsilon^{s}}{\theta^{\overline{\overline{s}}}}\left(\mathbf{t}^{\overline{\overline{s}}}-\mathbf{t}^{s}\right){:}\mathbf{d}^{\overline{\overline{s}}} + \sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{\epsilon^{\iota}}{\theta^{\overline{\overline{\iota}}}}\left(\mathbf{t}^{\overline{\iota}}-\gamma^{\iota}\mathbf{I}\right){:}\mathbf{d}^{\overline{\iota}}
$$

$$
+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{t}^{\overline{\overline{wns}}}+\gamma^{wns}\mathbf{I}\right){:}\mathbf{d}^{\overline{\overline{wns}}} + \sum_{\iota\in\{\mathfrak{I}_{\mathrm{f}}\cup\mathfrak{I}_{\mathrm{I}}\cup\mathfrak{I}_{\mathrm{C}}\}}\frac{\epsilon^{\iota}\mathbf{q}^{\overline{\iota}}}{\left(\theta^{\overline{\overline{\iota}}}\right)^{2}}\cdot\nabla\theta^{\overline{\iota}}
$$

$$
+\frac{1}{\left(\theta^{\overline{\overline{s}}}\right)^{2}}\left[\epsilon^{s}\mathbf{q}^{\overline{\overline{s}}} - \left\langle\left(\mathbf{t}_{s}-\boldsymbol{\sigma}_{s}{:}\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}\right]\cdot\nabla\theta^{\overline{\overline{s}}}
$$

$$
-\sum_{\iota\in\mathfrak{I}_{P}}\sum_{\kappa\in\mathfrak{I}_{c\iota}}\frac{1}{\theta^{\overline{\overline{\kappa}}}}\overset{\kappa\to\iota}{M}\left[\left(K_{E}^{\overline{\iota}}+\psi^{\iota}+\mu^{\overline{\iota}}\right)-\left(K_{E}^{\overline{\overline{\kappa}}}+\psi^{\kappa}+\mu^{\overline{\kappa}}\right)\right]
$$

46

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\sum_{\kappa\in\mathcal{I}_{cwns}}\overset{wns\to\kappa}{M}\left[\left(K_E^{\overline{\overline{\kappa}}}+\psi^{\overline{\kappa}}+\mu^{\overline{\kappa}}\right)-\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}+\mu^{\overline{wns}}\right)\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{P}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left[\overset{\kappa\to\iota}{Q}+\left(\frac{E^{\overline{\overline{\iota}}}}{\epsilon^{\iota}\rho^{\iota}}-\mu^{\overline{\iota}}\right)\overset{\kappa\to\iota}{M}+\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\left(\overset{\kappa\to\iota}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{\iota},\overline{\kappa}}}{2}\overset{\kappa\to\iota}{M}\right)\right]\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left[\overset{wns\to\iota}{Q}+\left(\frac{E^{\overline{\overline{\iota}}}}{\epsilon^{\iota}\rho^{\iota}}-\mu^{\overline{\iota}}\right)\overset{wns\to\iota}{M}+\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\left(\overset{wns\to\iota}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{\iota},\overline{wns}}}{2}\overset{wns\to\iota}{M}\right)\right]\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left\langle p_{\iota}\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right){\cdot}\mathbf{n}_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}}+\epsilon^{\iota}\rho^{\iota}\nabla\left(K_E^{\overline{\overline{\iota}}}+\psi^{\overline{\iota}}+\mu^{\overline{\iota}}\right)+\eta^{\overline{\iota}}\nabla\theta^{\overline{\iota}}\right.$$

$$\left.-\nabla\left(\epsilon^{\iota}p^{\iota}\right)+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left(\overset{\kappa\to\iota}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{\iota},\overline{\kappa}}}{2}\overset{\kappa\to\iota}{M}\right)\right]{\cdot}\mathbf{v}^{\overline{\iota},\overline{s}}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}}+\epsilon^{\iota}\rho^{\iota}\nabla\left(K_E^{\overline{\overline{\iota}}}+\psi^{\overline{\iota}}+\mu^{\overline{\iota}}\right)+\eta^{\overline{\iota}}\nabla\theta^{\overline{\iota}}+\nabla\left(\epsilon^{\iota}\gamma^{\iota}\right)\right.$$

$$\left.-\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}\cap\mathcal{I}_{\mathrm{P}}}\left(\overset{\iota\to\kappa}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{\kappa},\overline{\iota}}}{2}\overset{\iota\to\kappa}{M}\right)+\left(\overset{wns\to\iota}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{\iota},\overline{wns}}}{2}\overset{wns\to\iota}{M}\right)\right]{\cdot}\mathbf{v}^{\overline{\iota},\overline{s}}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\epsilon^{wns}\rho^{wns}\mathbf{g}^{\overline{wns}}+\epsilon^{wns}\rho^{wns}\nabla\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}+\mu^{\overline{wns}}\right)+\eta^{\overline{wns}}\nabla\theta^{\overline{wns}}\right.$$

$$\left.-\nabla\left(\epsilon^{wns}\gamma^{wns}\right)-\sum_{\kappa\in\mathcal{I}_{cwns}}\left(\overset{wns\to\kappa}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{\kappa},\overline{wns}}}{2}\overset{wns\to\kappa}{M}\right)\right]{\cdot}\mathbf{v}^{\overline{wns},\overline{s}}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla{\cdot}\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{I}'{\cdot}\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\frac{\mathbf{C}_s}{j_s}{:}\boldsymbol{\sigma}_s\left(\mathbf{v}_{\kappa}-\mathbf{v}_s\right){\cdot}\mathbf{n}_s\right\rangle_{\Omega_{\kappa},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{n}_s\mathbf{n}_s{\cdot}\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\theta^{\overline{\iota}}{\cdot}\left\langle\mathbf{n}_{\kappa}\mathbf{n}_{\kappa}{\cdot}\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\eta_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla{\cdot}\left\langle\mathbf{n}_{\kappa}\mathbf{n}_{\kappa}{\cdot}\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \gamma_\iota \rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}} - \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_{wns},\Omega} \right]$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \nabla \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}} + \mu^{\overline{\iota}} \right) \cdot \left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \frac{1}{\theta^{\overline{\overline{wn}}}} \left\langle \left(p_w - p_n - \gamma_{wn} \nabla' \cdot \mathbf{n}_w + \rho_{wn} \mathbf{n}_w \cdot \mathbf{g}_{wn} \right) \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_w \right\rangle_{\Omega_{wn},\Omega}$$

$$- \frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \left(p_w + \gamma_{ws} \nabla' \cdot \mathbf{n}_s - \rho_{ws} \mathbf{n}_s \cdot \mathbf{g}_{ws} \right) \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega}$$

$$- \frac{1}{\theta^{\overline{\overline{ns}}}} \left\langle \left(p_n + \gamma_{ns} \nabla' \cdot \mathbf{n}_s - \rho_{ns} \mathbf{n}_s \cdot \mathbf{g}_{ns} \right) \left(\mathbf{v}_{ns} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_{ns},\Omega}$$

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \rho_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \cdot (\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns}) \cdot \mathbf{g}_{wns} \right\rangle_{\Omega_{wns},\Omega}$$

$$- \frac{1}{\theta^{\overline{\overline{wns}}}} \nabla \cdot \left\langle (\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns}) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega}$$

$$- \frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \left(\mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} \right) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega}$$

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \nabla \theta^{\overline{\overline{wns}}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns}) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \eta_{wns} \right\rangle_{\Omega_{wns},\Omega}$$

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \nabla \left(K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}} + \mu^{\overline{wns}} \right) \cdot \left\langle (\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns}) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \rho_{wns} \right\rangle_{\Omega_{wns},\Omega}$$

$$- \frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle (\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns}) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega} : \mathbf{d}^{\overline{\overline{s}}} = \Lambda \geq 0.$$

Eqn (2.77) is the final CEI for the two-fluid-phase system. Additional work is needed so that both factors in all force-flux pairs will be zero at equilibrium. The appearance of terms in Eqn (2.77) is impacted by the choice of the microscale thermodynamic functional dependence, a choice which is reasonable but not unique. No mathematical approximations have been employed in obtaining this equation from Eqn (2.34). Thus, Eqn (2.77) provides a starting point for the formulation of a range of complete closed models for two-fluid-phase flow. The subsequent steps to obtain those models require approximations appropriate for the physical system under consideration and may take different forms depending on the systems studied and the approximate relations employed.

2.6. Restrictions and Approximations

The conservation equations given in §2.4 require closure relations to arrive at a set of solvable models. The development of closure relations is guided by the simplified EI (SEI). The final models derived are based upon both restrictions that detail aspects of the specific system being considered and approximations relied upon to produce closure relations and thus solvable systems. An important aspect of the TCAT approach is that these restrictions and approximations are carefully detailed and the models derived can be revisited if they are found to be inadequate.

Restrictions are considered statements that specify the physical system being modeled. When these restrictions are specified before the AEI is formulated, they are termed primary restrictions. Secondary restrictions are applied after the final CEI is derived. The distinction is important because secondary restrictions are relatively easy to relax, while primary restrictions limit the systems of concern without a complete model reformulation.

Approximations are needed to produce a closed, solvable model. These approximations involve mathematical steps needed to produce the SEI and to formulate closure relations based upon the SEI. The validity of the approximations will be testable in most cases, and improved approximations may be both possible and necessary in certain instances. A set of restrictions and approximations for this work and their significance is noted.

PRIMARY RESTRICTION 1 (Deterministic Macroscale Averaging). *A discrete macroscopic length scale exists such that all macroscale quantities of concern are well-defined and insensitive to the single size of the representative elementary volume employed for the deterministic models derived.*

Primary restriction 1 is a standard assumption needed to produce deterministic macroscale models based upon a clear separation of length scales. When a clear separation of length scales does not exist, the fundamental averaging operators and theorems relied upon in this work need to be revisited.

PRIMARY RESTRICTION 2 (Entities). *The particular system of interest is comprised of a wetting fluid, a non-wetting fluid, and a solid phase. The juxtaposition of these phases results in three interfaces and a common curve. The species composition of the phase entities is not considered.*

Primary restriction 2 indicates that interest is limited to the behavior of individual entities in a porous medium system. The distribution of species that comprise the phase entities is not considered here. Each phase entity is modeled as being comprised of a single chemical component.

PRIMARY RESTRICTION 3 (Classical Irreversible Thermodynamics).
Classical irreversible thermodynamics is applicable to the porous medium system at the microscale.

Primary restriction 3 fulfills the need within the TCAT approach to choose a thermodynamic approach. Additionally, the selection is made at the microscale, and the consequences of this choice are rigorously established by averaging to the macroscale. It is possible to select an alternative microscale thermodynamic approach.

PRIMARY RESTRICTION 4 (Continuous Phases). *The system of concern consists of continuous wetting and non-wetting phases along with a solid phase.*

Primary restriction 4 is a statement that only continuous wetting and non-wetting fluid phases will be present in the system; no disconnected fluids are present. In the case of the solid phase, there is a matrix such that all the solid particles are in contact with other solid particles and the solid phase may be treated as a continuum.

APPROXIMATION 1 (Simplified Entropy Inequality). *The four approximations used to produce the SEI are: (1) the geometric tensor is independent of entity measures, densities, velocities, interfacial tension, and entropy, such that integrals of products of these quantities may be split into products of integrals; (2) changes in entity measures are not independent and can be approximated using averaging theorems; (3) the systems*

of concern are macroscopically simple; and (4) terms involving products of microscale quantities related to solid-phase deformation that are known to vanish at equilibrium are negligible.

Approximation 1 summarizes a set of conditions imposed to produce the SEI upon which the closure relations are based. This approximation is a reasonable first approximation; it is testable based upon microscale simulations; and it can be relaxed if system behavior dictates this is necessary. The simple system component of this assumption allows for the heat and entropy fluxes and sources to be related and posits that these processes do not contribute to the production of entropy.

APPROXIMATION 2 (Closure Approximations). *Closure approximations will be posited to be zero order with respect to the macroscale rate of strain tensor and first-order Taylor series approximations with respect to all other forces being considered.*

Neglect of the rate of strain in constitutive relations for porous media flow, as stated in Approximation 2, is typical within the system but may have to be relaxed if wall effects are important or for a very high velocity flow. Linear dependence on the forces is an implicit statement that the system is "near enough" to equilibrium that higher order dependences can be neglected. This statement does not eliminate Onsager-like cross-coupling effects.

SECONDARY RESTRICTION 1 (Isothermal). *The system of concern is isothermal.*

Secondary restriction 1 eliminates the need to solve conservation of energy equations and to develop closure relations for quantities involving heat flux. If one is interested in modeling, for example, geothermal processes, this restriction would be eliminated and constitutive forms involving heat would be needed.

SECONDARY RESTRICTION 2 (Immiscible). *The entities of concern are completely immiscible.*

Secondary restriction 2 is a statement that no mass exchange between phases takes place.

SECONDARY RESTRICTION 3 (Solid Properties). *The solid phase is linearly compressible, elastic, isotropic, only slightly deformable and solely as a result of normal stress, primarily deformed in the vertical direction with small spatial gradients in such deformations, and the curvature of the solid phase is independent of the fluid phase contacting the surface.*

This restriction allows for the inclusion of solid-phase deformation but for a very specific and relatively simple case. The solid-phase deformation is considered to be slow and horizontal spatial gradients are assumed to be negligible. This restriction also allows for the solid-phase curvature to be treated as essentially constant in time and independent of the fluid saturation conditions.

APPROXIMATION 3 (Equations of State). *The system is described by standard equations of state (EOS), averaged up to the macroscale, relating mass densities to fluid pressures.*

Approximation 3 asserts that the EOS commonly used in the hydrologic and petroleum literature are sufficient for describing macroscale behavior when averaged up to the macroscale for the system of interest.

APPROXIMATION 4 (Spatial Gradients). *Spatial gradients of mass densities are negligible.*

Spatial derivatives of macroscale mass densities appear as products with other variables. This approximation implies that the other variables in the product change much more rapidly than the phase densities of concern in this work. This assumption is reasonable, but it is also straightforward to consider these spatial variations as well.

APPROXIMATION 5 (Acceleration of Momentum). *Local and advective rates of change of momentum at the macroscopic scale are negligible.*

Approximation 5 states there is negligible acceleration with time of the entities and negligible advective acceleration of the entities at the macroscale, i.e. when considering acceleration of the macroscale velocities. This assertion simplifies the momentum equations and is a common approximation used to arrive at a momentum equation similar to the multiphase extension to Darcy's Law.

APPROXIMATION 6 (Fluctuation Terms). *Integral material derivative fluctuation terms relating microscale and macroscale quantities arising in the Gibbs-Duhem equation can be neglected.*

The fluctuations terms are contained in an integral over the domain corresponding to the entity of interest, with each of the time derivatives written as a difference between a macroscale quantity and its microscale precursor. In cases where the system is spatially homogeneous at the microscale for a given property, the corresponding integral term vanishes. Even in cases where the system is not microscopically spatially homogeneous these terms may vanish. In general, while not zero, in many practical cases the fluctuation terms may be small. Thus neglecting these terms is a feasible first approximation.

APPROXIMATION 7 (Deviation Terms). *Terms accounting for deviations in kinetic energy can be neglected.*

$K_E^{\bar{\bar{\iota}}}$ is the kinetic energy due to microscale velocity fluctuations and can be considered a measure of the deviations in kinetic energy. In cases where the velocity difference between microscale and macroscale velocities are small, this difference squared, as it appears in $K_E^{\bar{\bar{\iota}}}$ can as a first approximation be justifiably neglected. Thus, this statement says that the integral of the product of the difference between the microscale and macroscale velocities is, to first order, zero.

APPROXIMATION 8 (Massless Interfaces and Common Curves). *The interfaces and common curves are assumed to be massless.*

Massless interfaces and common curves eliminate the need for conservation of mass equations for these entities and simplifies the form of the conservation of momentum equations for these entities.

2.7. Simplified Entropy Inequality

An objective of this work is to produce a SEI based upon the CEI that can be used to guide the formulation of closed models. A useful SEI will consist solely of force-flux pairs with all forces and fluxes equal to zero at equilibrium. The steps needed to derive such an SEI from the CEI are approximate in nature. If better approximations become available, or should an exact relation be derived for a particular system, alternatives to the approximations used here and detailed in §2.6 may be employed to produce the SEI. The resultant SEI may be used to derive closure relations for a wide range of models based upon any additional secondary restrictions applied to the system and the precise form of the closure relations chosen. We summarize the steps needed to derive the SEI.

First, restrict the system to be isothermal according to Secondary Restriction 1 and to have no mass exchange between phases according to Secondary restriction 2. The condition of no mass exchange implies that for phase ι,

$$(2.78) \qquad \left(\mathbf{v}_\kappa - \mathbf{v}_\iota\right) \cdot \mathbf{n}_\iota = 0 \qquad \text{on } \Omega_\kappa,$$

where $\iota \in \mathfrak{I}_\mathrm{P}$ and $\kappa \in \mathfrak{I}_{\mathrm{c}\iota}$. Consistent with Approximation 7, the terms involving deviation kinetic energy are assumed to be negligible since they are second order in velocity deviations. Also all terms that contain interface or common curve densities are eliminated based on Approximation 8.

Next, the terms in the averaging operators that involve integrals of $\mathbf{n}_\iota\mathbf{n}_\iota$ over the κ domain are considered. Since these terms are related to the orientation of the κ entity, they are referred to collectively as geometric orientation terms.

Define the geometric orientation tensor for the κ interface, $\mathbf{G}^\kappa$, as

(2.79) $$\mathbf{G}^\kappa = \langle \mathbf{G}_\kappa \rangle_{\Omega_\kappa, \Omega_\kappa} = \langle \mathbf{n}_\iota \mathbf{n}_\iota \rangle_{\Omega_\kappa, \Omega_\kappa} \qquad \text{for } \iota \in (\mathfrak{I}_{c\kappa} \cap \mathfrak{I}_P) \, .$$

For the *wns* common curve, the geometric orientation tensor, $\mathbf{G}^{wns}$, is defined as

(2.80) $$\mathbf{G}^{wns} = \langle \mathbf{G}_{wns} \rangle_{\Omega_{wns}, \Omega_{wns}} = \langle (\mathbf{I} - \mathbf{l}_{wns}\mathbf{l}_{wns}) \rangle_{\Omega_{wns}, \Omega_{wns}} \, .$$

Knowledge of the microscale is sufficient to compute the geometric tensor without error and thereby test the macroscale models derived from this theory. In general, the geometric tensor appears within averaging operators as a product involving other terms. We approximate these geometric product terms by assuming independence among certain groupings of variables according to Approximation 1, which allows for integrals of products to be expressed as products of integral expressions. To be specific, the following approximations are used involving the geometric tensors

(2.81) $$\left\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega} \approx \epsilon^\iota \mathbf{G}^\iota \cdot \mathbf{v}^{\overline{\iota}, \overline{s}} \gamma^\iota,$$

(2.82) $$\langle \mathbf{n}_\kappa \mathbf{n}_\kappa \gamma_\iota \rangle_{\Omega_\iota, \Omega} \approx \epsilon^\iota \mathbf{G}^\iota \gamma^\iota,$$

(2.83) $$\left\langle (\mathbf{I} - \mathbf{l}_{wns}\mathbf{l}_{wns}) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{wns} \right\rangle_{\Omega_{wns}, \Omega} \approx \epsilon^{wns} \mathbf{G}^{wns} \cdot \mathbf{v}^{\overline{wns}, \overline{s}} \gamma^{wns}$$

and

(2.84) $$\langle (\mathbf{I} - \mathbf{l}_{wns}\mathbf{l}_{wns}) \gamma_{wns} \rangle_{\Omega_{wns}, \Omega} \approx \epsilon^{wns} \mathbf{G}^{wns} \gamma^{wns} \, .$$

Entropy and heat source and flux terms are assumed to not contribute to entropy production. The assumption of a thermodynamically simple system is invoked in Approximation 1 to equate these respective terms and assert that the resulting expressions are identically equal to zero. The conditions employed are based on Eqn (2.77), but are

also consistent with the identification of simple systems at the microscale. For macro-scopically simple systems, the entropy and heat fluxes are related by

$$(2.85) \qquad \epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} - \frac{\epsilon^\iota \mathbf{q}^{\overline{\overline{\iota}}}}{\theta^{\overline{\overline{\iota}}}} = 0 \quad \text{for } \iota \in \{w, n, ws, wn, ns, wns\}$$

and

$$(2.86) \qquad \epsilon^s \boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}} \left[\epsilon^s \mathbf{q}^{\overline{\overline{s}}} - \left\langle \left(\mathbf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s, \Omega} \right] = 0.$$

If more complex relationships are found to be necessary based on observations of a system of interest, the right sides of these expressions can be set to some non-zero constitutive function of the force variables in the SEI.

Similarly, energy and entropy source terms are related according to

$$(2.87) \quad \epsilon^\iota b^\iota - \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(\epsilon^\iota h^{\overline{\overline{\iota}}} + \left\langle \eta_\iota \frac{\mathrm{D}^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} \right)$$
$$- \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \rho_\iota \frac{\mathrm{D}^{\overline{s}} \left(\mu_\iota + \psi_\iota - \mu^{\overline{\iota}} - \psi^{\overline{\iota}} - K_E^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_P,$$

$$(2.88) \quad \epsilon^\iota b^\iota - \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(\epsilon^\iota h^{\overline{\overline{\iota}}} + \left\langle \eta_\iota \frac{\mathrm{D}'^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} \right)$$
$$- \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \rho_\iota \frac{\mathrm{D}'^{\overline{s}} \left(\mu_\iota + \psi_\iota - \mu^{\overline{\iota}} - \psi^{\overline{\iota}} - K_E^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_I,$$

$$(2.89) \quad \epsilon^{wns} b^{wns} - \frac{1}{\theta^{\overline{\overline{wns}}}} \left(\epsilon^{wns} h^{\overline{\overline{wns}}} + \left\langle \eta_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\theta_{wns} - \theta^{\overline{\overline{wns}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns}, \Omega} \right)$$
$$- \frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \rho_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\mu_{wns} + \psi_{wns} - \mu^{\overline{wns}} - \psi^{\overline{wns}} - K_E^{\overline{\overline{wns}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns}, \Omega} = 0.$$

We can derive geometric density approximations using theorem G[3,(3,0),0] [82]

(2.90) $$\langle \nabla f \rangle_{\Omega_\iota,\Omega} = \nabla \langle f \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in \mathfrak{I}_{c\iota}} \langle \mathbf{n}_\iota f \rangle_{\Omega_\kappa,\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}}.$$

Setting $f = 1$ yields

(2.91) $$0 = \nabla \epsilon^\iota + \sum_{\kappa \in \mathfrak{I}_{c\iota}} \langle \mathbf{n}_\iota \rangle_{\Omega_\kappa,\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}}.$$

Theorem T[3,(3,0),0] [82] is

(2.92) $$\left\langle \frac{\partial f}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \frac{\partial}{\partial t} \langle f \rangle_{\Omega_\iota,\Omega} - \sum_{\kappa \in \mathfrak{I}_{c\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa f \rangle_{\Omega_\kappa,\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}},$$

and for $f = 1$

(2.93) $$0 = \frac{\partial \epsilon^\iota}{\partial t} - \sum_{\kappa \in \mathfrak{I}_{c\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa \rangle_{\Omega_\kappa,\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}}.$$

Combining Eqn (2.93) with the dot product of $\mathbf{v}^{\overline{s}}$ and Eqn (2.91) gives

(2.94) $$\frac{\mathrm{D}^{\overline{s}} \epsilon^\iota}{\mathrm{D}t} = \sum_{\kappa \in \mathfrak{I}_{c\iota}} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}}.$$

From Eqn (2.94) we obtain for the w phase, since $\mathbf{n}_w = -\mathbf{n}_s$ on the ws interface

(2.95) $$\frac{\mathrm{D}^{\overline{s}} \epsilon^w}{\mathrm{D}t} = -\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} + \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega},$$

while a corresponding expression for the s phase may be written

(2.96) $$\frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} = \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} + \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ns},\Omega}.$$

For this equation, we make the approximation that

(2.97) $$\chi_{ws}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} \approx \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega}.$$

Thus substitution of Eqn (2.97) into Eqn (2.95) yields:

$$
(2.98) \qquad \frac{D^{\bar{s}}\epsilon^w}{Dt} + \chi_{ws}^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt} \approx \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wn},\Omega}.
$$

The following geometric approximation can be derived in a similar manner using gradient and transport theorems for the appropriate domains.

$$
(2.99) \quad \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \approx (\epsilon^{ws} + \epsilon^{ns})\frac{D^{\bar{s}}\chi_{ws}^{ss}}{Dt}
$$

$$
+\chi_{ns}^{ss}\nabla\cdot(\epsilon^{ws}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ws},\bar{s}} - \chi_{ws}^{ss}\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ns},\bar{s}}
$$

$$
+\chi_{ns}^{ss}\epsilon^{ws}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ws}}} - \chi_{ws}^{ss}\epsilon^{ns}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ns}}}.
$$

In obtaining this equation, use has been made of Secondary restriction 3 stipulating that the curvature of the solid grain surface is independent of the fluid phase it contacts.

Applying all of the above mentioned restrictions and approximations outlined in this section to Eqn (2.77), the SEI may be written as follows:

$$
(2.100) \quad \sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{\epsilon^\iota}{\theta}\left(\mathbf{t}^{\bar{\iota}} + p^\iota\mathbf{I}\right):\mathbf{d}^{\bar{\iota}} + \frac{\epsilon^s}{\theta}\left(\mathbf{t}^{\bar{s}} - \mathbf{t}^s\right):\mathbf{d}^{\bar{s}} + \frac{\epsilon^{wn}}{\theta}\left[\mathbf{t}^{\overline{\overline{wn}}} - \gamma^{wn}\left(\mathbf{I} - \mathbf{G}^{wn}\right)\right]:\mathbf{d}^{\overline{\overline{wn}}}
$$

$$
+\frac{1}{\theta}\left[\epsilon^{ws}\mathbf{t}^{\overline{\overline{ws}}} - \epsilon^{ws}\gamma^{ws}\left(\mathbf{I} - \mathbf{G}^{ws}\right)\right.
$$

$$
\left.-\chi_{ns}^{ss}\left(\gamma_{ws}^{wns} + \gamma_{wn}^{wns}\cos\varphi^{\overline{ws},\overline{wn}} - \gamma_{ns}^{wns} + \gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right)\mathbf{G}^{ss}\right]:\mathbf{d}^{\overline{\overline{ws}}}
$$

$$
+\frac{1}{\theta}\left[\epsilon^{ns}\mathbf{t}^{\overline{\overline{ns}}} - \epsilon^{ns}\gamma^{ns}\left(\mathbf{I} - \mathbf{G}^{ns}\right)\right.
$$

$$
\left.+\chi_{ws}^{ss}\left(\gamma_{ws}^{wns} + \gamma_{wn}^{wns}\cos\varphi^{\overline{ws},\overline{wn}} - \gamma_{ns}^{wns} + \gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right)\mathbf{G}^{ss}\right]:\mathbf{d}^{\overline{\overline{ns}}}
$$

$$
+\frac{\epsilon^{wns}}{\theta}\left[\mathbf{t}^{\overline{\overline{wns}}} + \gamma^{wns}\left(\mathbf{I} - \mathbf{G}^{wns}\right)\right]:\mathbf{d}^{\overline{\overline{wns}}}
$$

$$
-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta}\left(\epsilon^\iota\rho^\iota\mathbf{g}^{\bar{\iota}} + \epsilon^\iota\rho^\iota\nabla\left(\psi^{\bar{\iota}} + \mu^{\bar{\iota}}\right) - \nabla\left(\epsilon^\iota p^\iota\right) + \sum_{\kappa\in\mathcal{I}_{c\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right)\cdot\mathbf{v}^{\bar{\iota},\bar{s}}
$$

$$
-\frac{1}{\theta}\left(\nabla\cdot\left[\epsilon^{wn}\gamma^{wn}\left(\mathbf{I} - \mathbf{G}^{wn}\right)\right] + \sum_{\kappa\in\mathcal{I}_{cwn}}\overset{\kappa\to wn}{\mathbf{T}}\right)\cdot\mathbf{v}^{\overline{wn},\bar{s}}
$$

$$-\frac{1}{\theta}\Bigg(\nabla\cdot[\epsilon^{ws}\gamma^{ws}(\mathbf{I}-\mathbf{G}^{ws})]+\sum_{\kappa\in\mathcal{J}_{cws}}\overset{\kappa\to ws}{\mathbf{T}}+\chi^{ss}_{ns}\Big(\gamma^{wns}_{ws}+\gamma^{wns}_{wn}\cos\varphi^{\overline{ws,wn}}$$

$$-\gamma^{wns}_{ns}+\gamma^{wns}\kappa^{\overline{\overline{wns}}}_{G}\Big)\nabla\cdot(\epsilon^{ws}\mathbf{G}^{ss})\Bigg)\cdot\mathbf{v}^{\overline{ws,\bar{s}}}$$

$$-\frac{1}{\theta}\Bigg(\nabla\cdot[\epsilon^{ns}\gamma^{ns}(\mathbf{I}-\mathbf{G}^{ns})]+\sum_{\kappa\in\mathcal{J}_{cns}}\overset{\kappa\to ns}{\mathbf{T}}-\chi^{ss}_{ws}\Big(\gamma^{wns}_{ws}+\gamma^{wns}_{wn}\cos\varphi^{\overline{ws,wn}}$$

$$-\gamma^{wns}_{ns}+\gamma^{wns}\kappa^{\overline{\overline{wns}}}_{G}\Big)\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ss})\Bigg)\cdot\mathbf{v}^{\overline{ns,\bar{s}}}$$

$$-\frac{1}{\theta}\Bigg(-\nabla\cdot[\epsilon^{wns}\gamma^{wns}(\mathbf{I}-\mathbf{G}^{wns})]-\sum_{\kappa\in\mathcal{J}_{cwns}}\overset{wns\to\kappa}{\mathbf{T}}\Bigg)\cdot\mathbf{v}^{\overline{wns,\bar{s}}}$$

$$-\frac{1}{\theta}\Big\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\cdot\Big(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\Big)\Big\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\theta}\left(\frac{\mathrm{D}^{\bar{s}}\epsilon^w}{\mathrm{D}t}+\chi^{ss}_{ws}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}\right)(p^{wn}_w-p^{wn}_n-\gamma^{wn}J^{wn}_w)$$

$$-\frac{1}{\theta}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}\Big[(p^{ws}_w+\gamma^{ws}J^{ws}_s)\chi^{ss}_{ws}+(p^{ns}_n+\gamma^{ns}J^{ns}_s)\chi^{ss}_{ns}+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}}$$

$$+\Big(\gamma^{wns}\kappa^{\overline{\overline{wns}}}_{N}-\gamma^{wns}_{wn}\sin\varphi^{\overline{ws,wn}}\Big)\frac{\epsilon^{wns}}{\epsilon^{ss}}\Big]$$

$$-\frac{1}{\theta}\epsilon^{ss}\frac{\mathrm{D}^{\bar{s}}\chi^{ss}_{ws}}{\mathrm{D}t}\Big(\gamma^{wns}_{ws}+\gamma^{wns}_{wn}\cos\varphi^{\overline{ws,wn}}-\gamma^{wns}_{ns}+\gamma^{wns}\kappa^{\overline{\overline{wns}}}_{G}\Big)=\Lambda\geq0.$$

This equation has been arranged such that it is a sum of products of fluxes (the first factor in each summed product) and forces (the second factor in each summed product). Knowledge that the forces are zero at equilibrium comes from the derived thermodynamic equilibrium conditions [137] summarized here in §2.3.

2.8. Closure Relations

Eqn (2.100) is a formal constraint on the form of the closure relations, but it does not provide the precise form of the needed closure relations. The approximations and restrictions detailed in §2.6 provide additional guidance on how Eqn (2.100) will be used to provide closure relation approximations and ultimately the form of the closed models. Based upon Approximation 2, that the fluxes are zero order in the rate of strain

tensors, the following approximations are obtained for the stress tensors since the factors multiplying the rates of strain must be zero

$$(2.101) \qquad \mathbf{t}^{\overline{\overline{w}}} + p^w \mathbf{I} = 0,$$

$$(2.102) \qquad \mathbf{t}^{\overline{\overline{n}}} + p^n \mathbf{I} = 0,$$

$$(2.103) \qquad \mathbf{t}^{\overline{\overline{s}}} - \mathbf{t}^s = 0,$$

$$(2.104) \qquad \mathbf{t}^{\overline{\overline{wn}}} - \gamma^{wn} \left(\mathbf{I} - \mathbf{G}^{wn} \right) = 0,$$

$$(2.105) \qquad \mathbf{t}^{\overline{\overline{ws}}} - \gamma^{ws} \left(\mathbf{I} - \mathbf{G}^{ws} \right) = 0,$$

$$(2.106) \qquad \mathbf{t}^{\overline{\overline{ns}}} - \gamma^{ns} \left(\mathbf{I} - \mathbf{G}^{ns} \right) = 0,$$

$$(2.107) \qquad \mathbf{t}^{\overline{\overline{wns}}} + \gamma^{wns} \left(\mathbf{I} - \mathbf{G}^{wns} \right) = 0.$$

The zero-order approximations for these fluxes model the flow as being macroscopically inviscid, which is reasonable for many porous medium systems. In addition, stress tensors for the interfaces and the common curve depend only upon interfacial, or curvilinear, tensions and the orientation of the surfaces and curve. If the macroscale rate of strain tensors are not close to zero, a higher order approximation could be posited. When highly resolved microscale descriptions of a system are available, the adequacy of this approximation can be evaluated. For most environmental systems, the closure relations noted above will be adequate.

Also by Approximation 2, the entropy inequality will be linear in each of the force terms. Therefore, closure Eqns (2.101)–(2.107) and requiring linearity, Eqn (2.100) simplifies to

$$(2.108)$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{1}{\theta} \left(\epsilon^\iota \rho^\iota \mathbf{g}^{\overline{\iota}} + \epsilon^\iota \rho^\iota \nabla \left(\psi^{\overline{\iota}} + \mu^{\overline{\iota}} \right) - \nabla \left(\epsilon^\iota p^\iota \right) + \sum_{\kappa \in \mathcal{I}_{c\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \right) \cdot \mathbf{v}^{\overline{\iota}, \overline{s}}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left(\nabla\cdot[\epsilon^\iota\gamma^\iota\left(\mathbf{I}-\mathbf{G}^\iota\right)]+\sum_{\kappa\in\mathcal{I}_{C\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right)\cdot\mathbf{v}^{\overline{\iota,\overline{s}}}$$

$$-\frac{1}{\theta}\left(-\nabla\cdot[\epsilon^{wns}\gamma^{wns}\left(\mathbf{I}-\mathbf{G}^{wns}\right)]-\sum_{\kappa\in\mathcal{I}_{cwns}}\overset{wns\to\kappa}{\mathbf{T}}\right)\cdot\mathbf{v}^{\overline{wns,\overline{s}}}$$

$$+\frac{1}{\theta}\left(\frac{\mathrm{D}^{\overline{s}}\epsilon^w}{\mathrm{D}t}+\chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}\right)(p_w^{wn}-p_n^{wn}-\gamma^{wn}J_w^{wn})$$

$$-\frac{1}{\theta}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}\Big[\left(p_w^{ws}+\gamma^{ws}J_s^{ws}\right)\chi_{ws}^{ss}+\left(p_n^{ns}+\gamma^{ns}J_s^{ns}\right)\chi_{ns}^{ss}+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}}$$

$$+\left(\gamma^{wns}\kappa_N^{\overline{\overline{wns}}}-\gamma_{wn}^{wns}\sin\varphi^{\overline{\overline{ws,wn}}}\right)\frac{\epsilon^{wns}}{\epsilon^{ss}}\Big]$$

$$-\frac{1}{\theta}\epsilon^{ss}\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}\left(\gamma_{ws}^{wns}+\gamma_{wn}^{wns}\cos\varphi^{\overline{\overline{ws,wn}}}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right)=\Lambda\geq0.$$

This equation is a sum of products of independent fluxes with independent forces where, in general, each flux is a linear function of all the forces and each force is zero at equilibrium. The non-negative property of this equation requires that each force will also be zero at equilibrium.

Consider the flux terms from Eqn (2.108) that form products with the relative velocities, $\mathbf{v}^{\overline{\iota,\overline{s}}}$. A cross-coupled flux approximation can be written by expressing the flux as a linear function of both its conjugate force and the other velocity forces. The linearized expression for the force is then

$$(2.109)\quad \epsilon^\iota\rho^\iota\mathbf{g}^{\overline{\iota}}+\epsilon^\iota\rho^\iota\nabla\left(\psi^{\overline{\iota}}+\mu^{\overline{\iota}}\right)-\nabla\left(\epsilon^\iota p^\iota\right)+\sum_{\kappa\in\mathcal{I}_{C\iota}}\overset{\kappa\to\iota}{\mathbf{T}}=-\sum_{\kappa\in\mathcal{I}}\hat{\mathbf{R}}_\kappa^\iota\cdot\mathbf{v}^{\overline{\kappa,\overline{s}}},\qquad\iota\in\mathcal{I}_{\mathrm{f}},$$

where $\hat{\mathbf{R}}_\kappa^\iota$ are second-rank, symmetric resistance tensors.

Similarly for momentum transfer of the ι interface a linear cross-coupled approximation can be formulated from the flux that multiplies the force term, $\mathbf{v}^{\overline{\iota,\overline{s}}}$, and the connected entities as

$$(2.110)\qquad\nabla\cdot[\epsilon^\iota\gamma^\iota\left(\mathbf{I}-\mathbf{G}^\iota\right)]+\sum_{\kappa\in\mathcal{I}_{C\iota}}\overset{\kappa\to\iota}{\mathbf{T}}=-\sum_{\kappa\in\mathcal{I}}\hat{\mathbf{R}}_\kappa^\iota\cdot\mathbf{v}^{\overline{\kappa,\overline{s}}},\qquad\iota\in\mathcal{I}_{\mathrm{I}}.$$

Similarly for momentum transfer to the *wns* common curve

$$(2.111) \qquad \nabla \cdot \left[\epsilon^{wns} \gamma^{wns} \left(\mathbf{I} - \mathbf{G}^{wns} \right) \right] + \sum_{\kappa \in \mathcal{J}_{cwns}} {}^{wns \rightarrow \kappa} \mathbf{T} = \sum_{\kappa \in \mathcal{J}} \hat{\mathbf{R}}_\kappa^{wns} \cdot \mathbf{v}^{\overline{\kappa}, \overline{s}}.$$

When the superscripts and subscripts on the resistance tensors, $\hat{\mathbf{R}}_\kappa^\iota$, differ, the tensor accounts for cross-coupling. The resistance tensors depend upon the morphology of the system and are assumed to be functions of the independent variables around which the linearizations were not performed such as the specific measures of the entities, volume fractions, interfacial areas, and the common curve length. The factors containing the geometric tensors, $\mathbf{G}^\iota$, that multiply the divergence of the interfacial tensions are the macroscale mechanism for including the particular orientations that the interfaces and common curves have at the microscale and in particular the microscopic gradients in interfacial tension will only drive flow in directions tangent to the surface [93].

The material derivative of the solid-phase fraction in Eqn (2.108) is considered a flux term for a conjugate force term that vanishes at equilibrium. The linearized force neglecting any coupling is expressed as

$$(2.112) \quad -\frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} = \frac{1}{\hat{c}^s} \Bigg[\left(p_w^{ws} + \gamma^{ws} J_s^{ws} \right) \chi_{ws}^{ss} + \left(p_n^{ns} + \gamma^{ns} J_s^{ns} \right) \chi_{ns}^{ss}$$

$$+ \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}} + \left(\gamma^{wns} \kappa_N^{\overline{\overline{wns}}} - \gamma_{wn}^{wns} \sin \varphi^{\overline{ws, wn}} \right) \frac{\epsilon^{wns}}{\epsilon^{ss}} \Bigg],$$

where $\hat{c}^s$ is a non-negative compressibility parameter. Eqn (2.112) is an expression of the dynamic relationship among the normal forces acting on the solid surface.

The material derivative of the wetting-phase fraction in combination with the material derivative of the solid-phase fraction appears in Eqn (2.108) as a flux term multiplying a force related to capillary effects at the fluid-fluid interface. The linearized force without considering cross-coupling is

$$\frac{\mathrm{D}^{\overline{s}} \epsilon^w}{\mathrm{D}t} + \chi_{ws}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} = \epsilon \frac{\mathrm{D}^{\overline{s}} s^w}{\mathrm{D}t} + \left(s^w - \chi_{ws}^{ss} \right) \frac{\mathrm{D}^{\overline{s}} \epsilon}{\mathrm{D}t}$$

$$(2.113) \qquad\qquad = \frac{1}{\hat{c}^{wn}}\left(p_w^{wn} - p_n^{wn} - \gamma^{wn}J_w^{wn}\right).$$

The product of the mean macroscale curvature, J_w^{wn}, and the interfacial tension, γ^{wn}, is the macroscale capillary pressure, such that Eqn (2.113) indicates a disequilibrium in capillary forces will cause a change in saturation to occur.

The final grouping of geometric terms in Eqn (2.108) can be identified as a flux term that multiplies a force that can be shown to be zero at equilibrium. Thus the linearized expression for the flux can be written as:

$$(2.114) \qquad -\frac{\mathrm{D}^{\bar{s}}\chi_{ws}^{ss}}{\mathrm{D}t} = \frac{1}{\hat{c}^{wns}}\left(\gamma_{ws}^{wns} + \gamma_{wn}^{wns}\cos\varphi^{\overline{ws,wn}} - \gamma_{ns}^{wns} + \gamma^{wns}\kappa_G^{\overline{wns}}\right).$$

This equation indicates a disequilibrium in the force balance at the common curve tangent to the solid surface, commonly referred to as spreading pressure [93], will cause a change in the fraction of the solid surface in contact with the wetting fluid.

2.9. Model Formulation

The purpose of this section is to produce a set of complete, closed, and solvable models in terms of measurable parameters and macroscale variables. The models are based upon the conservation equations given in §2.4, the restrictions and approximations summarized in §2.6, and the closure relations given in §2.8.

The steps involved in producing the target models include (1) specification of the appropriate set of conservation equations, (2) application of the restrictions and approximations, (3) inclusion of the closure relations, (4) determination of additional closure relations needed to close the system, and (5) assembling of the individual components into a closed model.

2.9.1. Full Model Equations and Unknowns. Using the restrictions and approximations presented in §2.6, for the case of two-fluid-phase flow, the following conservation

of mass equations apply

$$(2.115) \qquad \frac{\mathrm{D}^{\bar{\iota}}(\epsilon^{\iota}\rho^{\iota})}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}} = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}},$$

as do the conservation of momentum equations

$$(2.116) \qquad \frac{\mathrm{D}^{\bar{\iota}}(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}})}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}} - \nabla{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\bar{\bar{\iota}}}\right) - \epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\bar{\iota}} - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\iota}} \overset{\kappa\to\iota}{\mathbf{T}} = 0 \quad \text{for } \iota \in \mathfrak{I}.$$

Recalling the constitutive equations resulting from the SEI, Eqns (2.109)–(2.111), together with Approximations 5 and 8, and Eqns (2.101)–(2.107), the conservation of momentum equations in Eqn (2.116) may be expressed as

$$(2.117) \qquad \sum_{\kappa\in\mathfrak{I}} \hat{\mathbf{R}}^{\iota}_{\kappa}{\cdot}\mathbf{v}^{\overline{\kappa,\bar{s}}} = -\epsilon^{\iota}\rho^{\iota}\nabla\left(\psi^{\bar{\iota}} + \mu^{\bar{\iota}}\right) \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{f}},$$

$$(2.118) \qquad \hat{\mathbf{R}}^{\iota}_{\iota}{\cdot}\mathbf{v}^{\overline{\iota,\bar{s}}} = - \sum_{(\kappa\in\mathfrak{I})\cap(\kappa\neq\iota)} \hat{\mathbf{R}}^{\iota}_{\kappa}{\cdot}\mathbf{v}^{\overline{\kappa,\bar{s}}} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}$$

and

$$(2.119) \qquad \hat{\mathbf{R}}^{wns}_{wns}{\cdot}\mathbf{v}^{\overline{wns,\bar{s}}} = - \sum_{\kappa\in\left(\mathfrak{I}_{\mathrm{P}}\cup\mathfrak{I}_{\mathrm{I}}\right)} \hat{\mathbf{R}}^{wns}_{\kappa}{\cdot}\mathbf{v}^{\overline{\kappa,\bar{s}}}.$$

The assumption is made that the distribution of the phases within the volume is uniform enough that $\nabla\psi^{\bar{\iota}} = -\mathbf{g}^{\bar{\iota}}$ for all ι, thus the variables $\psi^{\bar{\iota}}$ do not have to be considered as unknowns; this assumption will not hold for all systems. Allowing for this assumption, Eqn (2.115) and Eqns (2.117)–(2.119) comprise a system of 21 scalar equations, three for mass and 18 for momentum—neglecting the solid phase, with a corresponding set of 29 unknowns:

$$(2.120) \qquad \{\epsilon^{w}, \epsilon^{n}, \epsilon^{s}, \rho^{w}, \rho^{n}, \rho^{s}, \mathbf{v}^{\bar{s}}, \mathbf{v}^{\overline{w,\bar{s}}}, \mathbf{v}^{\overline{n,\bar{s}}}, \mathbf{v}^{\overline{wn,\bar{s}}}, \mathbf{v}^{\overline{ws,\bar{s}}}, \mathbf{v}^{\overline{ns,\bar{s}}}, \mathbf{v}^{\overline{wns,\bar{s}}}, \mu^{\bar{w}}, \mu^{\bar{n}}\}.$$

In addition to the equations indicated so far, three additional dynamic equations that resulted from the entropy inequality, namely Eqns (2.112)–(2.114), are available. These

equations, however, add 24 additional variables to the list of unknowns. In addition to the variables that appear in the equations identified so far, ϵ^{wn} is included in anticipation of the fact that it will arise subsequently. Thus, the 25 additional variables are

$$(2.121) \quad \{\epsilon, \epsilon^{ws}, \epsilon^{wn}, \epsilon^{wns}, \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}}, p_w^{ws}, p_w^{wn}, p_n^{ns}, p_n^{wn}, \gamma^{ws}, \gamma^{ns}, \gamma^{wn}, \gamma_{wn}^{wns},$$

$$\gamma_{ws}^{wns}, \gamma_{ns}^{wns}, \gamma^{wns}, s^w, \chi_{ws}^{ss}, \chi_{ns}^{ss}, J_s^{ws}, J_s^{ns}, J_w^{wn}, \kappa_N^{\overline{wns}}, \kappa_G^{\overline{wns}}, \varphi^{\overline{ws},\overline{wn}}\}.$$

The counts of equations and unknown variables stand at 24 and 54, respectively, so that 30 additional constraints are needed to close the system.

2.9.2. Full Model Closure Relations. In this section the relations, at least as functional dependences, that are employed in closing the full model are provided. These relations are of three types: (1) exact identities; (2) approximate equations of state; and (3) approximate dynamic relations. The latter two of these types are subject to improvement depending on data and insight.

2.9.2.1. *Identities.* First, the specific entity measures of the phases can be eliminated because they are related to the porosity and wetting-phase saturation according to

$$(2.122) \qquad\qquad\qquad \epsilon^s = 1 - \epsilon,$$

$$(2.123) \qquad\qquad\qquad \epsilon^w = s^w \epsilon$$

and

$$(2.124) \qquad\qquad\qquad \epsilon^n = (1 - s^w)\epsilon.$$

Additionally, the solid surface area fractions must sum to 1, so one of these may be eliminated using the identity

$$(2.125) \qquad\qquad\qquad \chi_{ns}^{ss} = 1 - \chi_{ws}^{ss}.$$

Making use of these four identities, 26 closure constraints are still required.

2.9.2.2. *Equations of State.* The macroscale equations of state that will be employed here make use of Approximation 6, that the fluctuation integrals can be ignored. Also recall the restriction of this study to isothermal systems. The first two equations used follow directly from the Gibbs-Duhem equation for the fluid phases and relate the chemical potential to the pressure according to

$$(2.126) \qquad \left(\frac{\partial \mu^{\bar{\iota}}}{\partial p^{\iota}} \right)_{\theta^{\bar{\iota}}} = \frac{1}{\rho^{\iota}} \quad \text{for } \iota \in \mathcal{I}_{\text{f}}.$$

These two equations introduce the new pressure variables as replacements for chemical potentials and therefore they do not reduce the number of closure relations needed. However, if the surface averages of pressure are approximated by the volume-average pressures, then surface averaged pressures can be eliminated using

$$(2.127) \qquad p_w^{ws} = p_w^{wn} = p^w$$

and

$$(2.128) \qquad p_n^{ns} = p_n^{wn} = p^n.$$

Because of Secondary restriction 3, $J_s^{\iota s} = J_s^{ss}$.

Equations of state can be introduced to relate densities to effective pressures

$$(2.129) \qquad \hat{\beta}^{\iota} = \frac{1}{\rho^{\iota}} \left(\frac{\partial \rho^{\iota}}{\partial p^{\iota}} \right)_{\theta^{\bar{\iota}}} \quad \text{for } \iota \in \mathcal{I}_{\text{f}},$$

$$(2.130) \qquad \hat{\beta}^{s} = -\frac{1}{\rho^{s}} \left(\frac{\partial \rho^{s}}{\partial \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}}} \right)_{\theta^{\bar{s}}},$$

where $\hat{\beta}^{\iota}$ is the fluid compressibility. Additionally, the bulk compressibility or bulk modulus, $\hat{\alpha}^{\mathrm{b}}$, relates the change in porosity with pressure and is defined by

$$(2.131) \qquad \hat{\alpha}^{\mathrm{b}} = -\frac{1}{(1-\epsilon)\rho^s}\left(\frac{\partial[(1-\epsilon)\rho^s]}{\partial\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}}}\right)_{\theta^{\overline{\overline{s}}}}.$$

In considering massless, isothermal interfaces and common curve, the equations of state for the tensions associated with these entities are simply that the interfacial tensions are constants. The macroscale tensions corresponding to a surface are also considered to have the same value whether averaged over the interface or just over the common curve. Thus six values of interfacial tension and one value of the common curve tension are specified, reducing the number of needed closure relations by seven.

Finally, constitutive equations are proposed for the fluid-fluid interfacial curvature, the normal and geodesic curvatures, and the contact angle. These quantities are thermodynamic properties of the system. The four EOS employed are

$$(2.132) \qquad \gamma^{wn} J_w^{wn} = p^c(s^w, \epsilon^{wn}, \chi_{ws}^{ss}),$$

$$(2.133) \qquad \kappa_N^{\overline{\overline{wns}}} = \kappa_N^{\overline{\overline{wns}}}(s^w, \chi_{ws}^{ss}, \epsilon^{wns}),$$

$$(2.134) \qquad \kappa_G^{\overline{\overline{wns}}} = \kappa_G^{\overline{\overline{wns}}}(s^w, \chi_{ws}^{ss}, \epsilon^{wns})$$

and

$$(2.135) \qquad \varphi^{\overline{\overline{ws,wn}}} = \varphi^{\overline{\overline{ws,wn}}}(s^w, \epsilon^{wn}, \chi_{ws}^{ss}).$$

The first of these relations defines the equilibrium capillary pressure. The hypothesized functional dependences must be obtained experimentally and are subject to revision. These four state equations bring the total number invoked here to 21 and reduce the number of closure conditions still needed to five. These remaining conditions will be obtained as dynamic constraints.

2.9.2.3. *Dynamic Conditions.* Approximate relations for evolution of the geometric variables have been obtained through the application of time and space averaging theorems [93]. This work provides three equations while introducing no additional unknown variables. The geometric equations are

$$
(2.136) \quad \frac{\mathrm{D}^{\overline{s}}(\epsilon^{ws} + \epsilon^{ns})}{\mathrm{D}t} - J_s^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} \approx -\nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\overline{s}} - \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\overline{\overline{ws}}}
$$
$$
-\nabla \cdot (\epsilon^{ns} \mathbf{G}^{ns}) \cdot \mathbf{v}^{\overline{ns},\overline{s}} - \epsilon^{ns} \mathbf{G}^{ns} : \mathbf{d}^{\overline{\overline{ns}}},
$$

$$
(2.137) \quad \frac{\mathrm{D}^{\overline{s}} \epsilon^{wn}}{\mathrm{D}t} - \epsilon^{ss} \cos \varphi^{\overline{\overline{ws,wn}}} \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t} - J_w^{wn} \frac{\mathrm{D}^{\overline{s}} \epsilon^w}{\mathrm{D}t}
$$
$$
- \left(\chi_{ws}^{ss} J_w^{wn} - \frac{\epsilon^{wns}}{\epsilon^{ss}} \sin \varphi^{\overline{\overline{ws,wn}}} \right) \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t}
$$
$$
\approx \chi_{ns}^{ss} \cos \varphi^{\overline{\overline{ws,wn}}} \left(\nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\overline{s}} + \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\overline{\overline{ws}}} \right)
$$
$$
- \chi_{ws}^{ss} \cos \varphi^{\overline{\overline{ws,wn}}} \left(\nabla \cdot (\epsilon^{ns} \mathbf{G}^{ns}) \cdot \mathbf{v}^{\overline{ns},\overline{s}} + \epsilon^{ns} \mathbf{G}^{ns} : \mathbf{d}^{\overline{\overline{ns}}} \right)
$$
$$
- \nabla \cdot (\epsilon^{wn} \mathbf{G}^{wn}) \cdot \mathbf{v}^{\overline{wn},\overline{s}} - \epsilon^{wn} \mathbf{G}^{wn} : \mathbf{d}^{\overline{\overline{wn}}}
$$

and

$$
(2.138) \quad \frac{\mathrm{D}^{\overline{s}} \epsilon^{wns}}{\mathrm{D}t} + \kappa_G^{\overline{\overline{wns}}} (\epsilon^{ws} + \epsilon^{ns}) \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t} + \frac{\epsilon^{wns}}{\epsilon^{ss}} \kappa_N^{\overline{\overline{wns}}} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t}
$$
$$
\approx -\kappa_G^{\overline{\overline{wns}}} \chi_{ns}^{ss} \nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\overline{s}} - \kappa_G^{\overline{\overline{wns}}} \chi_{ns}^{ss} \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\overline{\overline{ws}}}
$$
$$
+ \kappa_G^{\overline{\overline{wns}}} \chi_{ws}^{ss} \nabla \cdot (\epsilon^{ns} \mathbf{G}^{ns}) \cdot \mathbf{v}^{\overline{ns},\overline{s}} + \kappa_G^{\overline{\overline{wns}}} \chi_{ws}^{ss} \epsilon^{ns} \mathbf{G}^{ns} : \mathbf{d}^{\overline{\overline{ns}}}
$$
$$
- \nabla \cdot (\epsilon^{wns} \mathbf{G}^{wns}) \cdot \mathbf{v}^{\overline{wns},\overline{s}} - \epsilon^{wns} \mathbf{G}^{wns} : \mathbf{d}^{\overline{\overline{wns}}}.
$$

Although ϵ^{ns} has not appeared in the list of unknowns, it is derivable from χ_{ws}^{ss} and ϵ^{ws}. In fact, it is more convenient to replace ϵ^{ws} with the total solid specific surface area, ϵ^{ss}. Then $\epsilon^{ws} = \chi_{ws}^{ss} \epsilon^{ss}$ and $\epsilon^{ns} = (1 - \chi_{ws}^{ss}) \epsilon^{ss}$.

The last two dynamic conditions to be invoked involve the solid phase velocity. The divergence of the solid velocity, $\nabla \cdot \mathbf{v}^{\overline{s}} = \mathbf{d}^{\overline{\overline{s}}} : \mathbf{I}$ is related to the material derivative of the mass of phase s per total volume through the conservation of mass equation. Therefore $\nabla \cdot \mathbf{v}^{\overline{s}}$ will be retained in the analysis whenever solid deformation is being considered and will be treated as an additional variable. However, whenever the undifferentiated solid velocity appears multiplying a gradient, that term will be considered small. Therefore, for example,

$$(2.139) \qquad \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \approx \frac{\partial}{\partial t}.$$

Although the divergence of the solid velocity is significant in comparison to other terms in the analysis, neglect of the solid velocity itself provides three dynamic conditions

$$(2.140) \qquad \mathbf{v}^{\overline{s}} = 0,$$

with the divergence of velocity, $\mathbf{d}^{\overline{\overline{s}}} : \mathbf{I}$, one additional variable. Thus the problem statement is complete, though somewhat complex.

2.9.3. Closed Full Model. Based on the closure relations employed above, some of the variables listed in Eqns (2.120) and (2.121) can be explicitly eliminated from further consideration. It is convenient to restate the full problem here in terms of the variables that require attention. The heart of a porous media model is the mass conservation equations. For a fluid phase, Eqn (2.115) can be rearranged to

$$(2.141) \qquad \frac{\partial(\epsilon s^\iota \rho^\iota)}{\partial t} + \nabla \cdot (\epsilon s^\iota \rho^\iota \mathbf{v}^{\iota,\overline{s}}) + \nabla \cdot (\epsilon s^\iota \rho^\iota \mathbf{v}^{\overline{s}}) = 0 \quad \text{for } \iota \in \mathcal{I}_\mathrm{f}.$$

The constitutive relations given by Eqns (2.129)–(2.131) can be used along with Eqn (2.139) to obtain

$$(2.142) \quad \epsilon \frac{\partial s^\iota}{\partial t} + s^\iota \left(\left[\hat{\alpha}^\mathrm{b} + (1-\epsilon)\hat{\beta}^s \right] \frac{\partial \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}}}{\partial t} + \epsilon \hat{\beta}^\iota \frac{\partial p^\iota}{\partial t} \right)$$

$$+\nabla\cdot(\epsilon s^\iota \mathbf{v}^{\overline{\iota,\overline{s}}}) = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{f}},$$

where the solid-phase mass conservation equation has been used to eliminate $\nabla\cdot\mathbf{v}^{\overline{s}}$, and $\epsilon s^\iota \mathbf{v}^{\overline{\iota,\overline{s}}}\cdot\nabla\rho^\iota$ has been assumed to be negligible in comparison to the other terms in the equation. The list of 31 unknowns that must be monitored along with the problem description is

$$(2.143) \quad \{s^w, \epsilon, \mathbf{v}^{\overline{w,\overline{s}}}, \mathbf{v}^{\overline{n,\overline{s}}}, \mathbf{v}^{\overline{wn,\overline{s}}}, \mathbf{v}^{\overline{ws,\overline{s}}}, \mathbf{v}^{\overline{ns,\overline{s}}}, \mathbf{v}^{\overline{wns,\overline{s}}}, \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}}, p^w, p^n,$$

$$\epsilon^{wn}, \chi_{ws}^{ss}, \epsilon^{ss}, \epsilon^{wns}, \gamma^{wn}J_w^{wn}, \kappa_N^{\overline{\overline{wns}}}, \kappa_G^{\overline{\overline{wns}}}, \varphi^{\overline{ws,wn}}\}.$$

These variables are modeled using 31 equations consisting of: two equations of mass conservation given in Eqn (2.142); 18 momentum Eqns (2.117)–(2.119); three conditions from the EI Eqns (2.112)–(2.114); five EOS Eqn (2.131) and Eqns (2.132)–(2.135); and three dynamic conditions Eqns (2.136)–(2.138). Note that all material derivatives relative to the s phase will be changed to partial time derivatives according to Eqn (2.140). Thus the general two-phase model with interfaces and a common curve has been closed in a general functional form using the EI.

2.9.4. Model Formulation Neglecting Common Curves. The general model developed above can be simplified by neglecting the properties and dynamics of the common curve. These restrictions are in addition to the restrictions and approximations of §2.6. If the effects of the common curve are neglected, as is done in standard models, the model formulation of §2.9.3 will simplify. The list of 31 unknowns is reduced to 25, namely

$$(2.144) \quad \{s^w, \epsilon, \mathbf{v}^{\overline{w,\overline{s}}}, \mathbf{v}^{\overline{n,\overline{s}}}, \mathbf{v}^{\overline{wn,\overline{s}}}, \mathbf{v}^{\overline{ws,\overline{s}}}, \mathbf{v}^{\overline{ns,\overline{s}}}, \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}}, p^w, p^n, \epsilon^{wn}, \chi_{ws}^{ss}, \epsilon^{ss},$$

$$\gamma^{wn}J_w^{wn}, \varphi^{\overline{ws,wn}}\},$$

where the relative velocity of the common curve, $\mathbf{v}^{\overline{wns,\overline{s}}}$, the geometric density of the common curve, ϵ^{wns}, and the normal and geodesic curvatures, $\kappa_N^{\overline{\overline{wns}}}$ and $\kappa_G^{\overline{\overline{wns}}}$, have all

been discarded. The conservation of momentum equations for the common curve is no longer necessary to describe the system of interest. Also, the dynamic condition, Eqn (2.138), is no longer relevant. Because the normal and geodesic curvatures are eliminated from the list of unknowns, the EOS for these variables, Eqn (2.133) and Eqn (2.134), are unnecessary. The form of Eqn (2.114) will change slightly when the common curve is neglected with the new form being

$$(2.145) \qquad \gamma_{ws}^{wns} + \gamma_{wn}^{wns} \cos \varphi^{\overline{\overline{ws,wn}}} - \gamma_{ns}^{wns} = -\hat{c}^{wns} \frac{\mathrm{D}^{\bar{s}} \chi_{ws}^{ss}}{\mathrm{D}t}.$$

Eqn (2.145) still indicates a disequilibrium in the force balance at the common curve, but since the common curve properties are not being considered, the product of the curvilinear tension and geodesic curvature has been neglected here.

The resulting 25 variables are modeled using 25 equations consisting of: two equations of mass conservation given in Eqn (2.142); 15 momentum equations, Eqns (2.117) and (2.118); three equations from the EI, Eqn (2.112), Eqn (2.113), and Eqn (2.145); three equations of state Eqn (2.131), Eqn (2.132), and Eqn (2.135); and two dynamic conditions Eqns (2.136) and (2.137). Note again all material derivatives relative to the s phase are changed to partial time derivatives according to Eqn (2.140).

2.9.5. Model Formulation Neglecting Common Curves and Interfaces.

Traditional two-fluid-phase flow models neglect the contributions of both common curves and interfaces by assigning these entities no properties. The list of 25 unknowns resulting from neglecting just common curves is reduced further to the set of 12 unknowns, namely

$$(2.146) \qquad \{s^w, \epsilon, \mathbf{v}^{\overline{w},\bar{s}}, \mathbf{v}^{\overline{n},\bar{s}}, \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}}, p^w, p^n, \gamma^{wn} J_w^{wn}\}.$$

where the relative velocities of the interfaces, the geomtric densities of the interfaces, the area of the solid surface, the geometric ratios, and the contact angle have all been neglected. The conservation of momentum equation for the interfaces is no longer necessary to describe the system of interest. The dynamic conditions, Eqns (2.136) and

(2.137), are no longer employed. The exclusion of the contact angle excludes its equation of state, Eqn (2.135). In addition, the constitutive relations resulting from the EI are effected such that Eqn (2.114) is no longer needed. Also, with regard to Eqn (2.113), a problem arises with this equation in that the last term contains χ_{ws}^{ss} which is not determined in this formulation that neglects interfaces. Therefore, essentially, an additional equation of state is needed to express χ_{ws}^{ss} in terms of the unknowns of the problems. In general this equation of state needs to be determined experimentally. However, some simple hypotheses may be useful. For example, one could set $\chi_{ws}^{ss} = s^w$ implying that the fraction of solid surface in contact with the wetting phase is equal to the fraction of the pore space occupied by the w phase. This is a widely used approximation. Another option might be to specify $\chi_{ws}^{ss} = 1$ which might be particularly apt if one is considering drainage starting with a fully saturated system.

Additionally, specification of the capillary pressure as a function of ϵ^{wn} in addition to saturation cannot be accomplished without some measure of the interfacial area. Therefore, within the constraints of this formulation, it seems appropriate to specify the capillary pressure $\gamma^{wn} J_w^{wn}$ as a function only of s^w. Thus the functional form previously given as an equation of state in Eqn (2.132) can be written as

$$(2.147) \qquad -\gamma^{wn} J_w^{wn} = p^c(s^w)$$

and Eqn (2.113), using $\chi_{ws}^{ss} = s^w$, can be written as

$$(2.148) \qquad p^w - p^n - \gamma^{wn} J_w^{wn} = \hat{c}^{wn} \epsilon \frac{\mathrm{D}^{\bar{s}} s^w}{\mathrm{D}t}.$$

Eqn (2.112) also takes a modified form,

$$(2.149) \quad s^w \left(p^w + \gamma^{ws} J_s^{ss}\right) + (1 - s^w)\left(p^n + \gamma^{ns} J_s^{ss}\right) + \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}} = -\hat{c}^s \frac{\mathrm{D}^{\bar{s}} \epsilon^s}{\mathrm{D}t}$$

and note that γ^ι and J_s^{ss} are parameters. The resulting 12 variables are then modeled using 12 equations consisting of: two equations of mass conservation given in Eqn (2.142);

six momentum equations, Eqn (2.117); two equations from the EI, Eqns (2.148) and (2.149); and two EOS Eqns (2.131) and (2.147).

To recover a model resembling a traditional model for two-phase flow, the hydraulic conductivity tensor, $\hat{\mathbf{K}}^\iota$, is defined as

(2.150)
$$\hat{\mathbf{K}}^\iota = \epsilon^{\iota 2}(\hat{\mathbf{R}}_\iota^\iota)^{-1},$$

so that Eqn (2.117) may be expressed in what is commonly called the Darcian form

(2.151)
$$\epsilon^\iota \mathbf{v}^{\overline{\iota,s}} = -\hat{\mathbf{K}}^\iota \cdot \left(\nabla p^\iota - \rho^\iota \mathbf{g}^{\overline{\iota}} \right) \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{f}}.$$

Substitution of Eqn (2.151) into the conservation of mass equation, Eqn (2.142) yields

$$\epsilon \frac{\partial s^\iota}{\partial t} + s^\iota \left(\left[\hat{\alpha}^{\mathrm{b}} + (1-\epsilon)\hat{\beta}^s \right] \frac{\partial \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}}}{\partial t} + \epsilon \hat{\beta}^\iota \frac{\partial p^\iota}{\partial t} \right)$$

(2.152)
$$-\nabla \cdot \left[\hat{\mathbf{K}}^\iota \cdot \left(\nabla p^\iota - \rho^\iota \mathbf{g}^{\overline{\iota}} \right) \right] = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{f}}.$$

The second term in this equation is often neglected in traditional models based on the argument that the rate of change of a pressure multiplied by a compressibility is much smaller than the rate of change of saturation. With this assumption, Eqn (2.152) becomes

(2.153)
$$\epsilon \frac{\partial s^\iota}{\partial t} - \nabla \cdot \left[\hat{\mathbf{K}}^\iota \cdot \left(\nabla p^\iota - \rho^\iota \mathbf{g}^{\overline{\iota}} \right) \right] = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{f}}.$$

Eqn (2.148) is a simplification of a dynamic equation whose equilibrium form is typically taken to be the relation between the capillary and fluid pressures employed in standard multiphase models even when the system is changing slowly such that

(2.154)
$$-\gamma^{wn} J_w^{wn} = p^c(s^w) = p^n - p^w.$$

The relation $p^c(s^w)$ is the standard closure relation, for which several specific forms have been advanced. For cases in which an entrapped non-wetting phase fluid is allowed, this relation is hysteretic in form. The time rate of change of porosity is generally considered

considered to be negligible such that ϵ is a specified quantity. The unknowns in traditional models are the three variables $\{s^w, p^w, p^n\}$ and the governing equations are Eqn (2.153), Eqn (2.147), and specification of the function $p^c(s^w)$. The conductivity, $\hat{\mathbf{K}}^\iota = \hat{\mathbf{K}}^\iota(s^w)$ is also a typical closure relation, which may be hysteretic for the case of an entrapped non-wetting phase fluid. For systems in which significant changes in the porosity occur, the morphology and topology of the pore space will change, thus the $p^c(s^w)$ and $\hat{\mathbf{K}}^\iota = \hat{\mathbf{K}}^\iota(s^w)$ relations will also be effected, becoming $p^c(\epsilon, s^w)$ and $\hat{\mathbf{K}}^\iota = \hat{\mathbf{K}}^\iota(\epsilon, s^w)$.

2.10. Discussion

The approach to modeling multiphase flow in porous media presented here builds on and extends information presented in preceding papers in this TCAT series. The general steps involved in the TCAT approach were presented in the first paper [84]. The necessary mathematical foundation for use in the TCAT can be found in the second paper [136], and the equilibrium conditions were presented in the fourth paper [137]. The TCAT approach has been used to specify a closed model in the case of single-phase flow [85] and single-phase flow and species transport in a porous medium [87]. The primary objective of the present work is to detail the TCAT approach for a specific application of multiphase flow in porous media. The relatively simple example of two-fluid-phase flow was chosen to demonstrate the approach and provide some specific applications. To accomplish the objective, a constrained entropy inequality connecting the second law of thermodynamics and quantities appearing in the conservation equations is formulated. Restrictions on the system of interest and approximations are detailed that allow for the formulation of a simplified entropy inequality, which is used to guide closure relations necessary to produce well-posed models. A hierarchy of three models are presented by imposing additional assumptions on the system. The general TCAT approach can be employed to describe many other systems, such as multiple fluid systems with compositional effects.

The class of problems considered, two-fluid-phase flow, and the specific closed models developed, represent relatively simple instances of multiphase-flow. To this end, the three

closed model formulations presented in §2.9 each deserve discussion. These discussions must first highlight the restrictions and approximations leading to the model formulations and then comment on the consequences of these constraints as well as the consequences arising from alternative choices.

The primary restrictions on the system are those that specify the physical system being modeled and that are posited at the start of the TCAT process. Primary restriction 1 requires a clear separation of lengths scales which may or may not exist in natural systems. This issue is an open topic of debate. The models derived are deterministic in form. Their extension to stochastic form will follow naturally from the deterministic models by maintaining a consistent deterministic model form while allowing macroscopic parameters and auxiliary conditions to be stochastic in nature. Alternative approaches would be to relax this single REV assertion to include REV's that vary as a function of the quantity being considered or to consider the averaging from the microscale to the macroscale in a stochastic sense. Primary restrictions 2 and 4 require examination of a specific instance of a multiphase flow problem, namely one composed of continuous wetting and non-wetting fluid phases and a solid phase without consideration of the components of the phases. Alternatively, many other entities could be included in the TCAT approach such as additional fluid phases, films, discontinuous phases, and species considerations within the entities. Primary restriction 3 is a statement of the thermodynamic theory to be considered. Thermodynamics was needed to connect the conservation equations to the EI. Other thermodynamic theories exist, and were reviewed previously in [84]. For cases in which CIT is not sufficient to describe observations, an alternative thermodynamic theory can be incorporated by averaging the theory from the microscale to the macroscale and using it in place of CIT in the EI.

Secondary restrictions on the system are those that specify the physical system being modeled, but do not have to be applied until after the final CEI is developed. As a result, unlike the primary restrictions, the secondary restrictions are relatively easy to relax because they do not require a complete model reformulation. The secondary

restrictions asserted in this paper are that of an isothermal system with immiscible fluids and an incompressible solid. These restrictions are an explicit statement of a simple two-fluid-phase flow case, yet are consistent in many cases with traditional models used in practice. Relaxing Secondary restriction 1 to fluid flow in a non-isothermal porous medium system, is an active area of research with many unresolved questions. Relaxing Secondary restriction 2 would amount to allowing mixing at the interface and would then be considering the case of not only mass transfer, but also species effects. Relaxing Secondary restriction 3, the description of the solid phase, would be necessary for systems where significant consolidation occurs.

Finally, a set of approximations were used to arrive at the final SEI and to formulate constitutive equations from the SEI. Approximation 1 was made to simplify the geometric aspects of the SEI and ultimately influenced the form of the constitutive equations. If better approximations become available they can be used instead. These approximations are believed to be reasonable first approximations, and they are testable based upon microscale simulations. Approximation 2, which asserts that at most a first-order dependence among force-flux pairs is known to be overly restrictive in certain cases. Many unresolved issues remain for extension to higher-order theory. However, the inclusion of cross-coupling is an improvement to traditional models. Approximation 3, claims that standard equations of state are sufficient for the system; if better EOS are developed they can be used to replace the standard equations. Approximations 4–8 are all statements that allow simplification of the system, if a more complex system is desired they can be omitted.

In §2.9.3 the first closed model is formulated which follows from the system described by all of the restrictions and approximations of §2.6. The system is a generalization of traditional models that includes well-defined variables; it is consistent across scales; and it includes the influence and evolution of interfaces and a common curve. These are all crucial components for useful macroscale models of two-fluid-phase flow in porous media.

While advantages exist for including as much information as possible in a model description, a trade-off exists between the completeness of a model and the ease of developing a useful and accurate simulation. Therefore, a simpler second model formulation is presented in §2.9.4, which neglects the effects of the common curve. Although common curve effects could be first order effects in some cases, even this reduced model still has many advantages over the traditional models used in practice because it includes well-defined variables; it is consistent across scales; and it accounts for the influence and evolution of interfaces.

Finally in §2.9.5, the assumption that interfaces need not be modeled explicitly is made to demonstrate the assumptions inherent in a derived model equivalent in form to the traditionally assumed model for two-fluid-phase flow. We emphasize that the impact of interfaces on pore-scale phenomena has been demonstrated [132, 147], yet traditional models do not account for this effect. Furthermore it is useful to arrive at a two-fluid-phase flow model that is consistent with the traditional model because such a derivation makes explicit the assumptions that support this model. Additionally, the methods used to derive the macroscale variables within the model provide the advantages of precisely defined variables that are rigorously connected to the microscale; clearly expressed assumptions required to arrive at the model; and a foundation upon which the assumptions can be relaxed to produce alternative models.

2.11. Summary

Detailed in this work are the elements of the TCAT approach necessary to construct models for multiphase porous medium systems. The results are novel in the inclusion of interfaces and common curves, the rigorous treatment of the thermodynamics, the utilization of equilibrium conditions to guide the formulation of the SEI, the use of a Lagrange multiplier approach to connect conservation equations to the entropy inequality, the separation of exact results from approximations, and the framework for refinement, simplification, and extension.

The TCAT approach combined with a set of assumptions is used to produce three models, each a simplification of the previous model. The simplest model, is a model similar to a traditional two-fluid-phase flow model. However, this model boasts advantages over traditional models in that the unknown quantities are well-defined and firmly connected to the microscale. We also note that this model is not obtained so much as a target for which a complex mathematical framework has been constructed but as a consequence of careful mathematical analysis and some particular assumptions. Through the inclusion of interfaces, a second, more conceptually satisfying, model has been developed that has the advantage of accounting for phenomena that occur as a result of the interfaces. The most encompassing model discussed accounted for common curve properties as well as the interfaces. While interfaces and common curves are both neglected in traditional models it is believed these entities produce first-order effects and play an important role in the true physics of the system.

Potential extensions to the two-fluid-phase flow model are considered and include systems for which consolidation is important, systems that are non-isothermal, and systems for which species transport is desired. In addition to potential model extensions, should better approximations become available then those listed in §2.6, they can be used in producing the final SEI without altering any of the formulation up to that point. The TCAT approach provides the foundation for model extension, revision, and simplification and has been demonstrated for a simple case of a two-fluid-phase flow model formulation.

CHAPTER 3

Thermodynamically Constrained Averaging Theory Approach for Modeling Flow and Transport Phenomena in Porous Medium Systems: 9. Transition Region Models

3.1. Introduction

Previous work in this series [84–88, 110, 136, 137] has focused on the development of foundational aspects of the thermodynamically constrained averaging theory (TCAT). Efforts to date have focused on fundamental aspects of single-fluid phase [85, 87, 88] and two-fluid-phase [110] porous medium systems at both the macroscale [85, 87, 110] and the megascale [88]. In addition, species transport for non-dilute systems has been considered [87, 137]. The purpose of this series of work is to generate models that are consistent across scales, include the full set of entities of concern (e.g., phases, interfaces, common curves, and common points), posed in terms of well-defined variables, and constrained by the second law of thermodynamics.

Recently, considerable interest has arisen over the modeling of transition regions between domains that contain different sets of entities [6, 74, 112, 124, 140, 146]. For example, at Earth's surface a domain that contains a solid, a water phase, a gas, and the corresponding interfaces and common curve is in contact with the atmosphere that may only contain a gas phase. Many other sorts of transition regions arise as well in both natural and engineered systems, e.g., coupled surface and subsurface flows, flows in blood vessels and biological tissues, industrial filtration, thermal insulation, and fuel cells [12, 95, 107]. Models that represent the transfer of mass, momentum, and energy between two distinct regions and which meet the overall goals common to TCAT models have not yet been formulated.

The overall goal of this work is to extend the development of TCAT to the modeling of transition regions. The specific objectives of this work are: (1) to derive a set of macroscale conservation and balance equations that apply to transition regions, (2) to formulate a general constrained entropy inequality (CEI) that can be used to derive models of transition regions under a variety of limiting conditions, (3) to construct a simplified entropy inequality (SEI) posed in terms of flux-force pairs that can be used to guide closure relations for transition region models, (4) to generate a closed model for a dilute porous medium transition region, and (5) to discuss ways in which the formulated models can be further developed and applied.

3.2. Background

The most widely considered transition region is the interface between an open fluid (free flow) and a porous medium. At the macroscale, the coupled system is described as two different continuum flow domains (free flow, porous medium) separated by an interface. It can be a sharp interface (Fig. 3.1, left) or a small transition zone of thickness d (Fig. 3.1, right). Correct specification of the coupling conditions for the transition between the two flow domains is essential for a complete and accurate mathematical description of flow and transport processes in compositional system [6, 22, 74, 112, 124, 146, 162].
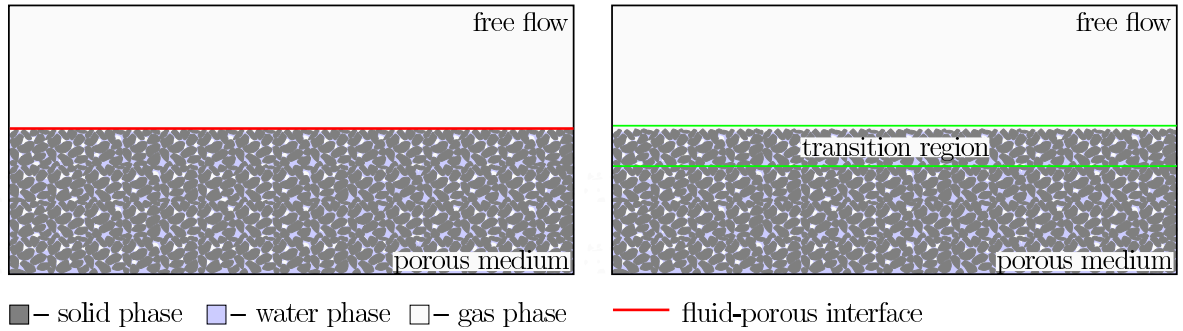
FIGURE 3.1. Sharp interface (left) and transition region (right) between free flow and porous medium

In general, two different approaches are proposed to deal with the underlying problem of coupling flow between a porous medium and a free-flow region: the single-domain approach, and the two-domain approach.

The single-domain approach is based on solution of the Brinkman equation [39], which is a superposition of the Stokes equation and Darcy's law, over the entire domain. There is no need to specify interface conditions between the free flow and the porous medium, since the velocity and stress continuity across the interface are naturally fulfilled. The transition from the free-flow region to the porous medium region is achieved by specifying spatial variations of permeability and porosity, and by introducing an effective viscosity in the porous medium system [74, 161]. Since this modeling approach avoids the explicit formulation of interface conditions, it has been used widely for numerical simulations of coupled systems. However, model results are very sensitive to parameter values used in the model, and these values are generally not known from physical considerations, especially when considering a multiphase system.

The two-domain approach employs a different model in each of the two regions and couples these models at the interface using appropriate conditions [6, 12, 22, 44, 45, 74, 95, 107, 111, 112, 126, 146, 162, 171]. In the free-flow region, the Navier-Stokes equations are used to describe momentum conservation while Darcy's law, or the Brinkman extension to this equation, is used as an approximate conservation of momentum equation in the porous medium.

When the porous medium model is based on Darcy's law, the Beavers-Joseph velocity jump condition [22] is widely used to couple the two different flow domains, in conjunction with restrictions that arise due to mass conservation and a balance of normal forces across the interface [124]. The Beavers-Joseph condition establishes the connection between the free-flow velocity and the porous medium velocity tangent to the interface. It has been shown that setting the tangential velocity equal to zero along the interface is not physical. The Beavers-Joseph condition has been studied experimentally for flow that is parallel to the interface between two flow domains [22] to estimate a dimensionless jump coefficient.

This coefficient depends on the structure of the permeable material within the boundary region and the location of the interface.

Saffman [162] proposed a modification of the Beavers-Joseph condition that contains only variables in the free-flow region, since the porous medium velocity is much smaller than the free-flow velocity, and can thus be neglected. Mathematical justification of the Beavers-Joseph-Saffman interface condition was derived rigorously by Jäger and Mikelić [111, 112] by homogenization techniques, and the velocity jump coefficient was determined through an auxiliary boundary-layer problem. A generalization of Beavers-Joseph-Saffman coupling condition was obtained by Hassanizadeh and Gray [100] using a volume averaging approach.

Some authors distinguish between two qualitatively different flow directions: "near parallel flow", where the velocity in the free fluid is much larger than the filtration velocity in the porous medium, and "near normal flow", where velocities in the two regions have comparable magnitudes. For these two classifications, different coupling conditions have been proposed [120, 126]. However, these conditions cannot be applied to a general flow situation.

As an alternative to Darcy's law, the Brinkman equation can be used to model the porous medium flow. The main advantage of this equation lies in the similarity in form employed for the stress tensor in the porous medium and the free-flow domains. For a Brinkman model, the continuity of the velocity at the interface is satisfied automatically; and continuity of the normal component of the stress tensor is often imposed at the interface [11, 107]. However, this last condition is purely mathematical since in the porous medium the influence of the solid matrix is not taken into account by considering stress continuity. Instead of this condition, Ochoa-Tapia and Whitaker proposed a stress jump condition [146] derived using the volume averaging technique. This condition involves an empirical coefficient that cannot be easily determined. Recently, Chanderis and Jamet [44, 45] derived the velocity jump and stress jump conditions at the interface with a two-step upscaling approach and the method of matched asymptotic expansions.

Some other fluid flow and heat transfer interface conditions are available in the literature, e.g., [6, 74, 171].

To date, single domain and two-domain coupling approaches with different interface conditions have been developed only for single-phase, single-component systems, but in practice we are often interested in multiphase, multi-component flows. Recently, the classical two-domain concept has been extended to two-component non-isothermal flow with two fluid phases inside the porous medium and a single fluid phase in the free-flow region [140]. A flat interface, that has no thickness, cannot store mass, momentum or energy and is in thermodynamic equilibrium, is considered. The coupling conditions are based on assumptions of mechanical, thermal and chemical equilibrium, and the Beavers-Joseph velocity jump condition. The concept is restricted to free flow parallel to the porous medium and a sharp interface.

Macroscale coupling approaches are available for free flow that is either parallel or perpendicular to the porous medium. No general approach has been developed for the coupling of flow systems with chemical species and more than one fluid phase. Thus, a general coupling formulation that includes the macroscale flow and transport behavior at the interface between the flow regions is needed. Such a formulation can be developed in the context of TCAT.

3.3. Primary Restrictions

The formulation of a TCAT model is guided by a set of primary restrictions, secondary restrictions, SEI approximations, and closure approximations. The primary restrictions fix the nature of the system being considered and dictate details of the formulation procedure that result, after some manipulation, in a constrained entropy inequality. The appropriate selection of the primary restrictions is important because these restrictions limit features of a system that can be considered. On the other hand, specifying a very general set of primary restrictions, while leading to the potential to formulate a rich hierarchy of models, results in significant complexity in formulating and reducing the

entropy inequality (EI). Thus, a balance is sought in formulating the primary restrictions so that a significant hierarchy of models can be formulated from the resultant entropy inequality without unnecessary complexity. The primary restrictions relate to continuum mechanical requirements, the spatial dimensionality of the system, the entities of concern, the phenomena one wishes to model, and the microscale thermodynamic theory relied upon. We will detail each of these restrictions in turn.

PRIMARY RESTRICTION 1 (Deterministic Macroscale Averaging). *A discrete macroscopic length scale exists such that all macroscale quantities of concern are well-defined and insensitive to the size of the representative elementary volume (REV) used to derive the deterministic models.*

Primary Restriction 1 is a common restriction applied to TCAT models. We specify that a separation of length scales exists such that the scale at which the model is formulated leads to values of all variables that are well defined in an average sense, and the values of these variables are not sensitive to small changes in the size of the averaging region. Put another way, we require a local form of the model at the scale at which we formulate the model. Once derived at the scale of focus in this work, such a model can be upscaled to non-local situations in which a heterogeneous domain exists at a scale above the macroscale.

PRIMARY RESTRICTION 2 (Spatial Domain). *The model will be formulated at the macroscale in two spatial dimensions and at the megascale in the third spatial dimension, which is the direction normal to the boundary between the two distinct domains, Ω_1 and Ω_2.*

Primary Restriction 2 specifies a spatial domain that is macroscale in two dimensions and megascale in the third dimension. By the macroscale we mean a scale above the microscale or pore scale, where a point implies an averaged value about some representative elementary volume and all entities may exist at such a point. The megascale is the system scale where the system is averaged over the entire length of the domain in the

megascale dimension. In this case, a megascale will be used to represent the transition region normal to the boundary between the two distinct domains. This restriction implies that all macroscale quantities will have variability in only two spatial dimensions. This restriction on all macroscale variables will be implicit and will not be specifically denoted in any way.

PRIMARY RESTRICTION 3 (Transition Region Entities). *The transition region is formulated in terms of the union of sets of entities that correspond to each region, $\mathcal{E} = \mathcal{E}_1 \cup \mathcal{E}_2$, where $\mathcal{E}$ is the set of entities of concern in the transition region Ω, $\mathcal{E}_1$ is the set of entities in region 1 with domain Ω_1 and $\mathcal{E}_2$ is the set of entities in region 2 with domain Ω_2. We specify that $\mathcal{E} = \{\mathcal{E}_P, \mathcal{E}_I, \mathcal{E}_C\}$ or that the set of entities consists of a set of phases, interfaces, and common curves. We further specify the system of focus such that $\mathcal{E}_P = \{\Omega_w, \Omega_g, \Omega_s\}$, where Ω_w denotes the domain of a water phase, Ω_g denotes the domain of a gas phase, and Ω_s denotes the domain of a solid phase; $\mathcal{E}_I = \{\Omega_{wg}, \Omega_{ws}, \Omega_{gs}\}$ where the two subscripts denote the corresponding phases that form an interface; and $\mathcal{E}_C = \{\Omega_{wgs}\}$, where Ω_{wgs} denotes the common curve domain that forms at the intersection of the three interfaces.*

Primary Restriction 3 specifies that the transition region will include all entities in both the single-fluid-phase portion of the domain and the two-fluid-phase porous medium portion of the domain. Furthermore, these entities are restricted to two fluid phases, a solid phase, three interfaces, and a common curve. This restriction dictates the scope of systems for which a hierarchy of models will be developed. More complex systems, for example those containing three fluid phases, are excluded from consideration at this point. This limits the complexity of the system that needs to be considered.

PRIMARY RESTRICTION 4 (Phenomena Modeled). *The phenomena to be modeled includes conservation of momentum, and energy in each entity and the conservation of a mass of each species in each entity.*

Primary Restriction 4 specifies the level of detail to be considered in the TCAT model. Compositional effects are specified but only with regard to the conservation of

mass. This excludes the modeling of species momentum or species energy. It also implies that the velocity of individual species will need to be approximated based upon closure relations rather than a set of separate momentum conservation equations for species-phase combinations.

PRIMARY RESTRICTION 5 (Microscale Thermodynamic Theory). *Classical irreversible thermodynamics (CIT) will be used as the underlying thermodynamic theory to describe the local equilibrium states of the system considered at the microscale.*

Primary Restriction 5 specifies the microscale thermodynamic theory that will be relied upon to connect the entropy inequality (EI) with the conservation equations in order to constrain the closure relations. While many different theories are possible [e.g. 84], we will rely upon CIT for this purpose. CIT is the simplest possible choice of an underlying thermodynamic theory, and it has shown significant utility for deriving a range of models using the TCAT approach [85–87, 110].

3.4. Averaging Theorems

Conservation and balance equations can be derived at the macroscale by applying the averaging operator defined by

$$
(3.1) \qquad \langle \mathcal{P}_i \rangle_{\Omega_j, \Omega_k, W} =
\begin{cases}
\dfrac{\int\limits_{\Omega_j} W \mathcal{P}_i \, d\mathfrak{r}}{\int\limits_{\Omega_k} W \, d\mathfrak{r}} & \text{for } \dim \Omega_j > 0, \ \dim \Omega_k > 0, \\[2em]
\dfrac{\sum\limits_{h \in \Omega_j} \mathcal{P}_{ih} W}{\int\limits_{\Omega_k} W \, d\mathfrak{r}} & \text{for } \dim \Omega_j = 0, \ \dim \Omega_k > 0, \\[2em]
\dfrac{\sum\limits_{h \in \Omega_j} \mathcal{P}_{ih} W}{\sum\limits_{h \in \Omega_k} W} & \text{for } \dim \Omega_j = 0, \ \dim \Omega_k = 0,
\end{cases}
$$

where $\mathcal{P}_i$ is a microscale quantity to be averaged, and W is a weighting function. If W is not specified, it is assumed to be 1 and the macroscale property appears with

a superscript, $\mathcal{P}^i$. For the case of a mass averaged quantity, the superscript on the macroscale property has a single overbar, $\mathcal{P}^{\bar{i}}$. All other weighting functions or specially defined macroscale properties are indicating through a superscript with a double overbar, $\mathcal{P}^{\bar{\bar{i}}}$. For the common case when $\Omega_k = \Omega$ the averaged quantity is normalized by an integral over the entire REV. The case when $\dim \Omega_j = 0$ represents a domain that consists of a set of common points. For this case the averaging operator corresponds to a summation over the set of points, h, that comprise Ω_j. Cases will arise in which the point form is used to denote a boundary of a common curve. Common forms of the averaging operator have been detailed previously [136].
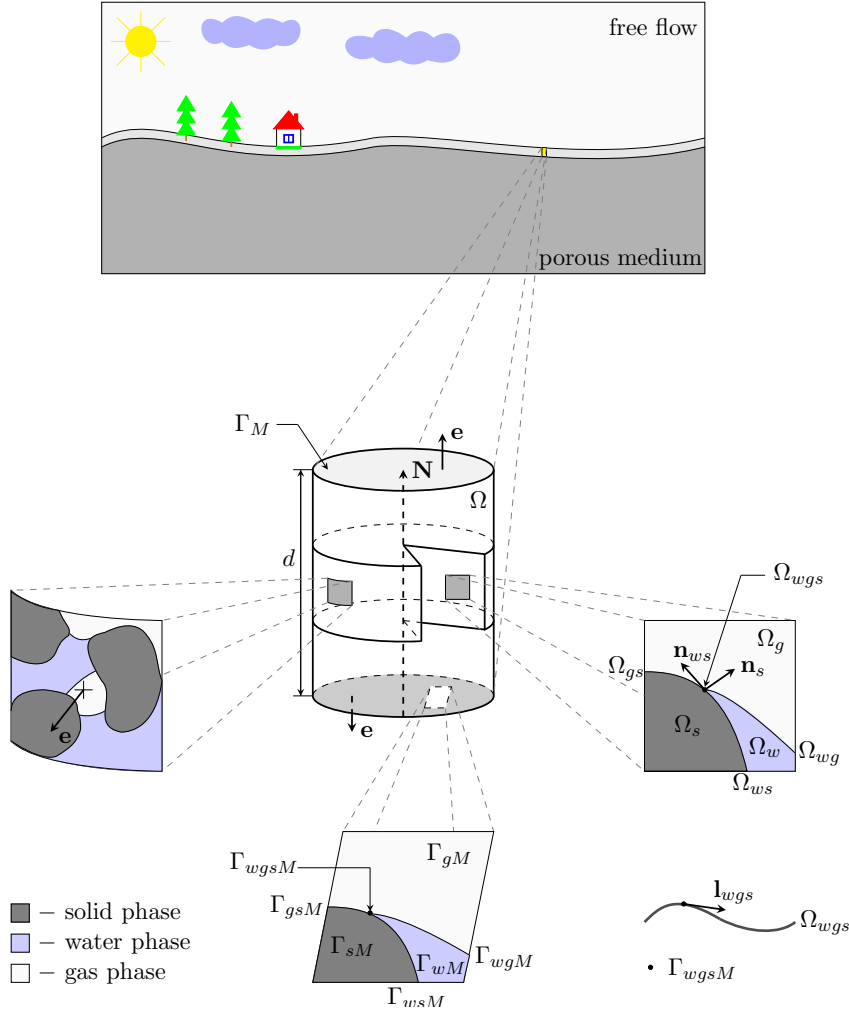
FIGURE 3.2. Schematic depiction of domain, coordinate system, averaging region, entities, and unit vectors.

The set of macroscale conservation and balance equations needed to derive the TCAT models of focus in this work have not yet appeared in the literature. In order to derive these equations, a set of averaging theorems from [82] are detailed below. Figure 3.2 is a schematic representation of the domain, entities, and unit vectors associated with the transition region of concern in this work, which can be used to map the physical system to terms appearing in the theorems of interest. The divergence, gradient, and transport theorems needed to transform microscale quantities defined over volumes to two macroscale dimensions and one megascale dimension are:

THEOREM 3.4.1 (D[3,(2,0),1]).

$$(3.2) \qquad \langle \nabla \cdot \mathbf{f}_\iota \rangle_{\Omega_\iota,\Omega} = \nabla^{\backprime} \cdot \langle \mathbf{f}_\iota \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in \mathcal{I}_{c\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{f}_\iota \rangle_{\Omega_\kappa,\Omega} + \langle \mathbf{e} \cdot \mathbf{f}_\iota \rangle_{\Gamma_{\iota M},\Omega} \qquad \iota \in \mathcal{I}_{\mathrm{P}},$$

THEOREM 3.4.2 (G[3,(2,0),1]).

$$(3.3) \qquad \langle \nabla f_\iota \rangle_{\Omega_\iota,\Omega} = \nabla^{\backprime} \langle f_\iota \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in \mathcal{I}_{c\iota}} \langle \mathbf{n}_\iota f_\iota \rangle_{\Omega_\kappa,\Omega} + \langle \mathbf{e} f_\iota \rangle_{\Gamma_{\iota M},\Omega} \qquad \iota \in \mathcal{I}_{\mathrm{P}},$$

and

THEOREM 3.4.3 (T[3,(2,0),1]).

$$(3.4) \quad \left\langle \frac{\partial f_\iota}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \frac{\partial^{\backprime}}{\partial t} \langle f_\iota \rangle_{\Omega_\iota,\Omega} - \sum_{\kappa \in \mathcal{I}_{c\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa f_\iota \rangle_{\Omega_\kappa,\Omega} - \langle \mathbf{e} \cdot \mathbf{v}_{\mathrm{ext}} f_\iota \rangle_{\Gamma_{\iota M},\Omega} \quad \iota \in \mathcal{I}_{\mathrm{P}},$$

where the partial time derivative restricted to a point on the moving macroscale interface is defined as

$$(3.5) \qquad \frac{\partial^{\backprime}}{\partial t} = \frac{\partial}{\partial t} + \mathbf{v}^{\bar{\iota}} \cdot \mathbf{N} \mathbf{N} \cdot \nabla,$$

the phase domain is denoted Ω_ι with a boundary consisting of a component on the external boundary of the REV and an internal component within the REV denoted $\Gamma_\iota = \Gamma_{\iota e} \cup \Gamma_{\iota i}$, $\mathcal{I}_{\mathrm{P}}$ is the index set of phases, $\mathcal{I}_{c\iota}$ is the index set of the connected entities, which is comprised of interfaces, the microscale spatial function f_ι and spatial vector function $\mathbf{f}_\iota$ are defined, continuous and differentiable in Ω_ι and in time, $\mathbf{v}_\kappa$ is the velocity of the

κ interface, $\nabla^{\backslash} = \nabla - \mathbf{NN} \cdot \nabla$ is a two-dimensional macroscale del operator, $\mathbf{N}$ is a unit vector tangent to the axis corresponding to the megascopic dimension of the REV, $\mathbf{e}$ is the unit normal vector directed outward from the boundary of the REV, $\mathbf{n}_\iota$ is a unit outward normal vector from phase ι on its boundary, the boundary of the REV, Γ, is the union of the boundary in the macroscale directions, Γ_m, and the megascale direction, Γ_M, $\Gamma = \Gamma_m \cup \Gamma_M$, the interface formed by the intersection of the phase with the REV boundary at the megascale ends is $\Gamma_{\iota M} = \Gamma_{\iota e} \cap \Gamma_M$, and $\mathbf{v}_{\text{ext}}$ is the velocity vector of the boundary of the REV.

The divergence, gradient, and transport theorems needed to transform microscale quantities defined over interfaces to two macroscale dimensions and one megascale dimension are:

THEOREM 3.4.4 (D[2,(2,0),1]).

$$(3.6) \quad \left\langle \nabla' \cdot \mathbf{f}_\iota \right\rangle_{\Omega_\iota, \Omega} = \nabla^{\backslash} \cdot \left\langle \mathbf{f}_\iota{}' \right\rangle_{\Omega_\iota, \Omega} + \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha \right) \mathbf{n}_\alpha \cdot \mathbf{f}_\iota \right\rangle_{\Omega_\iota, \Omega}$$
$$+ \sum_{\kappa \in \left(\mathcal{I}_{c\iota} \cap \mathcal{I}_C \right)} \left\langle \mathbf{n}_\iota \cdot \mathbf{f}_\iota \right\rangle_{\Omega_\kappa, \Omega} + \left\langle \frac{\mathbf{e} \cdot \mathbf{f}_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \qquad \iota \in \mathcal{I}_I,$$

THEOREM 3.4.5 (G[2,(2,0),1]).

$$(3.7) \quad \left\langle \nabla' f_\iota \right\rangle_{\Omega_\iota, \Omega} = \nabla^{\backslash} \left\langle f_\iota \right\rangle_{\Omega_\iota, \Omega} - \nabla^{\backslash} \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha f_\iota \right\rangle_{\Omega_\iota, \Omega} + \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha \right) \mathbf{n}_\alpha f_\iota \right\rangle_{\Omega_\iota, \Omega}$$
$$+ \sum_{\kappa \in \left(\mathcal{I}_{c\iota} \cap \mathcal{I}_C \right)} \left\langle \mathbf{n}_\iota f_\iota \right\rangle_{\Omega_\kappa, \Omega} + \left\langle \frac{\mathbf{e} f_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \qquad \iota \in \mathcal{I}_I,$$

and

THEOREM 3.4.6 (T[2,(2,0),1]).

$$(3.8) \quad \left\langle \frac{\partial' f_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} = \frac{\partial^{\backslash}}{\partial t} \left\langle f_\iota \right\rangle_{\Omega_\iota, \Omega} + \nabla^{\backslash} \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{v}_\iota f_\iota \right\rangle_{\Omega_\iota, \Omega} - \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha \right) \mathbf{n}_\alpha \cdot \mathbf{v}_\iota f_\iota \right\rangle_{\Omega_\iota, \Omega}$$
$$- \sum_{\kappa \in \left(\mathcal{I}_{c\iota} \cap \mathcal{I}_C \right)} \left\langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa f_\iota \right\rangle_{\Omega_\kappa, \Omega} - \left\langle \frac{\mathbf{e} \cdot \mathbf{v}_{\text{ext}} f_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \qquad \iota \in \mathcal{I}_I,$$

where the partial time derivative restricted to a point on the moving microscale interface is defined as

$$(3.9) \qquad \frac{\partial'}{\partial t} = \frac{\partial}{\partial t} + \mathbf{v}_\iota \cdot \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \nabla,$$

the partial time derivative restricted to a point on the moving macroscale interface is defined as

$$(3.10) \qquad \frac{\partial^{\backprime}}{\partial t} = \frac{\partial}{\partial t} + \mathbf{v}^{\bar{\iota}} \cdot \mathbf{NN} \cdot \nabla,$$

the interface domain is defined as $\Omega_\iota = \bar{\Omega}_\alpha \cap \bar{\Omega}_\beta$ with a boundary consisting of a component on the external boundary of the REV and an internal component within the REV denoted $\Gamma_\iota = \Gamma_{\iota e} \cup \Gamma_{\iota i}$ for $\alpha, \beta \in \mathfrak{I}_P$, $\mathfrak{I}_P$ is the index set of phases, $\mathfrak{I}_I$ is the index set of interfaces, $\mathfrak{I}_C$ is the index set of common curves, $\mathfrak{I}_{c\iota}$ is the index set of connected entities, which consists of phases and common curves, the microscale spatial function f_ι and spatial vector function $\mathbf{f}_\iota$ are defined, continuous and differentiable in Ω_ι and in time, $\mathbf{v}_\kappa$ is the velocity of the κ common curve, $\nabla' = \nabla - \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \nabla$ is a two-dimensional microscale del operator, $\mathbf{n}_\alpha$ is a unit vector normal to Ω_α oriented outward at the boundary and also normal to Ω_ι, $\nabla^{\backprime} = \nabla - \mathbf{NN} \cdot \nabla$ is a two-dimensional macroscale del operator, $\mathbf{N}$ is a unit vector tangent to the axis corresponding to the megascopic dimension of the REV, $\mathbf{f}_\iota' = \mathbf{f}_\iota - \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{f}_\iota$ is a microscale vector tangent to the Ω_ι surface, $\mathbf{e}$ is the unit normal vector directed outward from the boundary of the REV, $\mathbf{n}_\iota$ is a unit vector tangent to the Ω_ι surface and outward normal from the bounding common curve, the boundary of the REV is the union of the boundary in the macroscale directions, Γ_m, and the megascale direction, Γ_M, $\Gamma = \Gamma_m \cup \Gamma_M$, the curve formed by the intersection of the interface with the REV boundary at the megascale ends is $\Gamma_{\iota M} = \Gamma_{\iota e} \cap \Gamma_M$, and $\mathbf{v}_{\text{ext}}$ is the velocity vector of the boundary of the REV.

The divergence, gradient, and transport theorems needed to transform microscale quantities defined over common curves to two macroscale dimensions and one megascale dimension are:

THEOREM 3.4.7 (D[1,(2,0),1]).

$$(3.11) \quad \langle \nabla''\!\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega} = \nabla^{\backprime}\!\cdot\langle\mathbf{f}_\iota''\rangle_{\Omega_\iota,\Omega} - \langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa\in(\mathcal{I}_{\mathrm{c}\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\langle\mathbf{n}_\iota\cdot\mathbf{f}_\iota\rangle_{\Omega_\kappa,\Omega} + \left\langle\frac{\mathbf{e}\cdot\mathbf{f}_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} \qquad \iota\in\mathcal{I}_\mathrm{C},$$

THEOREM 3.4.8 (G[1,(2,0),1]).

$$(3.12) \quad \langle\nabla''f_\iota\rangle_{\Omega_\iota,\Omega} = \nabla^{\backprime}\!\cdot\langle\mathbf{l}_\iota\mathbf{l}_\iota f_\iota\rangle_{\Omega_\iota,\Omega} - \langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\,f_\iota\rangle_{\Omega_\iota,\Omega} + \sum_{\kappa\in(\mathcal{I}_{\mathrm{c}\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\langle\mathbf{n}_\iota f_\iota\rangle_{\Omega_\kappa,\Omega}$$

$$+ \left\langle\frac{\mathbf{e}f_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} \qquad \iota\in\mathcal{I}_\mathrm{C},$$

and

THEOREM 3.4.9 (T[1,(2,0),1]).

$$(3.13) \quad \left\langle\frac{\partial''f_\iota}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = \frac{\partial^{\backprime}}{\partial t}\langle f_\iota\rangle_{\Omega_\iota,\Omega} + \nabla^{\backprime}\!\cdot\langle(\mathbf{v}_\iota - \mathbf{l}_\iota\mathbf{l}_\iota\cdot\mathbf{v}_\iota)\,f_\iota\rangle_{\Omega_\iota,\Omega}$$

$$+ \langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\cdot\mathbf{v}_\iota f_\iota\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa\in(\mathcal{I}_{\mathrm{c}\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa f_\iota\rangle_{\Omega_\kappa,\Omega}$$

$$- \left\langle\frac{\mathbf{e}\cdot\mathbf{v}_{\mathrm{ext}}f_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} \qquad \iota\in\mathcal{I}_\mathrm{C},$$

where the partial time derivative restricted to a point on the moving microscale common curve is defined as

$$(3.14) \qquad\qquad \frac{\partial''}{\partial t} = \frac{\partial}{\partial t} + \mathbf{v}_\iota\cdot(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\nabla,$$

the partial time derivative restricted to a point on the moving macroscale interface is defined as

$$(3.15) \qquad\qquad \frac{\partial^{\backprime}}{\partial t} = \frac{\partial}{\partial t} + \mathbf{v}^{\bar{\iota}}\cdot\mathbf{N}\mathbf{N}\cdot\nabla,$$

the common curve domain is defined as $\Omega_\iota = \bar{\Omega}_\alpha\cap\bar{\Omega}_\beta\cap\bar{\Omega}_\gamma$ with a boundary consisting of a component on the external boundary of the REV and an internal component with

the REV denoted $\Gamma_\iota = \Gamma_{\iota e} \cup \Gamma_{\iota i}$ for $\alpha, \beta, \gamma \in \mathcal{I}_P$, $\mathcal{I}_P$ is the index set of phases, $\mathcal{I}_C$ is the index set of common curves, $\mathcal{I}_{Pt}$ is the index set of common points, $\mathcal{I}_{c\iota}$ is the index set of connected entities, which consists of interfaces and common points, the microscale spatial function f_ι and spatial vector function $\mathbf{f}_\iota$ are defined, continuous and differentiable in Ω_ι and in time, $\mathbf{v}_\kappa$ is the velocity of the κ common point, $\nabla'' = \mathbf{l}_\iota \mathbf{l}_\iota \cdot \nabla$ is a one-dimensional microscale del operator, $\mathbf{l}_\iota$ is a unit vector tangent to the ι common curve, $\nabla^\backprime = \nabla - \mathbf{N}\mathbf{N} \cdot \nabla$ is a two-dimensional macroscale del operator, $\mathbf{N}$ is a unit vector tangent to the axis corresponding to the megascopic dimension of the REV, $\mathbf{f}''_\iota = \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{f}_\iota$ is a microscale vector tangent to the ι common curve, Γ, $\mathbf{e}$ is the unit normal vector directed outward from the boundary of the REV, $\mathbf{n}_\iota$ is the unit vector tangent to the common curve and positive outward at common point boundaries such that $\mathbf{n}_\iota \cdot \mathbf{l}_\iota = \pm 1$, the boundary of the REV is the union of the boundary in the macroscale directions, Γ_m, and the megascale direction, Γ_M, $\Gamma = \Gamma_m \cup \Gamma_M$, the external boundary of the ι common curve is given by a set of points defined as $\Gamma_{\iota e} = \bar{\Omega}_\iota \cap \Gamma_M$, and $\mathbf{v}_{ext}$ is the velocity of the boundary of the REV.

3.5. Conservation and Balance Equations

The TCAT models of focus in this work require conservation of mass equations for a species, conservation of momentum and energy equations, and a balance of entropy equation, all for phases, interfaces, and common curves. These equations must be macroscopic in two spatial dimensions and megascopic in the third spatial dimension, which will be the dimension in which a transition is made between two distinct types of regions. This set of conservation equations has not yet been published in the averaging literature. However, the derivation of this set of equations can be accomplished by applying a form of the averaging operator given by Eq. (3.1) and available averaging theorems [82] summarized in §3.4 to available forms of microscale conservation and balance equations [137]. Routine calculations, similar to those detailed in [137], show that identical forms of the conservation and balance equations can be derived for all entities using this approach.

Details of the calculations are included in Appendix B. General forms of these macroscale conservation and balance equations are given below.

The entity based conservation of energy equation for a domain that is megascale in one spatial dimension and macroscale in the remaining two spatial dimensions can be written as

$$(3.16) \quad \mathcal{E}^\iota = \frac{D^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{Dt} + \mathbf{v}^{\bar{\iota}} \cdot \frac{D^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\bar{\iota}} \right)}{Dt} + \sum_{i \in \mathcal{I}_S} \left(K_E^{\bar{\bar{\iota}}} - \frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + \psi^{\overline{i\iota}} \right) \frac{D^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{i\iota} \right)}{Dt}$$

$$+ \sum_{i \in \mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\iota} \frac{D^{\bar{\iota}} \left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}} \right)}{Dt}$$

$$+ \left[E^{\bar{\bar{\iota}}} + \epsilon^\iota \rho^\iota \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} \right) + \sum_{i \in \mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\iota} \psi^{\overline{i\iota}} \right] \mathbf{I} : \mathbf{d}^{\bar{\bar{\iota}}}$$

$$- \nabla' \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} \right) - \nabla' \cdot \left(\epsilon^\iota \mathbf{q}^{\bar{\bar{\iota}}} \right) - \epsilon^\iota h_T^{\bar{\bar{\iota}}} - \sum_{i \in \mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\iota} \left(\mathbf{g}_T^{\overline{\overline{i\iota}}} - \mathbf{g}^{\overline{i\iota}} \right) \cdot \mathbf{v}^{\bar{\iota}}$$

$$- \sum_{i \in \mathcal{I}_S} \left(\epsilon^\iota \psi^{\overline{i\iota}} r^{i\iota} + \left\langle \rho_\iota \omega_{i\iota} \frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota, \Omega} \right) - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\sum_{i \in \mathcal{I}_S} \overset{i\kappa \to i\iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right)$$

$$+ \left\langle \frac{\left(E_\iota + \rho_\iota \frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \left(\psi_{i\iota} + \frac{\mathbf{u}_{i\iota} \cdot \mathbf{u}_{i\iota}}{2} \right) \right) \mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = 0 \quad \text{for } \iota \in \mathcal{I},$$

where ι is an entity qualifier, i is a species qualifier, $E^{\bar{\bar{\iota}}}$ is the internal energy density, $\mathbf{v}^{\bar{\iota}}$ is the macroscale mass averaged velocity, ϵ^ι is a specific entity measure of the ι entity (e.g., volume fraction, specific interfacial area, specific common curve length), ρ^ι is the macroscale mass density, $K_E^{\bar{\bar{\iota}}}$ is the macroscale kinetic energy per unit mass due to microscale velocity fluctuations, $\psi^{\overline{i\iota}}$ is the gravitational potential, $\omega^{i\iota}$ is the mass fraction of species i in the ι entity, $\mathbf{d}^{\bar{\bar{\iota}}}$ is the rate of strain tensor restricted to the transition region, $\mathbf{t}^{\bar{\bar{\iota}}}$ is the macroscale 3x3 stress tensor restricted to the transition region such that the tensor has zero in the direction normal to the averaging surface, similarly for the

microscale stress tensor terms, $\mathbf{t}_\iota$, when $\iota \in \mathfrak{I}_I$, $\mathbf{t}_\iota = \mathbf{t}'_\iota$ contains zero in the dimension normal to the surface, and when $\iota \in \mathfrak{I}_C$, $\mathbf{t}_\iota = \mathbf{t}''_\iota$, which contains zeros in two of the dimensions, $\mathbf{q}^{\overline{\overline{\iota}}}$ is the non-advective heat flux density vector which similarly to the stress tensor has been restricted to the transition region at the macroscale and at the microscale maintains its dimensionality when restricted to the surface or common curve with zeros in the additional dimensions such that $\mathbf{q}_\iota = \mathbf{q}'_\iota$ for $\iota \in \mathfrak{I}_I$ and $\mathbf{q}_\iota = \mathbf{q}''_\iota$ for $\iota \in \mathfrak{I}_C$, $h_T^{\overline{\iota}}$ is the total heat source density, $\mathbf{g}^{\overline{\overline{i\iota}}}$ is the external body force, $\mathbf{g}_T^{\overline{\overline{i\iota}}}$ is the total body force, $r^{i\iota}$ is the rate of mass production of species i resulting from all reactions in entity ι, $\overset{i\kappa \to i\iota}{M_E}$ represents the transfer of energy from entity κ to entity ι due to mass transfer of species i per unit volume per unit time, $\overset{\kappa \to \iota}{T_v}$ represents the transfer of energy from entity κ to entity ι due to work and deviations from mean processes per unit volume per unit time, $\overset{\kappa \to \iota}{Q}$ represents the transfer of energy from entity κ to entity ι resulting from heat transfer and deviations from mean processes per unit volume per unit time, $\mathbf{u}^{\overline{\overline{i\iota}}}$ is the dispersion velocity, $\mathfrak{I}$ is the index set of entities, $\mathfrak{I}_s$ is the index set of species, $\mathbf{I}$ is the identity tensor, integration at points indicates a summation over the points, and $\mathbf{n}_\iota \cdot \mathbf{e} = 1$ when $\iota \in \mathfrak{I}_P$. In shorthand notation we have

$$(3.17) \quad \mathcal{E}^\iota = \frac{\mathrm{D}^{\overline{\iota}} E^{\overline{\overline{\iota}}}}{\mathrm{D}t} + \mathbf{v}^{\overline{\iota}} \cdot \frac{\mathrm{D}^{\overline{\iota}} \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \right)}{\mathrm{D}t} + \sum_{i \in \mathfrak{I}_s} \left(K_E^{\overline{\overline{\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} + \psi^{\overline{i\iota}} \right) \frac{\mathrm{D}^{\overline{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{i\iota} \right)}{\mathrm{D}t}$$

$$+ \mathcal{E}_r^\iota = 0 \qquad \text{for } \iota \in \mathfrak{I},$$

where $\mathcal{E}_r^\iota$ accounts for the residual terms in Eq. (3.16) that are not explicitly written in Eq. (3.17).

The entity based conservation of momentum equation for a domain that is megascale in one spatial dimension and macroscale in the remaining two spatial dimensions can be written as

$$(3.18) \quad \boldsymbol{\mathcal{P}}^\iota = \frac{\mathrm{D}^{\overline{\iota}} \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \mathbf{I} : \mathbf{d}^{\overline{\overline{\iota}}} - \nabla \boldsymbol{\cdot} \left(\epsilon^\iota \mathbf{t}^{\overline{\overline{\iota}}} \right) - \sum_{i \in \mathfrak{I}_s} \epsilon^\iota \rho^\iota \omega^{i\iota} \mathbf{g}_T^{\overline{\overline{i\iota}}}$$

$$-\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\left(\sum_{i\in\mathcal{I}_s}\overset{i\kappa\rightarrow i\iota}{\mathbf{M}_v}+\overset{\kappa\rightarrow\iota}{\mathbf{T}}\right)+\left\langle\frac{\mathbf{e}\cdot\left[\rho_\iota\left(\mathbf{v}_\iota-\mathbf{v}_{\mathrm{ext}}\right)\mathbf{v}_\iota-\mathbf{t}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$=0\quad\text{for }\iota\in\mathcal{I},$$

which may be written in shorthand form as

$$(3.19)\qquad\qquad\boldsymbol{\mathcal{P}}^\iota=\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\mathbf{v}^{\bar{\iota}}\right)}{\mathrm{D}t}+\boldsymbol{\mathcal{P}}^\iota_r=0\qquad\text{for }\iota\in\mathcal{I},$$

where $\overset{i\kappa\rightarrow i\iota}{\mathbf{M}_v}$ represents the transfer of momentum as a result of the transfer of mass of species i from connected entity κ to entity ι per unit volume per unit time, $\overset{\kappa\rightarrow\iota}{\mathbf{T}}$ represents the transfer of momentum from entity ι to entity κ due to stress and deviations from mean processes per unit volume per unit time, and $\boldsymbol{\mathcal{P}}^\iota_r$ accounts for the residual terms from Eq. (3.18) that are not explicitly expressed in Eq. (3.19).

The conservation of mass equation for a species i in entity ι for a domain that is megascale in one spatial dimension and macroscale in the remaining two spatial dimensions can be written as

$$(3.20)\quad\mathcal{M}^{i\iota}=\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\right)}{\mathrm{D}t}+\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}}+\nabla^{\backslash}{\cdot}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{u}^{\overline{\bar{i\iota}}}\right)-\epsilon^\iota r^{i\iota}-\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\overset{i\kappa\rightarrow i\iota}{M}$$

$$+\left\langle\frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota-\mathbf{v}_{\mathrm{ext}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\left\langle\frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\mathbf{u}_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=0\qquad\text{for }\iota\in\mathcal{I}.$$

where the material derivative has been referenced to the macroscale mass averaged entity velocity, $\mathbf{v}^{\bar{\iota}}$ and $\overset{i\kappa\rightarrow i\iota}{M}$ represents the transfer of mass of species i from connected entity κ to entity ι per unit volume per unit time.

Eq. (3.20) can be written in shorthand notation as

$$(3.21)\qquad\qquad\mathcal{M}^{i\iota}=\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\right)}{\mathrm{D}t}+\mathcal{M}^{i\iota}_r=0\qquad\text{for }\iota\in\mathcal{I},$$

where $\mathcal{M}^{i\iota}_r$ accounts for the residual terms in Eq. (3.20).

Summing the balance of entropy equations that are macroscale in two spatial dimensions and megascale in the remaining spatial dimension over all entities provides the balance of entropy of the transition region system

$$(3.22) \quad \sum_{\iota \in \mathcal{I}} \mathcal{S}^\iota = \sum_{\iota \in \mathcal{I}} \left(\frac{D^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{Dt} + \eta^{\bar{\bar{\iota}}} \mathbf{I} : \mathbf{d}^{\bar{\bar{\iota}}} - \nabla' \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\bar{\bar{\iota}}} \right) - \epsilon^\iota b_T^{\bar{\bar{\iota}}} \right.$$

$$\left. + \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}} \right) \eta_\iota - \boldsymbol{\varphi}_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \right) = \Lambda \geq 0,$$

where η is the entropy density, $\boldsymbol{\varphi}^{\bar{\iota}}$ is the non-advective entropy density flux vector which is a three dimensional vector restricted to the transition region, at the microscale $\boldsymbol{\varphi}_\iota = \boldsymbol{\varphi}'_\iota$ for $\iota \in \mathcal{I}_I$ and $\boldsymbol{\varphi}_\iota = \boldsymbol{\varphi}''_\iota$ for $\iota \in \mathcal{I}_C$, $b_T^{\bar{\iota}}$ is the total entropy source density, and Λ is the entropy production rate density for the system.

We can write a shorthand expression for the entropy inequality as

$$(3.23) \qquad \sum_{\iota \in \mathcal{I}} \mathcal{S}^\iota = \sum_{\iota \in \mathcal{I}} \left(\frac{D^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{Dt} + \mathcal{S}_r^\iota \right) = \Lambda \geq 0,$$

where $\mathcal{S}_r^\iota$ represents the residual terms in the entropy inequality Eq. (3.22). Residual terms refer to the collection of all terms in the original equation not explicitly listed in the shorthand form.

3.6. Thermodynamics

We will rely on CIT at the microscale for the underlying thermodynamic theory [61], which is needed to link terms that appear in the entropy inequality with terms that appear in conservation equations. Since our desire is to produce models that are macroscale in two spatial dimensions and megascale in the third spatial dimension, it will be necessary to upscale established CIT expressions from the microscale to the desired scale. To accomplish this upscaling, we will average the microscale CIT up to the appropriate mixed macroscale and megascale forms needed. While such forms have not

appeared in the literature, this formulation builds upon previous work to develop averaged CIT expressions that are consistent across multiple length scales [76, 84, 87, 137]. Since this formulation is a routine calculation that is very similar to previous work, we will summarize the results without providing the details of the averaging procedure and simplifications that were performed using the theorems given in §3.4.

The averaged macroscale and megascale CIT expression relating material derivatives of thermodynamic quantities for a fluid phase is

$$
(3.24) \quad \mathcal{T}^\iota = \frac{\mathrm{D}^{\bar{\iota}} E^{\bar{\iota}}}{\mathrm{D}t} - \theta^{\bar{\iota}} \frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\iota}}}{\mathrm{D}t} - \sum_{i \in \mathcal{I}_S} \mu^{\overline{i\iota}} \frac{\mathrm{D}^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{\overline{i\iota}}\right)}{\mathrm{D}t}
$$

$$
+ \sum_{\kappa \in \mathcal{I}_{c\iota}} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}}\right) p_\iota \right\rangle_{\Omega_\kappa, \Omega} + \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{s}}\right) p_\iota \right\rangle_{\Gamma_{\iota M}, \Omega}
$$

$$
+ \left\langle \eta_\iota \frac{\mathrm{D}^{\bar{s}} \left(\theta_\iota - \theta^{\bar{\iota}}\right)}{\mathrm{D}t} + \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \frac{\mathrm{D}^{\bar{s}} \left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega}
$$

$$
- \mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \left(\eta^{\bar{\iota}} \nabla^{\backslash} \theta^{\bar{\iota}} + \sum_{i \in \mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \nabla^{\backslash} \mu^{\overline{i\iota}} - \nabla^{\backslash} \left(\epsilon^\iota p^\iota\right) \right) = 0 \quad \text{for } \iota \in \mathcal{I}_f,
$$

where p is the fluid pressure, θ is the temperature, μ is the chemical potential, $\mathbf{v}^{\overline{\iota}, \overline{s}} = \mathbf{v}^{\bar{\iota}} - \mathbf{v}^{\bar{s}}$, and $\mathcal{I}_f$ is the index set of fluid phases.

The averaged macroscale and megascale CIT expression relating material derivatives of thermodynamic quantities for the solid phase is

$$
(3.25) \quad \mathcal{T}^s = \frac{\mathrm{D}^{\bar{s}} E^{\bar{s}}}{\mathrm{D}t} - \theta^{\bar{s}} \frac{\mathrm{D}^{\bar{s}} \eta^{\bar{s}}}{\mathrm{D}t} - \sum_{i \in \mathcal{I}_S} \mu^{\overline{is}} \frac{\mathrm{D}^{\bar{s}} \left(\epsilon^s \rho^s \omega^{\overline{is}}\right)}{\mathrm{D}t}
$$

$$
+ \left\langle \eta_s \frac{\mathrm{D}^{\bar{s}} \left(\theta_s - \theta^{\bar{s}}\right)}{\mathrm{D}t} + \sum_{i \in \mathcal{I}_S} \rho_s \omega_{is} \frac{\mathrm{D}^{\bar{s}} \left(\mu_{is} - \mu^{\overline{is}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_s, \Omega}
$$

$$
- \epsilon^s \mathbf{t}^{\backslash s} : \mathbf{d}^{\overline{\backslash s}} + \epsilon^s \boldsymbol{\sigma}^{\bar{s}} : \frac{\mathbf{C}^s}{j^s} \mathbf{I} : \mathbf{d}^{\overline{\backslash s}} - \nabla^{\backslash} \cdot \left\langle \left(\mathbf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \mathbf{I}\right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right) \right\rangle_{\Omega_s, \Omega}
$$

$$
- \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right) \right\rangle_{\Omega_{ss}, \Omega} - \left\langle \mathbf{e} \cdot \mathbf{t}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right) \right\rangle_{\Gamma_{sM}, \Omega}
$$

$$+\left\langle\left(\nabla\cdot\mathbf{t}_s - \frac{\mathbf{C}_s}{j_s}:\nabla\boldsymbol{\sigma}_s\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_S,\Omega}$$

$$-\sum_{\kappa\in\mathfrak{I}_{cs}}\left\langle\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa - \mathbf{v}_s\right)\right\rangle_{\Omega_\kappa,\Omega} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}_s\right)\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

where j_s is the solid-phase Jacobian, ss denotes the solid surface, $\boldsymbol{\sigma}$ is the Lagrangian stress tensor, and $\mathbf{C}$ is the Green's deformation tensor.

The averaged macroscale and megascale CIT expression relating material derivatives of thermodynamic quantities for an interface is

$$(3.26)\quad \mathcal{T}^\iota = \frac{\mathrm{D}^{\bar{\iota}}E^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \theta^{\bar{\bar{\iota}}}\frac{\mathrm{D}^{\bar{\iota}}\eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\iota}}\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\right)}{\mathrm{D}t} + \langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\overline{\bar{s}}}$$

$$+\nabla^\backprime\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla^\backprime\theta^{\bar{\bar{\iota}}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa\in(\mathfrak{I}_{c\iota}\cap\mathfrak{I}_C)}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$+\sum_{i\in\mathfrak{I}_s}\nabla^\backprime\mu^{\overline{i\iota}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega} - \left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{s}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\mathrm{D}'^{\bar{s}}\left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t} + \sum_{i\in\mathfrak{I}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}'^{\bar{s}}\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\mathbf{v}^{\overline{\iota,\bar{s}}}\cdot\left(\eta^{\bar{\bar{\iota}}}\nabla^\backprime\theta^{\bar{\bar{\iota}}} + \sum_{i\in\mathfrak{I}_s}\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\nabla^\backprime\mu^{\overline{i\iota}} + \nabla^\backprime\left(\epsilon^\iota\gamma^\iota\right)\right) = 0 \qquad \text{for } \iota\in\mathfrak{I}_{\mathrm{I}},$$

where γ is the interfacial tension.

The averaged macroscale and megascale CIT expression relating material derivatives of thermodynamic quantities for a common curve is

$$(3.27)\quad \mathcal{T}^\iota = \frac{\mathrm{D}^{\bar{\iota}}E^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \theta^{\bar{\bar{\iota}}}\frac{\mathrm{D}^{\bar{\iota}}\eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\iota}}\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\right)}{\mathrm{D}t}$$

$$-\nabla^\backprime\cdot\left\langle\left(\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla^\backprime\theta^{\bar{\bar{\iota}}}\cdot\left\langle\left(\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{i \in \mathcal{I}_s} \nabla^{\backslash} \mu^{\overline{\overline{i\iota}}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \omega_{i\iota} \right\rangle_{\Omega_\iota, \Omega} - \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega} : \mathbf{d}^{\backslash \overline{\overline{s}}}$$

$$+ \sum_{\kappa \in \left(\mathcal{I}_{c\iota} \cap \mathcal{I}_{Pt} \right)} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\kappa, \Omega} + \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \left\langle \eta_\iota \frac{\mathrm{D}''^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\iota}} \right)}{\mathrm{D}t} + \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \frac{\mathrm{D}''^{\overline{s}} \left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega}$$

$$- \mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \left(\eta^{\overline{\overline{\iota}}} \nabla^{\backslash} \theta^{\overline{\iota}} + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \nabla^{\backslash} \mu^{\overline{\overline{i\iota}}} - \nabla^{\backslash} \left(\epsilon^\iota \gamma^\iota \right) \right) = 0 \qquad \text{for } \iota \in \mathcal{I}_C,$$

where γ is the curvilineal tension.

Each of the thermodynamic equations can be written in shorthand notation as

$$(3.28) \quad \mathcal{T}^\iota \quad = \quad \frac{\mathrm{D}^{\overline{\iota}} E^{\overline{\overline{\iota}}}}{\mathrm{D}t} - \theta^{\overline{\iota}} \frac{\mathrm{D}^{\overline{\iota}} \eta^{\overline{\overline{\iota}}}}{\mathrm{D}t} - \sum_{i \in \mathcal{I}_s} \mu^{\overline{\overline{i\iota}}} \frac{\mathrm{D}^{\overline{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{i\iota} \right)}{\mathrm{D}t} + \mathcal{T}_r^\iota \quad = \quad 0 \qquad \text{for } \iota \in \mathcal{I},$$

where $\mathcal{T}_r^\iota$ accounts for the residual terms found in Eq. (3.24), Eq. (3.25), Eq. (3.26), and Eq. (3.27) depending on the entity ι.

3.7. Entropy Inequality

As has been detailed in previous work in this series [84, 85, 87, 110], the formulation of a constrained entropy inequality (CEI) is a key step in the formulation of a TCAT model. The CEI represents an exact expression, given the limitations stated by a set of primary restrictions, for the second law of thermodynamics that connects the thermodynamics and conservation principles of a system to support the derivation of a set of closure relations and resultingly also a hierarchy of closed models. The derivation of a CEI for a given system requires a significant amount of manipulation, however these details are routine in nature and have been shown in previous work for other systems [85, 87, 88, 110]. While it is not necessary to present the details of the derivation of the CEI for the transition region model of concern in this work, the CEI itself has significant archival value because it is the starting point for the application of a set of secondary restrictions

and approximations that lead to a simplified entropy inequality (SEI), which is used to generate sets of permissable closure relations. Because multiple sets of secondary restrictions and approximations are possible, it is convenient to be able to return to the CEI to reformulate alternative sets of closure relations as needed in the future. Thus we will briefly outline the steps taken to derive the CEI in this section for the transition region model of concern in this work, while ommitting the routine manipulations needed to derive the final form of this expression. We also introduce the secondary restrictions and formal approximations that are used to reduce the CEI to the SEI and present the resulting SEI.

3.7.1. Constrained Entropy Inequality. An augmented entropy inequality (AEI) can be written for the transition region model as

$$\sum_{\iota \in \mathcal{I}} \left(\mathcal{S}^\iota + \lambda_\mathcal{E}^\iota \mathcal{E}^\iota + \boldsymbol{\lambda}_\mathcal{P}^\iota \cdot \boldsymbol{\mathcal{P}}^\iota + \sum_{i \in \mathcal{I}_s} \lambda_\mathcal{M}^{i\iota} \mathcal{M}^{i\iota} + \lambda_\mathcal{T}^\iota \mathcal{T}^\iota \right) = \Lambda \geq 0, \tag{3.29}$$

where λ denotes a Lagrange multiplier, the subscript is an equation qualifier, and the superscript is an entity or species-entity qualifer. The specific forms of the equations given by $\mathcal{S}, \mathcal{E}, \boldsymbol{\mathcal{P}}, \mathcal{M}$, and $\mathcal{T}$ are given by Eqs. (3.16), (3.18), (3.20), (3.22), and (3.24)–(3.27), respectively. These equations are expressed in terms of entropy, energy, and momentum per entity measure and species mass per entity measure. Thus compositional effects will be resolved through the conservation of mass equation, but all other thermodynamic quantities will not be compositional in nature. For example, the conservation of momentum for a phase, interface, or common curve will be modeled explicitly, while the conservation of momentum for a species in a phase, interface or common curve will not be explicitly modeled through a conservation equation but rather through the development of an appropriate set of closure relations. An alternative approach is possible and has been explored elsewhere [84].

The Lagrange multipliers in Eq. (3.29) can be solved to eliminate a subset of the material derivatives. In particular, Eq. (3.17), Eq. (3.19), Eq. (3.21), Eq. (3.23), and

Eq. (3.28) have been written in such a way that the material derivatives that appear explicitly may be made to cancel. A unique solution for the λ's that satisfies this goal is then accomplished as outlined in [85]. The result being

$$
(3.30) \quad \left\{ \begin{array}{c} \lambda_{\mathcal{M}}^{i\iota} \\ \boldsymbol{\lambda}_{\mathcal{P}}^{\iota} \\ \lambda_{\mathcal{E}}^{\iota} \\ \lambda_{\mathcal{T}}^{\iota} \end{array} \right\} = \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\{ \begin{array}{c} K_{E}^{\overline{\iota}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \dfrac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \\ \mathbf{v}^{\overline{\iota}} \\ -1 \\ 1 \end{array} \right\} \quad \text{for } \iota \in \mathcal{I}, \ i \in \mathcal{I}_{s}.
$$

Substitution of the above Lagrange multipliers and the conservation, balance, and thermodynamic equations into the AEI, Eq. (3.29), together with manipulations similar to what has been done in previous TCAT papers [85, 87, 110] gives the following CEI:

$$
\begin{aligned}
(3.31) \quad &-\sum_{\iota \in (\mathcal{I}_{\mathrm{f}} \cup \mathcal{I}_{\mathrm{I}} \cup \mathcal{I}_{\mathrm{C}})} \nabla \cdot \left[\epsilon^{\iota} \boldsymbol{\varphi}^{\backslash \overline{\iota}} - \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(\epsilon^{\iota} \mathbf{q}^{\backslash \overline{\iota}} + \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \right) \right] \\
&+ \sum_{\iota \in (\mathcal{I}_{\mathrm{f}} \cup \mathcal{I}_{\mathrm{I}} \cup \mathcal{I}_{\mathrm{C}})} (\nabla \cdot \mathbf{N}) \, \mathbf{N} \cdot \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\overline{\overline{i\iota}}} \\
&- \nabla \cdot \left\{ \epsilon^{s} \boldsymbol{\varphi}^{\backslash \overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}} \left[\epsilon^{s} \mathbf{q}^{\backslash \overline{\overline{s}}} + \sum_{i \in \mathcal{I}_s} \epsilon^{s} \rho^{s} \omega^{i\overline{s}} \left(\mu^{\overline{i s}} + \psi^{\overline{i s}} \right) \mathbf{u}^{\backslash \overline{\overline{i s}}} \right. \right. \\
&\qquad\qquad \left. \left. - \left\langle \mathbf{I} \cdot \left(\mathbf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s, \Omega} \right] \right\} \\
&+ (\nabla \cdot \mathbf{N}) \, \mathbf{N} \cdot \left[\frac{1}{\theta^{\overline{\overline{s}}}} \sum_{i \in \mathcal{I}_s} \epsilon^{s} \rho^{s} \omega^{i\overline{s}} \left(\mu^{\overline{i s}} + \psi^{\overline{i s}} \right) \mathbf{u}^{\overline{\overline{i s}}} \right. \\
&\qquad\qquad \left. + \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \left(\mathbf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s, \Omega} \right] \\
&- \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \left[\epsilon^{\iota} b_T^{\overline{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(\epsilon^{\iota} h_T^{\overline{\overline{\iota}}} + \left\langle \eta_{\iota} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\iota} - \theta^{\overline{\overline{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right) \right] \\
&- \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i \in \mathcal{I}_s} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}} - K_E^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega}
\end{aligned}
$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left[\epsilon^{\iota}b_T^{\bar{\bar{\iota}}}-\frac{1}{\theta^{\bar{\bar{\iota}}}}\left(\epsilon^{\iota}h_T^{\bar{\bar{\iota}}}+\left\langle\eta_{\iota}\frac{\mathrm{D}'^{\bar{s}}\left(\theta_{\iota}-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right)\right.$$

$$\left.-\frac{1}{\theta^{\bar{\bar{\iota}}}}\sum_{i\in\mathcal{I}_s}\left\langle\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}'^{\bar{s}}\left(\mu_{i\iota}+\psi_{i\iota}-\mu^{\overline{i\iota}}-\psi^{\overline{i\iota}}-K_E^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]$$

$$-\epsilon^{wgs}b_T^{\overline{\overline{wgs}}}+\frac{1}{\theta^{\overline{\overline{wgs}}}}\left(\epsilon^{wgs}h_T^{\overline{\overline{wgs}}}+\left\langle\eta_{wgs}\frac{\mathrm{D}''^{\bar{s}}\left(\theta_{wgs}-\theta^{\overline{\overline{wgs}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wgs},\Omega}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\sum_{i\in\mathcal{I}_s}\left\langle\rho_{wgs}\omega_{iwgs}\frac{\mathrm{D}''^{\bar{s}}\left(\mu_{iwgs}+\psi_{iwgs}-\mu^{\overline{iwgs}}-\psi^{\overline{iwgs}}-K_E^{\overline{\overline{wgs}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\epsilon^{\iota}}{\theta^{\bar{\bar{\iota}}}}\left(\mathbf{t}^{\backslash\bar{\iota}}+p^{\iota}\mathbf{I}^{\backslash}\right)\!:\!\mathbf{d}^{\backslash\bar{\iota}}+\frac{\epsilon^{s}}{\theta^{\bar{\bar{s}}}}\left(\mathbf{t}^{\backslash\bar{s}}-\mathbf{t}^{\backslash s}\right)\!:\!\mathbf{d}^{\backslash\bar{s}}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\epsilon^{\iota}}{\theta^{\bar{\bar{\iota}}}}\left(\mathbf{t}^{\backslash\bar{\iota}}-\gamma^{\iota}\mathbf{I}^{\backslash}\right)\!:\!\mathbf{d}^{\backslash\bar{\iota}}+\frac{\epsilon^{wgs}}{\theta^{\overline{\overline{wgs}}}}\left(\mathbf{t}^{\backslash\overline{wgs}}+\gamma^{wgs}\mathbf{I}^{\backslash}\right)\!:\!\mathbf{d}^{\backslash\overline{wgs}}$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\bar{\bar{\iota}}}}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{u}^{\backslash\overline{\bar{i\iota}}}\!\cdot\!\nabla^{\backslash}\left(\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)$$

$$-\sum_{\iota\in\left(\mathcal{I}_{\mathrm{f}}\cup\mathcal{I}_{\mathrm{I}}\cup\mathcal{I}_{\mathrm{C}}\right)}\left(\epsilon^{\iota}\mathbf{q}^{\backslash\bar{\iota}}-\mathbf{v}^{\iota,\bar{s}}\theta^{\bar{\iota}}\eta^{\bar{\iota}}+\sum_{i\in\mathcal{I}_s}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\left(\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\mathbf{u}^{\backslash\overline{i\iota}}\right)\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\bar{\bar{\iota}}}}\right)$$

$$-\left[\epsilon^{s}\mathbf{q}^{\backslash\bar{s}}+\sum_{i\in\mathcal{I}_s}\epsilon^{s}\rho^{s}\omega^{i\bar{s}}\left(\mu^{\overline{is}}+\psi^{\overline{is}}\right)\mathbf{u}^{\backslash\overline{is}}\right.$$

$$\left.-\left\langle\mathbf{I}^{\backslash}\!\cdot\!\left(\mathbf{t}_s-\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\bar{\bar{s}}}}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\left(\mathbf{v}^{\backslash\bar{\iota}}-\mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\iota}}}\!\cdot\!\left[\sum_{i\in\mathcal{I}_s}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\nabla^{\backslash}\left(K_E^{\bar{\bar{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)+\sum_{i\in\mathcal{I}_s}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{g}^{\backslash\overline{i\iota}}\right.$$

$$\left.-\nabla^{\backslash}\left(\epsilon^{\iota}p^{\iota}\right)+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left(\overset{\kappa\to\iota}{\mathbf{T}}\!\cdot\!\mathbf{I}^{\backslash}+\frac{\left(\mathbf{v}_{\iota}^{\backslash\overline{\kappa}}-\mathbf{v}^{\backslash\overline{\kappa}}\right)+\left(\mathbf{v}_{\iota}^{\backslash\overline{\kappa}}-\mathbf{v}^{\backslash\iota}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{i\kappa\to i\iota}{M}\right)\right]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\iota,\bar{s}}\!\cdot\!\mathbf{N}\mathbf{N}\cdot}{\theta^{\bar{\iota}}}\left[\sum_{i\in\mathcal{I}_s}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{g}^{\backslash\overline{i\iota}}\!\cdot\!\mathbf{N}\mathbf{N}\right.$$

$$
+ \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \mathbf{N}\mathbf{N} \cdot \left(\overset{\kappa \to \iota}{\mathbf{T}} + \frac{\left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{\kappa}}\right) + \left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{\iota}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{i\kappa \to i\iota}{M} \right) \Bigg]
$$

$$
- \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\left(\mathbf{v}^{\backslash \overline{\iota}} - \mathbf{v}^{\backslash \overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}} \cdot \Bigg[\sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \nabla^{\backslash} \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\backslash \overline{i\iota}}
$$

$$
+ \nabla^{\backslash} \left(\epsilon^\iota \gamma^\iota \right) - \sum_{\kappa \in \left(\mathcal{I}_{\mathrm{C}\iota} \cap \mathcal{I}_{\mathrm{P}} \right)} \left(\overset{\iota \to \kappa}{\mathbf{T}} \cdot \mathbf{I}^{\backslash} + \frac{\left(\mathbf{v}_\kappa^{\backslash \overline{\iota}} - \mathbf{v}^{\backslash \overline{\kappa}}\right) + \left(\mathbf{v}_\kappa^{\backslash \overline{\iota}} - \mathbf{v}^{\backslash \overline{\iota}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{i\iota \to i\kappa}{M} \right)
$$

$$
+ \left(\overset{wgs \to \iota}{\mathbf{T}} \cdot \mathbf{I}^{\backslash} + \frac{\left(\mathbf{v}_\iota^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{wgs}}\right) + \left(\mathbf{v}_\iota^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{\iota}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\iota}{M} \right) \Bigg]
$$

$$
- \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{N}\mathbf{N} \cdot}{\theta^{\overline{\overline{\iota}}}} \Bigg[\sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\overline{i\iota}} \cdot \mathbf{N}\mathbf{N}
$$

$$
- \sum_{\kappa \in \left(\mathcal{I}_{\mathrm{C}\iota} \cap \mathcal{I}_{\mathrm{P}} \right)} \mathbf{N}\mathbf{N} \cdot \left(\overset{\iota \to \kappa}{\mathbf{T}} + \frac{\left(\mathbf{v}_\kappa^{\overline{\iota}} - \mathbf{v}^{\overline{\kappa}}\right) + \left(\mathbf{v}_\kappa^{\overline{\iota}} - \mathbf{v}^{\overline{\iota}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{i\iota \to i\kappa}{M} \right)
$$

$$
+ \mathbf{N}\mathbf{N} \cdot \left(\overset{wgs \to \iota}{\mathbf{T}} + \frac{\left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{wgs}}\right) + \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{\iota}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\iota}{M} \right) \Bigg]
$$

$$
- \frac{\left(\mathbf{v}^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}} \cdot \Bigg[\sum_{i \in \mathcal{I}_s} \epsilon^{wgs} \rho^{wgs} \omega^{i\overline{wgs}} \nabla^{\backslash} \left(K_E^{\overline{\overline{wgs}}} + \mu^{\overline{iwgs}} + \psi^{\overline{iwgs}} \right)
$$

$$
+ \sum_{i \in \mathcal{I}_s} \epsilon^{wgs} \rho^{wgs} \omega^{i\overline{wgs}} \mathbf{g}^{\backslash \overline{iwgs}} - \nabla^{\backslash} \left(\epsilon^{wgs} \gamma^{wgs} \right)
$$

$$
- \sum_{\kappa \in \mathcal{I}_{\mathrm{C}wgs}} \left(\overset{wgs \to \kappa}{\mathbf{T}} \cdot \mathbf{I}^{\backslash} + \frac{\left(\mathbf{v}_\kappa^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{\kappa}}\right) + \left(\mathbf{v}_\kappa^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{wgs}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\kappa}{M} \right) \Bigg]
$$

$$
- \frac{\mathbf{v}^{\overline{wgs},\overline{s}} \cdot \mathbf{N}\mathbf{N} \cdot}{\theta^{\overline{\overline{wgs}}}} \Bigg[\sum_{i \in \mathcal{I}_s} \epsilon^{wgs} \rho^{wgs} \omega^{i\overline{wgs}} \mathbf{g}^{\overline{iwgs}} \cdot \mathbf{N}\mathbf{N}
$$

$$
- \sum_{\kappa \in \mathcal{I}_{\mathrm{C}wgs}} \mathbf{N}\mathbf{N} \cdot \left(\overset{wgs \to \kappa}{\mathbf{T}} + \frac{\left(\mathbf{v}_\kappa^{\overline{wgs}} - \mathbf{v}^{\overline{\kappa}}\right) + \left(\mathbf{v}_\kappa^{\overline{wgs}} - \mathbf{v}^{\overline{wgs}}\right)}{2} \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\kappa}{M} \right) \Bigg]
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \nabla^{\backslash} \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} + \mu^{\overline{i\iota}} \right) \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \omega_{i\iota} \right\rangle_{\Omega_\iota, \Omega}
$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\bar{\iota}}}} \nabla^{\backslash} \theta^{\overline{\bar{\iota}}} \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \eta_\iota \right\rangle_{\Omega_\iota, \Omega} - \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\bar{\iota}}}} \mu^{\overline{i\iota}} \epsilon^\iota r^{i\iota}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \frac{1}{\theta^{\overline{\bar{\kappa}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\bar{\kappa}}} + \mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}} \right) - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{wgs}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\overline{wgs}}} + \mu^{\overline{iwgs}} + \psi^{\overline{iwgs}} \right) - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\bar{\kappa}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\bar{\kappa}}} + \mu_{i\iota}^{\overline{\kappa}} + \psi_\iota^{\overline{\kappa}} \right) - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\overline{wgs}}} + \mu_{i\iota}^{\overline{wgs}} + \psi_\iota^{\overline{wgs}} \right) \right.$$

$$\left. - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\bar{\kappa}}}} \right) \left\{ \overset{\kappa \to \iota}{Q} + \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\bar{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa} - \mu_{i\iota}^{\overline{\kappa}} \right) \overset{i\kappa \to i\iota}{M} + \left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{\kappa \to \iota}{\mathbf{T}} \right.$$

$$\left. + \left[\frac{\left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right)}{2} - \frac{\mathbf{v}^{\overline{\iota,s}} \cdot \mathbf{v}^{\overline{\kappa,s}}}{2} \right] \sum_{i \in \mathcal{I}_s} \overset{i\kappa \to i\iota}{M} \right\}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left\{ \overset{wgs \to \iota}{Q} + \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{wgs}}}}{\epsilon^\iota \rho_\iota^{wgs}} - \mu_{i\iota}^{\overline{wgs}} \right) \overset{iwgs \to i\iota}{M} \right.$$

$$+ \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{wgs \to \iota}{\mathbf{T}}$$

$$\left. + \left[\frac{\left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right)}{2} - \frac{\mathbf{v}^{\overline{\iota,s}} \cdot \mathbf{v}^{\overline{wgs,s}}}{2} \right] \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\iota}{M} \right\}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\bar{\kappa}}}} \right) \left\langle p_\iota \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_\iota \right\rangle_{\Omega_\kappa, \Omega}$$

$$- \frac{1}{\theta^{\overline{\bar{s}}}} \sum_{\kappa \in \mathcal{I}_{cs}} \left\langle \left(\frac{\mathbf{C}_s}{j_s} : \boldsymbol{\sigma}_s \right) \left(\mathbf{v}_\kappa - \mathbf{v}_s \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa, \Omega}$$

$$- \frac{1}{\theta^{\overline{\bar{s}}}} \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{I}' \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ss}, \Omega} - \frac{1}{\theta^{\overline{\bar{s}}}} \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ss}, \Omega}$$

$$+ \frac{1}{\theta^{\overline{\bar{s}}}} \left\langle \left(\nabla \cdot \mathbf{t}_s - \nabla \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s, \Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\nabla\textbf{'}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}+\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}\mathbf{:d}^{\backslash\overline{\overline{s}}}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\left\langle\left(p_w-p_g-\gamma_{wg}\nabla'\cdot\mathbf{n}_w+\sum_{i\in\mathcal{I}_s}\rho_{wg}\omega_{iwg}\mathbf{n}_w\cdot\mathbf{g}_{iwg}\right)\right.$$

$$\left.\left(\mathbf{v}_{wg}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_w\right\rangle_{\Omega_{wg},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle\left(p_w+\gamma_{ws}\nabla'\cdot\mathbf{n}_s-\sum_{i\in\mathcal{I}_s}\rho_{ws}\omega_{iws}\mathbf{n}_s\cdot\mathbf{g}_{iws}\right)\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{gs}}}}\left\langle\left(p_g+\gamma_{gs}\nabla'\cdot\mathbf{n}_s-\sum_{i\in\mathcal{I}_s}\rho_{gs}\omega_{igs}\mathbf{n}_s\cdot\mathbf{g}_{igs}\right)\left(\mathbf{v}_{gs}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{gs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla\textbf{'}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}\mathbf{:d}^{\backslash\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\mathbf{l}_{wgs}\cdot\nabla''\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla\textbf{'}\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)$$

$$\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\rho_{wgs}\omega_{iwgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\sum_{i\in\mathcal{I}_s}\left\langle\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\rho_{wgs}\omega_{iwgs}\mathbf{g}_{iwgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla\textbf{'}\theta^{\overline{\overline{wgs}}}\cdot\left\langle\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\eta_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{f}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_\iota\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{I}_\mathrm{f}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot p_\iota\mathbf{I}\textbf{'}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_\iota'\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\sum_{\iota\in\mathcal{I}_\mathrm{I}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_\iota\mathbf{I}\textbf{'}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}''_{wgs}\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{wgs}}\right)}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$+\frac{\left(\mathbf{v}^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{wgs}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{wgs}\mathbf{I}''}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota,\overline{s}}}\cdot\mathbf{N}}{\theta^{\overline{\iota}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}p_{\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota,\overline{s}}}\cdot\mathbf{N}}{\theta^{\overline{\iota}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\frac{\mathbf{v}^{\overline{wgs,\overline{s}}}\cdot\mathbf{N}}{\theta^{\overline{wgs}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{wgs}}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\iota}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\mu_{i\iota}+\psi_{i\iota}-K_E^{\overline{\iota}}-\mu^{\overline{i\iota}}-\psi^{\overline{i\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\iota}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\frac{\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{2}+\frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\left\langle\frac{\mathbf{e}\cdot\sum_{i\in\mathcal{I}_s}\rho_{\iota}\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_{\iota}}-\frac{\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}}{\theta^{\overline{\iota}}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\left\langle\frac{\left(\frac{1}{\theta^{\overline{\iota}}}-\frac{1}{\theta_{\iota}}\right)\mathbf{e}\cdot\left[\mathbf{q}_{\iota}-\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\theta_{\iota}\eta_{\iota}\right]}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=\Lambda\geq0,$$

where $\boldsymbol{\tau}_{\iota}$ is the viscous stress tensor for entity ι, $\mathbf{I}^{\backslash}$ is the macroscale surface identity tensor, and $\mathbf{I}'$ and $\mathbf{I}''$ are the microscale surface and common curve identity tensors respectively. In the case where both subscript and superscript qualifiers are present in an averaged variable, the superscript indicates the domain over which the subscripted microscale quantity has been averaged.

Eq. (3.31) is the final CEI for the two-fluid-phase flow and species transport system that is macroscale in two spatial dimensions and megascale in the third spatial dimension. It has been written in terms of force-flux products, but additional work is needed to ensure both factors in all force-flux pairs will be zero at equilibrium. The choice of the microscale thermodynamic functional dependence is responsible in part for the appearance of terms in Eq. (3.31). No mathematical approximations have been employed in obtaining Eq. (3.31) beyond the primary restrictions detailed in §3.3. The subsequent

steps needed to obtain complete closed models require additional restrictions and approximations appropriate for the physical system under consideration and may take different forms depending on the systems studied and the approximate relations employed.

3.7.2. Secondary Restrictions and SEI Approximations. The primary restrictions presented in §3.3 define the general type of system to be modeled and the microscale thermodynamic theory to be used in formulating these models. Lengthy, but routine, manipulations result in the formulation of a CEI. While the CEI is useful for archival purposes because of its exact nature and generality, it is not suitable for use to guide the formulation of closure relations needed to produce specific well-posed models. What is needed is a form of the EI that is arranged strictly as the sum of force-flux pairs that each vanish at equilibrium. We call such a form the SEI. The SEI is derived by reducing the scope of the system being considered beyond that originally specified by the primary restrictions and by mathematically approximating certain terms that appear in the CEI to allow arrangement to the desired form. The scope of the system is reduced by specifying a set of secondary restrictions. A set of formal SEI approximations are stated that enable the final derivation of the SEI. Once an appropriate form SEI has been produced, a hierarchy of models of varying sophistication can be derived that are consistent with the SEI. Alternative sets of secondary restrictions and SEI approximations are possible, and each set would in turn lead to an alternative form of the SEI and a potentially different hierarchy of models. Formal statements of the elements selected to derive an SEI are detailed below.

SECONDARY RESTRICTION 1 (Solid Properties). *The solid-phase particles are non-deformable and of uniform constant composition.*

Secondary Restriction 1 indicates the solid phase does not undergo deformations, diffusion within the solid is negligible, and mass transfer does not occur between solid phase and other entities present within the system.

SECONDARY RESTRICTION 2 (Non-reactive). *The system is non-reactive.*

Secondary Restriction 2 specifies that no biogeochemical reactions occur between the species present in the system.

SECONDARY RESTRICTION 3 (Massless and Frictionless). *Interfaces and common curves are massless and frictionless.*

Secondary Restriction 3 reduces the conservation of mass equation for interfaces to a jump condition between phases at the interface. The common curve conservation of mass equation can be neglected because it becomes trivially zero.

SECONDARY RESTRICTION 4 (Species). *The system is restricted to an inert solid phase that does not change in composition, and two species in each of the fluid phases.*

This restriction is sufficiently general to account for evaporation of water to the gas phase and to account for volatilization of a dilute species from the aqueous phase to the gas phase, which are two target applications for the closed models. This restriction could be relaxed easily and more general models developed.

SEI APPROXIMATION 1 (Deviation Terms). *Subscale kinetic energy due to velocity deviations can be neglected*

Kinetic energy due to velocity fluctuations and differences between the species velocity within an entity and the entity velocity itself can be considered a measure of the deviations in kinetic energy. In cases where these velocity differences are small, this difference squared can as a first approximation be justifiably neglected. Approximation 1 states that the integral of the product of the difference between the microscale and macroscale velocities as well as the integral of the product of the difference between the species velocity within a given entity and that entity's velocity, are to first order, zero.

SEI APPROXIMATION 2 (Higher Order Terms). *In the force-flux arrangement of terms, products of two or more forces do not play a role in the linearization process and are thus neglected.*

Products of terms appear in the CEI that involve two or more forces multiplying a flux term. In the linearization process, these terms can be assumed to be higher order and can be dropped in the SEI.

SEI Approximation 3 (Macroscopically Simple System). *The system of concern is what we consider to be a macroscopically simple in the thermodynamic sense.*

We define a macroscopically simple system to be a system in which the entropy flux is balanced by the sum of the heat and diffusive flux, and the entropy source is balanced by the sum of the heat source and the material derivative of temperature and potential fluctuation terms.

SEI Approximation 4 (Geometric Tensor Independence). *Geometric tensors are independent of entity measures, densities, velocities, and interfacial and curvilinear tension, such that integrals of products of these quantities may be split into products of integrals.*

The orientation of entities arise from thermodynamics and play an important role in evolution equations and closure relations. The form of these orientation tensors exist as microscale products with a variety of other quantities. To a first approximation, these quantities are assumed independent, allowing expression in terms of macroscale quantities. Microscale experimental and computational approaches can be used to check the validity of these approximations.

SEI Approximation 5 (Solid Surface Independence). *Normal velocities and curvatures of material points on the solid surface do not depend on which fluid phase they contact.*

A secondary restriction on the system is that the solid particles do not deform. Thus, this approximation means that particle motion of the solid surface is independent of the fluid contacting the solid at the microscale. This will be the case if solid particle motion is through translation alone or if the rotational component is independent of the phase in contact with the solid.

SEI APPROXIMATION 6 (Relative Solid-Phase Mobility). *The solid is relatively immobile compared to the velocities of the fluid phases.*

This approximation requires that consolidaton and expansion due to solid phase motion happen on a time scale that is long compared to the motion of the fluid phases present in the system, which is a reasonable approximation for the target systems of interest in this work.

SEI APPROXIMATION 7 (Solid-Phase Curvature Deviations). *The average of the product of the deviation between the microscale and macroscale solid phase curvatures and the relative velocity of the fluid-solid interface in the normal direction to the solid phase is assumed to be negligibly small.*

If the curvature of the solid phase is not correlated with the microscale velocity, then this approximation is void of error. Even if correlation between the terms exists, both terms in the product will be small for the systems of focus in this work; this is a mild approximation.

SEI APPROXIMATION 8 (Entity Measure Evolution). *The evolution of specific interfacial areas and specific common curve lengths are formualted using averaging theorems and are simplified using approximations related to the solid behavior, integral splitting approximations, and closure approximations.*

Two specific problems arise in the CEI related to entity measures. First, terms that result in time derivatives of entity measures arise in various terms of the CEI and these time derivatives are not independent. Arrangement into a strict force-flux form requires an appropriate grouping of these terms. The inter-dependence of these terms can be derived using established averaging theorems [90]. Second, a deficit of equations exists because entity measures are not conserved quantities, which in turn requires the formulation of evolution equations that provide a means to close the system. Certain terms in the evolution equation must be approximated with a closure approximation to

produce a solvable evolution equation. Microscale methods can be used to check the assumptions made in the derivation of these evolution equations.

SEI APPROXIMATION 9 (Capillary Pressure Dynamics). *The dynamics of capillary pressure is influenced primarily by changes in the curvature of the interface, while differences between microscale and macroscale values of interfacial tension and pressures evaluated at the interface are of lower order importance.*

Because fluid pressures equilibrate relatively rapidly in a closed porous medium system and interfacial tensions vary primarily with composition and temperature, curvature effects will generally be dominant. This will not be the case if significant changes in solute concentrations that include surfactants occur, or if the difference between the temperature and the critical temperature changes significantly. Because our focus is not on surfactant systems and the critical temperature of water is large compared to normal temperatures, this assumption is mild.

3.7.3. Simplified Entropy Inequality. A SEI provides useful information for the formulation of closed models, but to do so, the SEI must consist solely of force-flux pairs with all forces and fluxes equal to zero at equilibrium. Examination of Eq. (3.31) reveals that several terms are not strictly in force-flux form. The steps needed to transform the CEI into the desired form of SEI are based on the system being considered as detailed by the secondary restrictions and upon the formal SEI approximations made. The resultant SEI may then be used to derive closure relationships for a wide range of models that are in agreement with the primary and secondary restrictions to the system. If better approximations, or exact expressions, are discovered in the future, then they need only be applied at this stage to the CEI in order to improve the SEI formulation.

The secondary restrictions and the SEI approximations listed above are applied so that the SEI can then be written in a convenient form for closure relationship purposes, with each force and flux term zero at equilibrium:

(3.32)

$$\sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \frac{\epsilon^{\iota}}{\theta^{\overline{\iota}}} \left(\mathbf{t}^{\backslash \overline{\iota}} + p^{\iota} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \overline{\iota}} + \frac{\epsilon^{s}}{\theta^{\overline{\overline{s}}}} \left(\mathbf{t}^{\backslash \overline{s}} - \mathbf{t}^{\backslash s} \right) : \mathbf{d}^{\backslash \overline{s}}$$

$$+ \sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{\epsilon^{\iota}}{\theta^{\overline{\iota}}} \left[\mathbf{t}^{\backslash \overline{\iota}} - \gamma^{\iota} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash \iota} \right) \right] : \mathbf{d}^{\backslash \overline{\iota}} + \frac{\epsilon^{wgs}}{\theta^{\overline{\overline{wgs}}}} \left[\mathbf{t}^{\backslash \overline{wgs}} + \gamma^{wgs} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash wgs} \right) \right] : \mathbf{d}^{\backslash \overline{wgs}}$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \sum_{i \in \mathfrak{I}_{s}} \frac{1}{\theta^{\overline{\iota}}} \epsilon^{\iota} \rho^{\iota} \omega^{i \overline{\iota}} \mathbf{u}^{\backslash \overline{i\iota}} \cdot \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right)$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \left(\epsilon^{\iota} \mathbf{q}^{\backslash \overline{\iota}} + \sum_{i \in \mathfrak{I}_{s}} \epsilon^{\iota} \rho^{\iota} \omega^{i \overline{\iota}} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\backslash \overline{i\iota}} \right) \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\iota}}} \right)$$

$$- \epsilon^{s} \mathbf{q}^{\backslash \overline{s}} \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right) - \sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \epsilon^{\iota} \mathbf{q}^{\backslash \overline{\iota}} \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\iota}}} \right)$$

$$- \epsilon^{wgs} \mathbf{q}^{\backslash \overline{wgs}} \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{wgs}}} \right)$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash s} \right)}{\theta^{\overline{\iota}}} \cdot \left(\sum_{i \in \mathfrak{I}_{s}} \epsilon^{\iota} \rho^{\iota} \omega^{i \overline{\iota}} \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) - \left\langle \frac{\mathbf{e} \cdot p_{\iota} \mathbf{I}^{\backslash}}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \right.$$

$$\left. + \sum_{i \in \mathfrak{I}_{s}} \epsilon^{\iota} \rho^{\iota} \omega^{i \overline{\iota}} \mathbf{g}^{\backslash \overline{i\iota}} - \nabla^{\backslash} \left(\epsilon^{\iota} p^{\iota} \right) + \sum_{\kappa \in \mathfrak{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{I}^{\backslash} \right)$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \mathbf{NN}}{\theta^{\overline{\iota}}} \cdot \left(\sum_{i \in \mathfrak{I}_{s}} \epsilon^{\iota} \rho^{\iota} \omega^{i \overline{\iota}} \mathbf{g}^{\backslash \overline{i\iota}} \cdot \mathbf{NN} + \sum_{\kappa \in \mathfrak{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{NN} \right.$$

$$\left. - \left\langle \frac{\mathbf{e} \cdot p_{\iota} \mathbf{NN}}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \right)$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash s} \right)}{\theta^{\overline{\iota}}} \cdot \left(\nabla^{\backslash} \cdot \left[\epsilon^{\iota} \gamma^{\iota} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash \iota} \right) \right] + \sum_{\kappa \in \mathfrak{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{I}^{\backslash} + \left\langle \frac{\mathbf{e} \cdot \gamma_{\iota} \mathbf{I}^{\backslash} \cdot \mathbf{I}^{\backslash}}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \right)$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \mathbf{NN}}{\theta^{\overline{\iota}}} \cdot \left(\sum_{\kappa \in \mathfrak{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{NN} - \left(\nabla^{\backslash} \cdot \mathbf{N} \right) \mathbf{N} \cdot \epsilon^{\iota} \mathbf{G}^{\iota} \cdot \mathbf{NN} \gamma^{\iota} \right.$$

$$\left. + \left\langle \frac{\mathbf{e} \cdot \gamma_{\iota} \mathbf{I}^{\backslash} \cdot \mathbf{NN}}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \right)$$

$$+ \frac{\left(\mathbf{v}^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash s} \right)}{\theta^{\overline{wgs}}} \cdot \left(\nabla^{\backslash} \cdot \left[\epsilon^{wgs} \gamma^{wgs} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash wgs} \right) \right] \right.$$

112

$$
+ \sum_{\kappa \in \mathcal{I}_{\mathrm{c}wgs}} \overset{wgs \to \kappa}{\mathbf{T}} \cdot \mathbf{l} + \left\langle \frac{\mathbf{e} \cdot \gamma_{wgs} \mathbf{l}'' \cdot \mathbf{l}}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgsM}, \Omega} \Bigg)
$$

$$
+ \frac{\mathbf{v}^{\overline{wgs,\overline{s}}} \cdot \mathbf{NN}}{\theta^{\overline{wgs}}} \cdot \Bigg(\sum_{\kappa \in \mathcal{I}_{\mathrm{c}wgs}} \overset{wgs \to \kappa}{\mathbf{T}} \cdot \mathbf{NN} - \left(\nabla' \cdot \mathbf{N} \right) \mathbf{N} \cdot \epsilon^{wgs} \mathbf{G}^{wgs} \cdot \mathbf{NN} \gamma^{wgs}
$$

$$
+ \left\langle \frac{\mathbf{e} \cdot \gamma_{wgs} \mathbf{l}'' \cdot \mathbf{NN}}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgsM}, \Omega} \Bigg)
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{c}\iota}} \frac{1}{\theta^{\overline{\overline{\kappa}}}} \sum_{i \in \mathcal{I}_s} \left[\left(\mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}} \right) - \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{c}\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \left[\overset{\kappa \to \iota}{Q} + \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa} - \mu_{i\iota}^{\overline{\kappa}} \right) \overset{i\kappa \to i\iota}{M} \right.
$$

$$
\left. + \left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{\kappa \to \iota}{\mathbf{T}} \right] + \sum_{\kappa \in \mathcal{I}_{\mathrm{c}s}} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \overset{\kappa \to s}{Q}
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left[\overset{wgs \to \iota}{Q} + \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{wgs \to \iota}{\mathbf{T}} \right]
$$

$$
+ \frac{1}{\theta^{\overline{\overline{wg}}}} \left(p_w^{wg} - p_g^{wg} - \gamma^{wg} J_w^{wg} \right) \left[\frac{\mathrm{D}^{\overline{s}} \epsilon^w}{\mathrm{D}t} + \chi_{ws}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{wM}, \Omega} \right.
$$

$$
\left. - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM}, \Omega} - \frac{\gamma^{wg}}{\left(p_w^{wg} - p_g^{wg} \right)} \hat{k}_1^{wg} \left(\epsilon^{wg} - \epsilon_{\mathrm{eq}}^{wg} \right) \right]
$$

$$
- \left[\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\chi_{\iota s}^{ss}}{\theta^{\overline{\overline{\iota s}}}} \left(p_\iota^{\iota s} + \gamma^{\iota s} J_s^{\iota s} \right) + \frac{1}{\theta^{\overline{\overline{s}}}} \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}} \right.
$$

$$
\left. + \frac{\chi_{wgs}^{ss}}{\theta^{\overline{\overline{wgs}}}} \left(\gamma^{wgs} \kappa_N^{\overline{\overline{wgs}}} - \gamma_{wg}^{wgs} \sin \varphi^{\overline{\overline{ws,wg}}} \right) \right] \times
$$

$$
\left(\frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM}, \Omega} \right)
$$

$$
- \frac{1}{\theta^{\overline{\overline{wgs}}}} \left(\gamma^{wgs} \kappa_G^{\overline{\overline{wgs}}} + \gamma_{ws}^{wgs} - \gamma_{gs}^{wgs} + \gamma_{wg}^{wgs} \cos \varphi^{\overline{\overline{ws,wg}}} \right) \left(\epsilon^{ss} \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t} \right.
$$

$$
\left. - \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM}, \Omega} + \chi_{ws}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{gsM}, \Omega} \right)
$$

$$+ \sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \boldsymbol{\tau}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathfrak{I}/\mathfrak{I}_{\mathrm{f}}} \left\langle \left(\frac{1}{\theta^{\bar{\bar{\iota}}}} - \frac{1}{\theta_\iota} \right) \mathbf{e} \cdot \left[\mathbf{q}_\iota - \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}} \right) \theta_\iota \eta_\iota \right] \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathfrak{I}_{\mathrm{P}}} \sum_{i \in \mathfrak{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}} \right) \rho_\iota \omega_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\bar{\bar{i\iota}}} - \psi^{\bar{\bar{i\iota}}} \right) \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathfrak{I}_{\mathrm{f}}} \left\langle \left(\frac{1}{\theta^{\bar{\bar{\iota}}}} - \frac{1}{\theta_\iota} \right) \mathbf{e} \cdot \left[\mathbf{q}_\iota - \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}} \right) \theta_\iota \eta_\iota \right. \right.$$

$$\left. \left. + \sum_{i \in \mathfrak{I}_s} \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} \right) \right] \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda \geq 0,$$

where $\mathbf{G}$ is a geometric orientation tensor, $\varphi^{\overline{\overline{ws,wg}}}$ is the contact angle, $\kappa_N^{\overline{\overline{wgs}}}$ is the normal curvature, $\kappa_G^{\overline{\overline{wgs}}}$ is the geodesic curvature, J_ι^κ for $\iota \in \mathfrak{I}_{\mathrm{P}}$ and $\kappa \in \mathfrak{I}_{\mathrm{c}\iota}$ are macroscale surface curvatures, χ_κ^{ss} is the fraction of the solid surface in contact with the κ entity where $\kappa \in \mathfrak{I}_{cs}$, $\hat{k}_1^{wg}$ is the generation rate coefficient for wg interfacial area, and $\epsilon_{\mathrm{eq}}^{wg}$ is the equilibrium specific interfacial area.

3.8. Model Closure

The SEI expression in Eq. (3.32) is the starting point for the selection of closure relations to produce closed thermodynamically consistent models of two-fluid-phase flow and species transport in a porous medium to free-flow transition region. The selection of the closure relations is non-unique and the generality of the SEI allows for a large range of problems to be considered based on the particular problem of interest and level of sophistication required. While restrictions and approximations were applied to derive Eq. (3.32), this expression is still more general in nature than we will consider. To simplify matters, we will specify a set of closure approximations to guide the production of a set of closed models. These approximations can be modified to produce alternative models if the resultant models produced based upon the closure approximations that follow are found to be inadequate for some case of concern.

CLOSURE APPROXIMATION 1 (Domain Curvature). *The curvature of the domain in the megascale direction is neglected.*

Curvature terms appear in the conservation equations and the SEI. The curvature in the megascale direction will be small for many applications of interest and when this situation is the case the corresponding terms will be relatively unimportant. The appropriateness of this approximation will be straightforward to assess from the physical system being considered.

CLOSURE APPROXIMATION 2 (Dilute). *Each of the fluid phases will be assumed to be dilute.*

It was previously assumed that the fluid phases are binary mixtures. The primary species of interest in the liquid phase (e.g.,water) is sufficiently volatile that volatilization to the gas phase can occur, and the dominant gas-phase species is assumed to be slightly soluble in the liquid phase. For these conditions, we can assume an ideal dilute solution with activity coefficients equal to unity.

CLOSURE APPROXIMATION 3 (Body Force). *The macroscale body force will be approximated as the product of the macroscale entity measure, and macroscale density, and the gradient in the microscale potential.*

This approximation is reasonable because the transition region is thin in the vertical dimension in which the gravitational potential acts, and densities and volume fractions are only available as averages through this thin region and would typically have limited variability, making this approximation reasonable.

CLOSURE APPROXIMATION 4 (Momentum Approximations). *Acceleration and inertial contributions to the conservation of momentum, aside from gravitational effects, will be neglected.*

Because the Reynolds number for flow in the transition region is expected to be small for most cases and the interfacial transport of momentum terms are dominant and non-gravitational acceleration and inertial terms can be shown to be a second-order effect.

CLOSURE APPROXIMATION 5 (Closure Order). *Closure approximations will be posited zero-order with respect to the macroscale rate of strain tensor and first-order with respect to all other forces being considered.*

Neglect of the rate of strain in constitutive relations for porous medium flow is appropriate if viscous forces at the boundary of the solid phase are dominant, as is typically the case for porous medium systems, which behave as if they are macroscopically inviscid. Because of this observation, we will use a zero-order closure for the flux multiplying the rate of strain tensor. If the zero-order approximation proves to be inadequate, this closure approximation will need to be revised. Similarly, the starting point for other closure relations will be a first-order approximation. We will include Onsager-like cross coupling where certain fluxes depend upon more than one force. Because of conditions on the system (e.g., massless interfaces and common curve, non-deforming solid phase) many cross-coupling terms can be neglected. Linear closure relations are a reasonable starting point and have been found adequate for many systems investigated to date.

CLOSURE APPROXIMATION 6 (State Equations). *State equations express the inter-relationship among variables at equilibrium and are written in a general functional form.*

The hypothesized functional dependencies must be obtained experimentally or through microscale computations, and reasonable specific forms are currently available in certain cases at the microscale. For example, relationships between fluid densities, pressures, temperatures, and composition are well established at the microscale; note that care is needed in extending such relations to the macroscale. The investigation of relationships among fluid pressures, saturations, interfacial areas, and curvatures is an active areas of research.

3.8.1. SEI Closure Relations. The SEI for a transition region, given in Eq. (3.32), is written in force-flux form and can be used to guide the formulation of closure relations within the transition region. To do this, we linearize the remaining force-flux products.

The zero-order closure for the stress tensors can be expressed as

$$(3.33) \qquad \mathbf{t}^{\backslash \overline{\overline{\iota}}} = -p^{\iota}\mathbf{I}^{\backslash} \quad \text{for } \iota \in \mathcal{I}_{\mathrm{f}},$$

$$(3.34) \qquad \mathbf{t}^{\backslash \overline{\overline{s}}} = \mathbf{t}^{\backslash s},$$

$$(3.35) \qquad \mathbf{t}^{\backslash \overline{\overline{\iota}}} = \gamma^{\iota}\left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash \iota}\right) \quad \text{for } \iota \in \mathcal{I}_{\mathrm{I}},$$

and

$$(3.36) \qquad \mathbf{t}^{\backslash \overline{\overline{wgs}}} = -\gamma^{wgs}\left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash wgs}\right).$$

As specified by Secondary Restriction 4, we consider only a two species, or binary, system for the fluid phases with an inert solid phase, where the index set of species in the fluid phases is given as $\mathcal{I}_{sf} = \{g, w\}$ and the system is considered to be dilute. A first-order closure scheme is used to specify the dispersion velocity for such a binary system as

$$(3.37) \qquad \omega^{g\iota}\mathbf{u}^{\overline{\overline{g\iota}}} = -x^{\overline{\overline{g\iota}}}x^{\overline{\overline{w\iota}}}\hat{\mathbf{D}}^{gw\iota}\cdot\nabla^{\backslash}\left(\mu^{\overline{g\iota}} + \psi^{\overline{g\iota}} - \mu^{\overline{w\iota}} - \psi^{\overline{w\iota}}\right) \quad \text{for } \iota \in \mathcal{I}_{\mathrm{f}},$$

where $\hat{\mathbf{D}}^{gw\iota}$ is a second-rank, symmetric tensor for which the third row and column contain zeros , and $x^{\overline{\overline{i\iota}}}$ is the mole fraction of species i in entity ι.

For the fluid phases, the linearized heat fluxes are

$$(3.38) \qquad \epsilon^{\iota}\mathbf{q}^{\backslash \overline{\overline{\iota}}} + \sum_{i\in\{g,w\}} \epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)\mathbf{u}^{\backslash \overline{\overline{i\iota}}} = -\epsilon^{\iota}\hat{\mathbf{K}}_{q}^{\iota}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\overline{\iota}}}\right) \quad \text{for } \iota \in \mathcal{I}_{\mathrm{f}},$$

while the linearized heat flux for the solid phase is

$$(3.39) \qquad \epsilon^{s}\mathbf{q}^{\backslash \overline{\overline{s}}} = -\epsilon^{s}\hat{\mathbf{K}}_{q}^{s}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\overline{\overline{s}}}}\right),$$

where $\hat{\mathbf{K}}_q^\iota$ is a second-rank, symmetric heat conduction tensor, and the corresponding closure relations for heat conduction in interfaces and common curves are written as

$$(3.40) \qquad \epsilon^\iota \mathbf{q}^{\overline{\overline{\iota}}} = -\epsilon^\iota \hat{\mathbf{K}}_q^\iota \cdot \nabla' \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} \right) \quad \text{for } \iota \in (\mathfrak{I}_\mathrm{I} \cup \mathfrak{I}_\mathrm{C}).$$

A first-order, cross-coupled approximation for fluid phase SEI terms involving the inter-entity transfer of momentum whose conjugate forces are the entity velocities relative to the macroscale solid-phase velocity can be written as

$$(3.41) \qquad \sum_{i\in\{g,w\}} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \nabla' \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) + \sum_{i\in\{g,w\}} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \mathbf{g}^{\overline{\overline{i\iota}}} - \nabla' \left(\epsilon^\iota p^\iota \right) - \left\langle \mathbf{e} \cdot p_\iota \mathbf{l}' \right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+ \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\iota}} \overset{\kappa\to\iota}{\mathbf{T}} \cdot \mathbf{l}' = -(\epsilon^\iota)^2 \sum_{\kappa\in\mathfrak{I}_\mathrm{f}} \left[\mathbf{l}' \cdot \hat{\mathbf{R}}_\kappa^\iota \cdot \left(\mathbf{v}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) + \mathbf{l}' \cdot \hat{\mathbf{R}}_\kappa^\iota \cdot \mathbf{NN} \cdot \mathbf{v}^{\overline{\kappa},\overline{s}} \right]$$

for $\iota \in \mathfrak{I}_\mathrm{f}$, where $\hat{\mathbf{R}}_\kappa^\iota$ are second-rank, symmetric, positive semi-definite resistance tensors. Cross-coupling is accounted for when the subscript and superscript on the resistance tensor differ. The resistance tensors are dependent upon the morphology and topology of the entity distributions. The macroscale mechanism for including the orientation of the interfaces at the microscale is the geometric tensors, $\mathbf{G}^\iota$.

For the interfaces we have

$$(3.42) \qquad \nabla' \cdot \left[\epsilon^\iota \gamma^\iota \left(\mathbf{l}' - \mathbf{G}^{\backslash \iota} \right) \right] - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\iota}} \overset{\iota\to\kappa}{\mathbf{T}} \cdot \mathbf{l}' + \left\langle \frac{\mathbf{e} \cdot \gamma_\iota \mathbf{l}' \cdot \mathbf{l}'}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_\mathrm{I},$$

and for the common curve

$$(3.43) \qquad -\nabla' \cdot \left[\epsilon^{wgs} \gamma^{wgs} \left(\mathbf{l}' - \mathbf{G}^{\backslash wgs} \right) \right] - \sum_{\kappa\in\mathfrak{I}_{cwgs}} \overset{wgs\to\kappa}{\mathbf{T}} \cdot \mathbf{l}' - \left\langle \frac{\mathbf{e} \cdot \gamma_{wgs} \mathbf{l}'' \cdot \mathbf{l}'}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgsM},\Omega} = 0.$$

In the megascale direction, the flux terms whose conjugate forces are the relative velocities can be written by expressing the flux as a linear function of both its conjugate force and the velocity force for the other fluid such that for $\iota \in \mathfrak{I}_\mathrm{f}$,

$$(3.44) \quad \sum_{i\in\{g,w\}} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \mathbf{g}^{\overline{\overline{i\iota}}} \cdot \mathbf{NN} - \langle \mathbf{e} \cdot p_\iota \mathbf{I} \cdot \mathbf{NN} \rangle_{\Gamma_{\iota M},\Omega} + \sum_{\kappa\in\mathcal{I}_{c\iota}} \overset{\kappa\to\iota}{\mathbf{T}} \cdot \mathbf{NN}$$

$$= -(\epsilon^\iota)^2 \sum_{\kappa\in\mathcal{I}_f} \left[\mathbf{NN} \cdot \hat{\mathbf{R}}_\kappa^\iota \cdot \mathbf{NN} \cdot \mathbf{v}^{\overline{\kappa,s}} + \mathbf{NN} \cdot \hat{\mathbf{R}}_\kappa^\iota \cdot \mathbf{I} \cdot \mathbf{v}^{\overline{\kappa,s}} \right].$$

For $\iota \in \mathcal{I}_\mathrm{I}$ we have

$$(3.45) \quad -\sum_{\kappa\in\mathcal{I}_{c\iota}} \overset{\iota\to\kappa}{\mathbf{T}} \cdot \mathbf{NN} + \left\langle \frac{\mathbf{e} \cdot \gamma_\iota \mathbf{I}' \cdot \mathbf{NN}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = 0,$$

and for the common curve

$$(3.46) \quad -\sum_{\kappa\in\mathcal{I}_{cwgs}} \overset{wgs\to\kappa}{\mathbf{T}} \cdot \mathbf{NN} - \left\langle \frac{\mathbf{e} \cdot \gamma_{wgs} \mathbf{I}'' \cdot \mathbf{NN}}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgsM},\Omega} = 0.$$

The mass exchange term considering massless interfaces can be linearized such that

$$(3.47) \quad \overset{iwg\to iw}{M} = \hat{K}_M \left[\left(\mu^{\overline{ig}} + \psi^{\overline{ig}} \right) - \left(\mu^{\overline{iw}} + \psi^{\overline{iw}} \right) \right],$$

where $\hat{K}_M$ is a scalar mass transfer coefficient and $\overset{iwg\to iw}{M} = -\overset{iwg\to ig}{M}$.

Energy exchanges between entities are linearized by their conjugate force and cross-coupled with the force associated with the work of volume change. For the case of a fluid phase ι, this means

$$(3.48) \quad \overset{wg\to\iota}{Q} + \sum_{i\in\{g,w\}} \left(\frac{E_\iota^{\overline{\overline{wg}}}}{\epsilon^\iota \rho_\iota^{\overline{wg}}} - \mu_{i\iota}^{\overline{wg}} \right) \overset{iwg\to i\iota}{M} + \left(\mathbf{v}_\iota^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{wg\to\iota}{\mathbf{T}}$$

$$= \hat{K}_{\iota,Q}^{wg} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) - \hat{K}_{\iota,W}^{wg} \left(p_w^{wg} - p_g^{wg} - \gamma^{wg} J_w^{wg} \right) \quad \text{for } \iota \in \mathcal{I}_f,$$

and

$$(3.49) \quad \overset{\kappa\to\iota}{Q} = \hat{K}_{\iota,Q}^\kappa \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \quad \text{for } \kappa \in \{ws, gs\}, \iota \in (\mathcal{I}_{c\kappa} \cap \mathcal{I}_\mathrm{P}),$$

where $\hat{K}_{\iota,Q}^\kappa$ are scalar inter-entity heat transfer parameters, and $\hat{K}_{\iota,W}^\kappa$ are scalar coefficients for work of expansion of entity ι.

For heat transfer between the common curve and interfaces,

$$(3.50) \quad \overset{wgs\to\iota}{Q} + \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \overset{wgs\to\iota}{\mathbf{T}} = \hat{K}_{\iota,Q}^{wgs} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}}\right)$$

$$+ \hat{K}_{\iota,W}^{wgs} \left(\gamma^{wgs} \kappa_G^{\overline{\overline{wgs}}} + \gamma_{ws}^{wgs} - \gamma_{gs}^{wgs} + \gamma_{wg}^{wgs} \cos \varphi^{\overline{\overline{ws,wg}}}\right) \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}.$$

Capillary effects at the fluid-fluid interface are included through the use of averaging theorems following the approach of [90], where the linearized force without considering cross-coupling is written as

$$(3.51) \quad \hat{\tau}_A \left[\frac{\mathrm{D}^{\overline{s}} \epsilon^w}{\mathrm{D}t} + \chi_{ws}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \frac{\gamma^{wg}}{\left(p_w^{wg} - p_g^{wg}\right)} \hat{k}_1^{wg} \left(\epsilon^{wg} - \epsilon_{\mathrm{eq}}^{wg}\right) \right.$$

$$\left. - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{wM},\Omega} - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega} \right]$$

$$= \left(p_w^{wg} - p_g^{wg} - \gamma^{wg} J_w^{wg}\right),$$

where

$$(3.52) \qquad\qquad\qquad \epsilon_{\mathrm{eq}}^{wg} = \epsilon_{\mathrm{eq}}^{wg}\left(s^w, J_w^{wg}\right),$$

and the coefficient $\hat{k}_1^{wg}$ is defined as

$$(3.53) \qquad\qquad\qquad \hat{k}^{wg} = \left(\frac{J_w^{wg} \gamma^{wg}}{p_w^{wg} - p_g^{wg}} - 1\right) \hat{k}_1^{wg},$$

where $\hat{k}^{wg}$ is a function of the system variables, $\hat{k}_1^{wg}$ is the generation rate coefficient for the fluid-fluid interfacial area, s^w is the wetting phase saturation, and $\hat{\tau}_A$ is a positive coefficient for capillary pressure dynamics. The approximation in Eq. (3.51) is based on the assumption that the solid-phase dynamics are negligible in comparison to fluid-phase dynamics related to capillary pressure transients. The product of the mean macroscale curvature, J_w^{wg}, and the interfacial tension, γ^{wg}, is the macroscale capillary pressure, such that Eq. (3.51) indicates a disequilibrium in capillary forces will cause a change in saturation or interfacial area to occur. The dynamic relationship among the normal

forces acting on the solid surface can be linearized as follows:

$$
(3.54) \quad -\hat{c}^s \left(\frac{D^{\bar{s}} \epsilon^s}{Dt} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right) = \sum_{\kappa \in \mathcal{I}_{cs}} \frac{\chi_\kappa^{ss}}{\theta^{\overline{\kappa}}} \left(p_\iota^\kappa + \gamma^\kappa J_s^\kappa \right)
$$

$$
+ \frac{1}{\theta^{\overline{s}}} \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}} + \frac{\chi_{wgs}^{ss}}{\theta^{\overline{\overline{wgs}}}} \left(\gamma^{wgs} \kappa_N^{\overline{\overline{wgs}}} - \gamma_{wg}^{wgs} \sin \varphi^{\overline{ws,wg}} \right),
$$

where $\iota \in (\mathcal{I}_f \cap \mathcal{I}_{c\kappa})$ and $\hat{c}^s$ is a non-negative compressibility parameter. The final grouping of geometric terms indicates a disequilibrium in the force balance at the common curve tangent to the solid surface will cause a change in the fraction of the solid surface in contact with the wetting fluid. This grouping can be linearized as

$$
(3.55)
$$

$$
- \hat{c}^{wgs} \left(\epsilon^{ss} \frac{D^{\bar{s}} \chi_{ws}^{ss}}{Dt} - \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} + \chi_{ws}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{s}} \right)}{\mathbf{n}_{gs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega} \right)
$$

$$
= \left(\gamma^{wgs} \kappa_G^{\overline{\overline{wgs}}} + \gamma_{ws}^{wgs} - \gamma_{gs}^{wgs} + \gamma_{wg}^{wgs} \cos \varphi^{\overline{ws,wg}} \right),
$$

where $\hat{c}^{wgs}$ is a non-negative surface wetting parameter.

The remaining closure approximations are for the boundary terms. For the viscous stress tensor of a fluid phase, a fist-order closure appoximation is

$$
(3.56) \qquad \frac{d\hat{\mathbf{r}}_\iota^{\text{top}}}{\epsilon_\iota^{\text{top}} \rho_\iota^{\text{top}}} \cdot \left\langle \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega} = \langle \mathbf{e} \cdot \boldsymbol{\tau}_\iota \rangle_{\Gamma_{\iota M_{\text{top}}},\Omega},
$$

where d is the interface thickness. Similarly for the viscous stress of a fluid at the bottom boundary we have

$$
(3.57) \qquad \frac{d\hat{\mathbf{r}}_\iota^{\text{bot}}}{\epsilon_\iota^{\text{bot}} \rho_\iota^{\text{bot}}} \cdot \left\langle \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega} = \langle \mathbf{e} \cdot \boldsymbol{\tau}_\iota \rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega},
$$

where $\iota \in \mathcal{I}_f$, $i \in \{w, g\}$, and $\hat{\mathbf{r}}_\iota$ are second-rank, symmetric, positive semi-definite resistance tensors. The superscript top indicates averaging over the boundary in the megascale direction at the top of the REV and the superscript bot indicates averaging

121

over the boundary in the megascale direction at the bottom of the REV. The remaining boundary terms are approximated in a similar manner.

Heat transfer over the REV boundary is approximated using the linear closure relations

$$(3.58) \quad d\eta_\iota^{\overline{\overline{\text{top}}}} \hat{k}_{\iota,q}^{\text{top}} \left\langle \frac{1}{\eta_\iota} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta_\iota} \right) \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega}$$
$$= \left\langle \mathbf{e} \cdot \left[\mathbf{q}_\iota - (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}) \, \theta_\iota \eta_\iota + \sum_{i \in \{g,w\}} \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} \right) \right] \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega},$$

and

$$(3.59) \quad d\eta_\iota^{\overline{\overline{\text{bot}}}} \hat{k}_{\iota,q}^{\text{bot}} \left\langle \frac{1}{\eta_\iota} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta_\iota} \right) \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega}$$
$$= \left\langle \mathbf{e} \cdot \left[\mathbf{q}_\iota - (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}) \, \theta_\iota \eta_\iota + \sum_{i \in \{g,w\}} \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} \right) \right] \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega},$$

for $\iota \in \mathcal{I}_{\text{f}}$, $i \in \{g, w\}$, and

$$(3.60) \quad d\eta_\iota^{\overline{\overline{\text{top}}}} \hat{k}_{\iota,q}^{\text{top}} \left\langle \frac{1}{\eta_\iota} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta_\iota} \right) \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega} = \left\langle \frac{\mathbf{e} \cdot \left[\mathbf{q}_\iota - (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}) \, \theta_\iota \eta_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega},$$

and

$$(3.61) \quad d\eta_\iota^{\overline{\overline{\text{bot}}}} \hat{k}_{\iota,q}^{\text{bot}} \left\langle \frac{1}{\eta_\iota} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta_\iota} \right) \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega} = \left\langle \frac{\mathbf{e} \cdot \left[\mathbf{q}_\iota - (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}) \, \theta_\iota \eta_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega},$$

for $\iota \in \{s, wg, ws, gs, wgs\}$, and $\hat{k}_{\iota,q}$ are scalar heat transfer closure parameters.

The transfer of mass normal to the boundary is approximated linearly as

$$(3.62) \quad - \frac{d\hat{k}_{i\iota,M}^{\text{top}}}{\epsilon_\iota^{\text{top}} \rho_\iota^{\text{top}} \overline{\omega_{i\iota}^{\text{top}}}} \left\langle \rho_\iota \omega_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - \psi^{\overline{i\iota}} \right) \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega}$$
$$= \left\langle \rho_\iota \omega_{i\iota} \mathbf{e} \cdot (\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}}) \right\rangle_{\Gamma_{\iota M_{\text{top}}},\Omega},$$

$$(3.63) \quad -\frac{d\hat{k}^{\text{bot}}_{i\iota,M}}{\epsilon^{\text{bot}}_\iota \rho^{\text{bot}}_\iota \overline{\omega^{\text{bot}}_{i\iota}}} \left\langle \rho_\iota \omega_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{i\iota}} \right) \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega}$$

$$= \left\langle \rho_\iota \omega_{i\iota} \mathbf{e} \cdot \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}} \right) \right\rangle_{\Gamma_{\iota M_{\text{bot}}},\Omega},$$

where $\iota \in \mathfrak{I}_{\text{f}}$, $i \in \{w,g\}$,

$$(3.64) \quad -\frac{d\hat{k}^{\text{top}}_{s,M}}{\epsilon^{\text{top}}_s \rho^{\text{top}}_s} \left\langle \rho_s \left(\mu_s + \psi_s - \mu^{\overline{s}} - \psi^{\overline{s}} \right) \right\rangle_{\Gamma_{s M_{\text{top}}},\Omega}$$

$$= \left\langle \rho_s \mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}} \right) \right\rangle_{\Gamma_{s M_{\text{top}}},\Omega} = 0,$$

and

$$(3.65) \quad -\frac{d\hat{k}^{\text{bot}}_{s,M}}{\epsilon^{\text{bot}}_s \rho^{\text{bot}}_s} \left\langle \rho_s \left(\mu_s + \psi_s - \mu^{\overline{s}} - \psi^{\overline{s}} \right) \right\rangle_{\Gamma_{s M_{\text{bot}}},\Omega} = \left\langle \rho_s \mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}} \right) \right\rangle_{\Gamma_{s M_{\text{bot}}},\Omega},$$

where $\hat{k}^{\text{top}}_{i\iota,M}, \hat{k}^{\text{bot}}_{i\iota,M}, \hat{k}^{\text{top}}_{s,M}$, and $\hat{k}^{\text{bot}}_{s,M}$ are scalar mass transfer coefficients for the transfer of mass normal to the top and bottom boundary of the REV. Because of the restriction on entities, solid phase cannot cross the top boundary, so this term has been set to zero.

3.8.2. System Equations. Application of the closure relations given by Eq. (3.37) together with the restrictions and formal approximations noted in sections §3.3, §3.7.2, and §3.8 allow the species mass conservation equations, Eq. (3.20), to be written as

$$(3.66) \quad \frac{\mathrm{D}^{\overline{g}} \left(\epsilon^g \rho^g \omega^{i\overline{g}} \right)}{\mathrm{D}t} + \epsilon^g \rho^g \omega^{i\overline{g}} \mathbf{I} : \mathbf{d}^{\overline{\overline{g}}} + \hat{K}_M \left[\left(\mu^{\overline{i g}} + \psi^{\overline{i g}} \right) - \left(\mu^{\overline{i w}} + \psi^{\overline{i w}} \right) \right]$$

$$-\nabla \cdot \left[\epsilon^g \rho^g x^{\overline{\overline{i g}}} x^{\overline{\overline{j g}}} \hat{\mathbf{D}}^{ijg} \cdot \nabla \left(\mu^{\overline{i g}} + \psi^{\overline{i g}} - \mu^{\overline{j g}} - \psi^{\overline{j g}} \right) \right]$$

$$-\hat{k}^{\text{top}}_{ig,M} \left(\mu^{\overline{\text{top}}}_{ig} + \psi^{\overline{\text{top}}}_{ig} - \mu^{\overline{i g}} - \psi^{\overline{i g}} \right)$$

$$-\hat{k}^{\text{bot}}_{ig,M} \left(\mu^{\overline{\text{bot}}}_{ig} + \psi^{\overline{\text{bot}}}_{ig} - \mu^{\overline{i g}} - \psi^{\overline{i g}} \right) = 0 \quad \text{for } i,j \in \{g,w\}, i \neq j,$$

$$(3.67) \quad \frac{\mathrm{D}^{\overline{w}} \left(\epsilon^w \rho^w \omega^{i\overline{w}} \right)}{\mathrm{D}t} + \epsilon^w \rho^w \omega^{i\overline{w}} \mathbf{I} : \mathbf{d}^{\overline{\overline{w}}} - \hat{K}_M \left[\left(\mu^{\overline{i g}} + \psi^{\overline{i g}} \right) - \left(\mu^{\overline{i w}} + \psi^{\overline{i w}} \right) \right]$$

$$-\nabla'\cdot\left[\epsilon^w\rho^w x^{\overline{\overline{iw}}} x^{\overline{\overline{jw}}} \hat{\mathbf{D}}^{ijw}\cdot\nabla'\left(\mu^{\overline{iw}}+\psi^{\overline{iw}}-\mu^{\overline{jw}}-\psi^{\overline{jw}}\right)\right]$$

$$-\hat{k}_{iw,M}^{top}\left(\mu_{iw}^{\overline{top}}+\psi_{iw}^{\overline{top}}-\mu^{\overline{iw}}-\psi^{\overline{iw}}\right)$$

$$-\hat{k}_{iw,M}^{bot}\left(\mu_{iw}^{\overline{bot}}+\psi_{iw}^{\overline{bot}}-\mu^{\overline{iw}}-\psi^{\overline{iw}}\right)=0 \quad \text{for } i,j\in\{g,w\}, i\neq j,$$

and

$$(3.68) \qquad \rho^s\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}+\epsilon^s\rho^s\mathbf{I}{:}\mathbf{d}^{\overline{\overline{s}}}-\hat{k}_{s,M}^{bot}\left(\mu_s^{\overline{bot}}+\psi_s^{\overline{bot}}-\mu^{\overline{s}}-\psi^{\overline{s}}\right)=0.$$

Application of the closure relations, the restrictions and formal approximations, as well as assuming the averages over the REV boundaries are separable integrals, allows the momentum conservation equations to be written as

$$(3.69)$$

$$\sum_{i\in\{g,w\}}\epsilon^g\rho^g\omega^{\overline{ig}}\nabla'\left(\mu^{\overline{ig}}+\psi^{\overline{ig}}\right)+\mathbf{v}_g^{\overline{wg}}\sum_{i\in\{g,w\}}\hat{K}_M\left[\left(\mu^{\overline{ig}}+\psi^{\overline{ig}}\right)-\left(\mu^{\overline{iw}}+\psi^{\overline{iw}}\right)\right]$$

$$-\sum_{i\in\{g,w\}}\hat{k}_{ig,M}^{top}\left(\mu_{ig}^{\overline{top}}+\psi_{ig}^{\overline{top}}-\mu^{\overline{ig}}-\psi^{\overline{ig}}\right)\mathbf{v}_g^{\overline{top}}$$

$$-\sum_{i\in\{g,w\}}\hat{k}_{ig,M}^{bot}\left(\mu_{ig}^{\overline{bot}}+\psi_{ig}^{\overline{bot}}-\mu^{\overline{ig}}-\psi^{\overline{ig}}\right)\mathbf{v}_g^{\overline{bot}}-\hat{\mathbf{r}}_g^{top}\cdot\left(\mathbf{v}_g^{\overline{top}}-\mathbf{v}^{\overline{g}}\right)$$

$$-\hat{\mathbf{r}}_g^{bot}\cdot\left(\mathbf{v}_g^{\overline{bot}}-\mathbf{v}^{\overline{g}}\right)=-(\epsilon^g)^2\sum_{\kappa\in\mathcal{I}_f}\hat{\mathbf{R}}_\kappa^g\cdot\mathbf{v}^{\overline{\kappa,s}},$$

and

$$(3.70)$$

$$\sum_{i\in\{g,w\}}\epsilon^w\rho^w\omega^{\overline{iw}}\nabla'\left(\mu^{\overline{iw}}+\psi^{\overline{iw}}\right)-\mathbf{v}_w^{\overline{wg}}\sum_{i\in\{g,w\}}\hat{K}_M\left[\left(\mu^{\overline{ig}}+\psi^{\overline{ig}}\right)-\left(\mu^{\overline{iw}}+\psi^{\overline{iw}}\right)\right]$$

$$-\sum_{i\in\{g,w\}}\hat{k}_{iw,M}^{top}\left(\mu_{iw}^{\overline{top}}+\psi_{iw}^{\overline{top}}-\mu^{\overline{iw}}-\psi^{\overline{iw}}\right)\mathbf{v}_w^{\overline{top}}$$

$$-\sum_{i\in\{g,w\}}\hat{k}_{iw,M}^{bot}\left(\mu_{iw}^{\overline{bot}}+\psi_{iw}^{\overline{bot}}-\mu^{\overline{iw}}-\psi^{\overline{iw}}\right)\mathbf{v}_w^{\overline{bot}}-\hat{\mathbf{r}}_w^{top}\cdot\left(\mathbf{v}_w^{\overline{top}}-\mathbf{v}^{\overline{w}}\right)$$

$$-\hat{\mathbf{r}}_w^{\mathrm{bot}}\cdot\left(\mathbf{v}_w^{\overline{\mathrm{bot}}}-\mathbf{v}^{\overline{w}}\right)=-(\epsilon^w)^2\sum_{\kappa\in\mathcal{I}_{\mathrm{f}}}\hat{\mathbf{R}}_\kappa^w\cdot\mathbf{v}^{\overline{\kappa},\overline{s}},$$

for the fluid phases g and w respectively.

For the solid phase, only the component in the $\mathbf{N}$ direction will play a role, so the conservation of momentum equation in the megascale direction can be expressed as

$$(3.71)\quad -\epsilon^s\rho^s\mathbf{g}^{\overline{s}}\cdot\mathbf{NN}-\sum_{i\in\{g,w\}}\epsilon^w\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot\mathbf{NN}-\sum_{i\in\{g,w\}}\epsilon^g\rho^g\omega^{i\overline{g}}\mathbf{g}^{\overline{ig}}\cdot\mathbf{NN}$$

$$-\hat{k}_{s,M}^{\mathrm{bot}}\left(\mu_s^{\overline{\mathrm{bot}}}+\psi_s^{\overline{\mathrm{bot}}}-\mu^{\overline{s}}-\psi^{\overline{s}}\right)\mathbf{v}_s^{\overline{\mathrm{bot}}}\cdot\mathbf{NN}-\frac{\epsilon_s^{top}}{d}\mathbf{N}\cdot\mathbf{t}_s^{top}\cdot\mathbf{NN}$$

$$+\frac{\epsilon_s^{bot}}{d}\mathbf{N}\cdot\mathbf{t}_s^{bot}\cdot\mathbf{NN}+\frac{\epsilon_w^{top}p_w^{top}}{d}\mathbf{N}-\frac{\epsilon_w^{bot}p_w^{bot}}{d}\mathbf{N}+\frac{\epsilon_g^{top}p_g^{top}}{d}\mathbf{N}$$

$$-\frac{\epsilon_g^{bot}p_g^{bot}}{d}\mathbf{N}=-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}(\epsilon^\iota)^2\sum_{\kappa\in\mathcal{I}_{\mathrm{f}}}\left[\mathbf{NN}\cdot\hat{\mathbf{R}}_\kappa^\iota\cdot\mathbf{NN}\cdot\mathbf{v}^{\overline{\kappa},\overline{s}}+\mathbf{NN}\cdot\hat{\mathbf{R}}_\kappa^\iota\cdot\mathbf{I}\cdot\mathbf{v}^{\overline{\kappa},\overline{s}}\right].$$

Since the interfaces and common curves are considered massless, they contribute no momentum, and conservation of momentum equations are not included in the set of system equations.

As an alternative to looking at the conservation of total energy, we instead use the conservation of internal energy. The transformation from total energy to internal energy is straightforward and can be found in [86].

The internal energy is described by

$$(3.72)\quad \mathcal{E}^\iota-\mathbf{v}^{\overline{\iota}}\cdot\boldsymbol{\mathcal{P}}^\iota+\sum_{i\in\mathcal{I}_s}\frac{1}{2}\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}\mathcal{M}^{i\iota}-\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\mathbf{g}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{\iota}}-\sum_{i\in\mathcal{I}_s}\frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\psi^{\overline{i\iota}}\right)}{\mathrm{D}t}$$

$$-\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\psi^{\overline{i\iota}}\mathbf{I}:\mathbf{d}^{\overline{\overline{\iota}}}+\sum_{\kappa\in\mathcal{I}_{C\iota}}\psi^{\overline{\kappa}}_\iota\sum_{i\in\mathcal{I}_s}\overset{i\kappa\to i\iota}{M}+\sum_{i\in\mathcal{I}_s}\epsilon^\iota\psi^{\overline{i\iota}}r^{i\iota}$$

$$+\sum_{i\in\mathcal{I}_s}\left\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega}-\left\langle\frac{\displaystyle\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\psi_{i\iota}\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\mathrm{ext}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=0.$$

The internal energy for a fluid phase after application of the restrictions and approxima-
tions for the system can be written

$$
(3.73) \quad \frac{\mathrm{D}^{\bar{\iota}} E^{\overline{\bar{\iota}}}}{\mathrm{D}t} + \left(E^{\overline{\bar{\iota}}} + \epsilon^{\iota} p^{\iota} \right) \mathbf{I}^{\backslash} \mathbf{:} \mathbf{d}^{\backslash \bar{\iota}} + \nabla^{\backslash} \cdot \left[\epsilon^{\iota} \hat{\mathbf{K}}_q^{\iota} \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} \right) \right] - \epsilon^{\iota} h^{\overline{\bar{\iota}}}
$$

$$
- \nabla^{\backslash} \cdot \left[\epsilon^{\iota} \rho^{\iota} \left(\mu^{\overline{g\iota}} + \psi^{\overline{g\iota}} - \mu^{\overline{w\iota}} - \psi^{\overline{w\iota}} \right) x^{\overline{\overline{g\iota}}} x^{\overline{\overline{w\iota}}} \hat{\mathbf{D}}^{gw\iota} \cdot \nabla^{\backslash} \left(\mu^{\overline{g\iota}} + \psi^{\overline{g\iota}} - \mu^{\overline{w\iota}} - \psi^{\overline{w\iota}} \right) \right]
$$

$$
- \sum_{i \in \{g,w\}} \mu_{i\iota}^{\overline{wg}} \hat{K}_M \left[\left(\mu^{\overline{ij}} + \psi^{\overline{ij}} \right) - \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] + \mathbf{v}^{\overline{\iota,\overline{s}}} \cdot \nabla^{\backslash} \cdot \left(\epsilon^{\iota} p^{\iota} \mathbf{I}^{\backslash} \right)
$$

$$
- \mathbf{v}^{\overline{\iota,\overline{s}}} \cdot \sum_{i \in \{g,w\}} \epsilon^{\iota} \rho^{\iota} \omega^{\overline{i\iota}} \mathbf{g}^{\overline{i\iota}} - \mathbf{v}^{\overline{\iota,\overline{s}}} \cdot \sum_{i \in \{g,w\}} \epsilon^{\iota} \rho^{\iota} \omega^{\overline{i\iota}} \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) - \mathbf{v}^{\overline{\iota,\overline{s}}} \cdot \sum_{\kappa \in \mathcal{I}_{\mathrm{f}}} \left(\epsilon^{\iota} \right)^2 \hat{\mathbf{R}}_{\kappa}^{\iota} \cdot \mathbf{v}^{\overline{\kappa,\overline{s}}}
$$

$$
- \sum_{\kappa \in \mathcal{I}_{\mathrm{c}\iota}} \hat{K}_{\iota,Q}^{\kappa} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} + \frac{1}{\theta^{\overline{\bar{\kappa}}}} \right) + \hat{K}_{\iota,W}^{wg} \left(p_w^{wg} - p_g^{wg} - \gamma^{wg} J_w^{wg} \right)
$$

$$
+ \mathbf{N} \cdot \left(\mathbf{v}_{\iota}^{\overline{\mathrm{top}}} - \mathbf{v}_{\mathrm{ext}}^{\overline{\mathrm{top}}} \right) \sum_{i \in \{g,w\}} \frac{\epsilon_{\iota}^{top} \rho_{\iota}^{top} \omega_{i\iota}^{\overline{top}}}{d} \mu_{i\iota}^{\overline{\mathrm{top}}}
$$

$$
- \mathbf{N} \cdot \left(\mathbf{v}_{\iota}^{\overline{\mathrm{bot}}} - \mathbf{v}_{\mathrm{ext}}^{\overline{\mathrm{bot}}} \right) \sum_{i \in \{g,w\}} \frac{\epsilon_{\iota}^{bot} \rho_{\iota}^{bot} \omega_{i\iota}^{\overline{bot}}}{d} \mu_{i\iota}^{\overline{\mathrm{bot}}}
$$

$$
+ \frac{\epsilon_{\iota}^{top} p_{\iota}^{top}}{d} \mathbf{N} \cdot \left(\mathbf{v}_{\mathrm{ext}}^{\overline{\mathrm{top}}} - \mathbf{v}^{\overline{s}} \right) - \frac{\epsilon_{\iota}^{bot} p_{\iota}^{bot}}{d} \mathbf{N} \cdot \left(\mathbf{v}_{\mathrm{ext}}^{\overline{\mathrm{bot}}} - \mathbf{v}^{\overline{s}} \right)
$$

$$
- \left[\hat{\mathbf{r}}_{\iota}^{\mathrm{top}} \cdot \left(\mathbf{v}_{\iota}^{\overline{\mathrm{top}}} - \mathbf{v}^{\overline{\iota}} \right) \right] \cdot \left(\mathbf{v}_{\iota}^{\backslash \overline{\mathrm{top}}} - \mathbf{v}^{\backslash \overline{\iota}} \right) - \left[\hat{\mathbf{r}}_{\iota}^{\mathrm{bot}} \cdot \left(\mathbf{v}_{\iota}^{\overline{\mathrm{bot}}} - \mathbf{v}^{\overline{\iota}} \right) \right] \cdot \left(\mathbf{v}_{\iota}^{\backslash \overline{\mathrm{bot}}} - \mathbf{v}^{\backslash \overline{\iota}} \right)
$$

$$
- \hat{k}_{\iota,q}^{top} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta_{\iota}^{\overline{\overline{top}}}} \right) + \mathbf{N} \cdot \sum_{i \in \{g,w\}} \frac{\epsilon_{\iota}^{top} \rho_{\iota}^{top} \omega_{i\iota}^{\overline{top}}}{d} \mathbf{u}_{i\iota}^{\overline{top}} \left(\mu_{i\iota}^{\overline{top}} + \psi_{i\iota}^{\overline{top}} \right)
$$

$$
- \hat{k}_{\iota,q}^{bot} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta_{\iota}^{\overline{\overline{bot}}}} \right) - \mathbf{N} \cdot \sum_{i \in \{g,w\}} \frac{\epsilon_{\iota}^{bot} \rho_{\iota}^{bot} \omega_{i\iota}^{\overline{bot}}}{d} \mathbf{u}_{i\iota}^{\overline{bot}} \left(\mu_{i\iota}^{\overline{bot}} + \psi_{i\iota}^{\overline{bot}} \right) = 0,
$$

for $\iota \in \mathcal{I}_{\mathrm{f}}, j \in \mathcal{I}_{\mathrm{f}}, j \neq \iota$. For the solid phase,

$$
(3.74) \quad \frac{\mathrm{D}^{\overline{s}} E^{\overline{\overline{s}}}}{\mathrm{D}t} + \left(E^{\overline{\overline{s}}} \mathbf{I}^{\backslash} - \epsilon^s \mathbf{t}^{\backslash s} \right) \mathbf{:} \mathbf{d}^{\backslash \overline{s}} + \nabla^{\backslash} \cdot \left[\epsilon^s \hat{\mathbf{K}}_q^s \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right) \right] - \epsilon^s h^{\overline{\overline{s}}}
$$

$$
- \sum_{\kappa \in \mathcal{I}_{cs}} \hat{K}_{s,Q}^{\kappa} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) - \frac{\epsilon_s^{top}}{d} \mathbf{N} \cdot \mathbf{t}_s^{\mathrm{top}} \cdot \left(\mathbf{v}_s^{\overline{\mathrm{top}}} - \mathbf{v}^{\overline{s}} \right) + \frac{\epsilon_s^{bot}}{d} \mathbf{N} \cdot \mathbf{t}_s^{\mathrm{bot}} \cdot \left(\mathbf{v}_s^{\overline{\mathrm{bot}}} - \mathbf{v}^{\overline{s}} \right)
$$

$$
-\mathbf{N}\cdot\left(\mathbf{v}_s^{\overline{\mathrm{top}}}-\mathbf{v}_{\mathrm{ext}}^{\overline{\mathrm{top}}}\right)\left(\frac{\epsilon_s^{\mathrm{top}}\rho_s^{\mathrm{top}}}{d}\mu_s^{\overline{\mathrm{top}}}+\frac{\epsilon_s^{\mathrm{top}}}{d}\boldsymbol{\sigma}_s^{\overline{\overline{\mathrm{top}}}}:\frac{\mathbf{C}_s^{\mathrm{top}}}{j_s^{\mathrm{top}}}\right)
$$

$$
+\mathbf{N}\cdot\left(\mathbf{v}_s^{\overline{\mathrm{bot}}}-\mathbf{v}_{\mathrm{ext}}^{\overline{\mathrm{bot}}}\right)\left(\frac{\epsilon_s^{\mathrm{bot}}\rho_s^{\mathrm{bot}}}{d}\mu_s^{\overline{\mathrm{bot}}}+\frac{\epsilon_s^{\mathrm{bot}}}{d}\boldsymbol{\sigma}_s^{\overline{\overline{\mathrm{bot}}}}:\frac{\mathbf{C}_s^{\mathrm{bot}}}{j_s^{\mathrm{bot}}}\right)
$$

$$
-\hat{k}_{s,q}^{top}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta_s^{\overline{\overline{top}}}}\right)-\hat{k}_{s,q}^{bot}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta_s^{\overline{\overline{bot}}}}\right)=0.
$$

For the solid-fluid interfaces, $\iota\in\{ws,gs\}$, the internal energy can be expressed as

$$
(3.75)\quad\frac{\mathrm{D}^{\bar{\iota}}E^{\overline{\overline{\iota}}}}{\mathrm{D}t}+\left[E^{\overline{\overline{\iota}}}\mathbf{I}-\epsilon^{\iota}\gamma^{\iota}\left(\mathbf{I}-\mathbf{G}^{\backslash\iota}\right)\right]:\mathbf{d}^{\overline{\overline{\iota}}}+\nabla^{\backslash}\cdot\left[\epsilon^{\iota}\hat{\mathbf{K}}_q^{\iota}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\overline{\iota}}}\right)\right]-\epsilon^{\iota}h^{\overline{\overline{\iota}}}
$$

$$
-\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\nabla^{\backslash}\cdot\left[\epsilon^{\iota}\gamma^{\iota}\left(\mathbf{I}-\mathbf{G}^{\backslash\iota}\right)\right]+\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{\mathrm{P}}\right)}\hat{K}_{\kappa,Q}^{\iota}\left(\frac{1}{\theta^{\overline{\overline{\kappa}}}}-\frac{1}{\theta^{\overline{\iota}}}\right)
$$

$$
-\hat{K}_{\iota,Q}^{wgs}\left(\frac{1}{\theta^{\overline{\iota}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)-\hat{K}_{\iota,W}^{wgs}\left(\gamma^{wgs}\kappa_G^{\overline{\overline{wgs}}}+\gamma_{ws}^{wgs}-\gamma_{gs}^{wgs}+\gamma_{wg}^{wgs}\cos\varphi^{\overline{\overline{ws,wg}}}\right)
$$

$$
-\hat{k}_{\iota,q}^{top}\left(\frac{1}{\theta^{\overline{\iota}}}-\frac{1}{\theta_{\iota}^{\overline{\overline{top}}}}\right)-\hat{k}_{\iota,q}^{bot}\left(\frac{1}{\theta^{\overline{\iota}}}-\frac{1}{\theta_{\iota}^{\overline{\overline{bot}}}}\right)=0.
$$

The internal energy of the fluid-fluid interface is similar to the fluid-solid interface except that mass can be exchanged.

$$
(3.76)\quad\frac{\mathrm{D}^{\overline{wg}}E^{\overline{\overline{wg}}}}{\mathrm{D}t}+\left[E^{\overline{\overline{wg}}}\mathbf{I}-\epsilon^{wg}\gamma^{wg}\left(\mathbf{I}-\mathbf{G}^{\backslash wg}\right)\right]:\mathbf{d}^{\overline{\overline{wg}}}+\nabla^{\backslash}\cdot\left[\epsilon^{wg}\hat{\mathbf{K}}_q^{wg}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\overline{\overline{wg}}}}\right)\right]
$$

$$
-\epsilon^{wg}h^{\overline{\overline{wg}}}-\mathbf{v}^{\overline{wg},\overline{s}}\cdot\nabla^{\backslash}\cdot\left[\epsilon^{wg}\gamma^{wg}\left(\mathbf{I}-\mathbf{G}^{\backslash wg}\right)\right]-\hat{K}_{wg,Q}^{wgs}\left(\frac{1}{\theta^{\overline{\overline{wg}}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)
$$

$$
+\sum_{i\in\{g,w\}}\left(\mu_{iw}^{\overline{wg}}-\mu_{ig}^{\overline{wg}}\right)\hat{K}_M\left[\left(\mu^{\overline{ig}}+\psi^{\overline{ig}}\right)-\left(\mu^{\overline{iw}}+\psi^{\overline{iw}}\right)\right]
$$

$$
+\sum_{\kappa\in\mathcal{I}_{cwg}\cap\mathcal{I}_{\mathrm{f}}}\left[\hat{K}_{\kappa,Q}^{wg}\left(\frac{1}{\theta^{\overline{\overline{\kappa}}}}-\frac{1}{\theta^{\overline{\overline{wg}}}}\right)-\hat{K}_{\kappa,W}^{wg}\left(p_w^{wg}-p_g^{wg}-\gamma^{wg}J_w^{wg}\right)\right]
$$

$$
-\hat{K}_{wg,W}^{wgs}\left(\gamma^{wgs}\kappa_G^{\overline{\overline{wgs}}}+\gamma_{ws}^{wgs}-\gamma_{gs}^{wgs}+\gamma_{wg}^{wgs}\cos\varphi^{\overline{\overline{ws,wg}}}\right)
$$

$$
-\hat{k}_{wg,q}^{top}\left(\frac{1}{\theta^{\overline{\overline{wg}}}}-\frac{1}{\theta_{wg}^{\overline{\overline{top}}}}\right)-\hat{k}_{wg,q}^{bot}\left(\frac{1}{\theta^{\overline{\overline{wg}}}}-\frac{1}{\theta_{wg}^{\overline{\overline{bot}}}}\right)=0.
$$

Finally, for the common curve, the expression for internal energy is given by

(3.77)
$$\frac{D^{\overline{wgs}} E^{\overline{wgs}}}{Dt} + \left[E^{\overline{wgs}}\mathbf{I}^{\backslash} + \epsilon^{wgs}\gamma^{wgs}\left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash wgs}\right)\right] : \mathbf{d}^{\overline{wgs}} + \nabla^{\backslash} \cdot \left[\epsilon^{wgs}\hat{\mathbf{K}}_q^{wgs} \cdot \nabla^{\backslash}\left(\frac{1}{\theta^{\overline{wgs}}}\right)\right]$$

$$- \epsilon^{wgs} h^{\overline{wgs}} + \mathbf{v}^{\overline{wgs},\overline{s}} \cdot \nabla^{\backslash} \cdot \left[\epsilon^{wgs}\gamma^{wgs}\left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash wgs}\right)\right] + \sum_{\kappa \in \mathcal{I}_{cwgs}} \hat{K}_{\kappa,Q}^{wgs}\left(\frac{1}{\theta^{\overline{\overline{\kappa}}}} - \frac{1}{\theta^{\overline{wgs}}}\right)$$

$$+ \sum_{\kappa \in \mathcal{I}_{cwgs}} \hat{K}_{\kappa,W}^{wgs}\left(\gamma^{wgs}\kappa_G^{\overline{\overline{wgs}}} + \gamma_{ws}^{wgs} - \gamma_{gs}^{wgs} + \gamma_{wg}^{wgs}\cos\varphi^{\overline{ws,wg}}\right)$$

$$- \hat{k}_{wgs,q}^{top}\left(\frac{1}{\theta^{\overline{\overline{wgs}}}} - \frac{1}{\theta_{wgs}^{\overline{top}}}\right) - \hat{k}_{wgs,q}^{bot}\left(\frac{1}{\theta^{\overline{\overline{wgs}}}} - \frac{1}{\theta_{wgs}^{\overline{bot}}}\right) = 0.$$

The model represented by Eqs. (3.67)–(3.77) contains more unknowns than equations, thus requiring additional closure relations and EOS for a well-posed model.

3.8.3. Evolution Equations. Approximate relations for the evolution of geometric variables have been obtained through the application of time and space averaging theorems [89]. Using this same process, but applying the averaging theorems found in §3.4, the approximate forms for the fluid-solid interfacial areas are

(3.78)
$$\frac{D^s \epsilon^{ws}}{Dt} + \epsilon^{ws}\mathbf{G}^{ss}:\mathbf{d}^{\overline{s}} - J_s^{ws}\chi_{ws}^{ss}\left(\frac{D^s \epsilon^s}{Dt} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)$$

$$- \epsilon^{ss}\frac{D^s \chi_{ws}^{ss}}{Dt} - \chi_{ws}^{ss}\left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws} \cdot \mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}$$

$$- \chi_{ws}^{ss}\left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs} \cdot \mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega} \approx 0,$$

and

(3.79)
$$\frac{D^s \epsilon^{gs}}{Dt} + \epsilon^{gs}\mathbf{G}^{ss}:\mathbf{d}^{\overline{s}} - J_s^{gs}\chi_{gs}^{ss}\left(\frac{D^s \epsilon^s}{Dt} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)$$

$$- \epsilon^{ss}\frac{D^s \chi_{gs}^{ss}}{Dt} - \chi_{gs}^{ss}\left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws} \cdot \mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}$$

$$-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\approx 0,$$

where $\chi_{\iota}^{ss}=\epsilon^{\iota}/\epsilon^{ss}$ for $\iota\in\{ws,gs,wgs\}$. We will consider wetting to be a dynamic process that can be modeled according to

$$(3.80)\qquad\frac{\mathrm{D}^{s}\chi_{ws}^{ss}}{\mathrm{D}t}\approx-\hat{k}^{ws}\left(\chi_{ws}^{ss}-\chi_{ws\text{eq}}^{ss}\right),$$

where the equilibrium wetted fraction as a function of saturation and average curvature of the fluid-fluid interface is

$$(3.81)\qquad\chi_{ws\text{eq}}^{ss}=\chi_{ws\text{eq}}^{ss}\left(s^{w},J_{w}^{wg}\right),$$

and $\hat{k}^{ws}$ is a wetting rate parameter. Note that

$$\frac{\mathrm{D}^{s}\chi_{gs}^{ss}}{\mathrm{D}t}=-\frac{\mathrm{D}^{s}\chi_{ws}^{ss}}{\mathrm{D}t}.$$

A general fluid-fluid interface evolution equation assuming a linear constitutive relation for the processes leading to entrapment and mobilization, can then be written as in [89] using averaging theorems from §3.4 as

$$(3.82)\quad\frac{\mathrm{D}^{\overline{s}}\epsilon^{wg}}{\mathrm{D}t}+\nabla'\cdot\left[\epsilon^{wg}\left(\mathbf{w}^{\overline{\overline{wg}}}+\mathbf{G}^{wg}\cdot\mathbf{v}^{\overline{s}}\right)\right]+\epsilon^{wg}\mathbf{G}^{wg}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-J_{w}^{wg}\left(\frac{\mathrm{D}^{\overline{s}}\epsilon^{w}}{\mathrm{D}t}+\chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}\right)+\hat{k}^{wg}\left(\epsilon^{wg}-\epsilon_{\text{eq}}^{wg}\right)$$

$$+\left(J_{w}^{wg}\chi_{ws}^{ss}-\chi_{wgs}^{ss}\sin\varphi^{\overline{\overline{ws,wg}}}\right)\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$-\epsilon^{ss}\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}\cos\varphi^{\overline{\overline{ws,wg}}}+\chi_{wgs}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}+J_{w}^{wg}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{wM},\Omega}$$

$$-\cos\varphi^{\overline{\overline{ws,wg}}}\left(\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}\right)$$

$$-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{wg}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgM},\Omega}\approx 0,$$

where the average macroscale interface velocity normal to the interface is defined as

$$(3.83) \qquad \mathbf{w}^{\overline{\overline{wg}}} = \left\langle \mathbf{n}_w \mathbf{n}_w \cdot \mathbf{v}_{wg} \right\rangle_{\Omega_{wg}, \Omega_{wg}}.$$

For the common curve, after application of the averaging theorems, the macroscale normal and geodesic curvatures can be added in a subtracted out to create a a convenient form. Following the arguments of [89] we define the resulting difference between the microscale and macroscale curvatures as

$$(3.84) \quad e^{\overline{\overline{wgs}}} = -\left\langle \left(\kappa_{Nwgs} - \kappa_N^{\overline{\overline{wgs}}} \right) \mathbf{n}_s \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs}, \Omega}$$

$$-\left\langle \left(\kappa_{Gwgs} - \kappa_G^{\overline{\overline{wgs}}} \right) \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs}, \Omega},$$

and linearly approximate this term by

$$(3.85) \qquad e^{\overline{\overline{wgs}}} \approx -\hat{k}^{wgs} \left(\epsilon^{wg} - \epsilon_{\text{eq}}^{wgs} \right),$$

where $\epsilon_{\text{eq}}^{wgs} = \epsilon_{\text{eq}}^{wgs}(s^w, J_w^{wg})$ is the equilibrium common curve length density and $\hat{k}^{wgs}$ is a common curve generation rate coefficient. Then the evolution of the common curve can be written as

$$(3.86) \quad \frac{\text{D}^{\overline{s}} \epsilon^{wgs}}{\text{D}t} + \nabla' \cdot \left[\epsilon^{wgs} \left(\mathbf{w}^{\overline{\overline{wgs}}} - \mathbf{G}^{wgs} \cdot \mathbf{v}^{\overline{s}} \right) \right] + \epsilon^{wgs} \mathbf{G}^{wgs} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+\kappa_G^{\overline{\overline{wgs}}} \epsilon^{ss} \frac{\text{D}^{\overline{s}} \chi_{ws}^{ss}}{\text{D}t} + \kappa_N^{\overline{\overline{wgs}}} \chi_{wgs}^{ss} \left(\frac{\text{D}^{\overline{s}} \epsilon^s}{\text{D}t} \right) + \hat{k}^{wgs} \left(\epsilon^{wg} - \epsilon_{\text{eq}}^{wgs} \right)$$

$$+\kappa_G^{\overline{\overline{wgs}}} \left(\chi_{ws}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{gsM}, \Omega} - \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM}, \Omega} \right)$$

$$-\kappa_N^{\overline{\overline{wgs}}} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM}, \Omega} - \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgs}, \Omega} \approx 0,$$

where the average velocity of the common curve in the direction normal to the common curve is defined as

$$(3.87) \qquad \mathbf{w}^{\overline{\overline{wgs}}} = \left\langle \left(\mathbf{I} - \mathbf{l}_{wgs} \mathbf{l}_{wgs} \right) \cdot \mathbf{v}_{wgs} \right\rangle_{\Omega_{wgs}, \Omega_{wgs}}.$$

The solid is specified as non-deformable and the curvature of the solid surface as independent of the fluid contacting it, thus we can reasonably make the approximation that $J_s^{ws} \approx J_s^{gs}$ and will be a specified quantity. The evolution equations together with the constitutive relationships found in Eq. (3.51), Eq. (3.54), and Eq. (3.55) introduce seven additional equations and the unknowns

$$(3.88) \quad \{p_w^{ws}, p_g^{gs}, \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}}, \mathbf{w}^{\overline{\overline{wg}}}, \mathbf{w}^{\overline{\overline{wgs}}}, \epsilon^{ss}, s^w, s^g, \kappa_N^{\overline{\overline{wgs}}}\}.$$

3.8.4. Identities, Equations of State, and Closure Relations.
The relationship between specific entity measures of the phases,

$$(3.89) \qquad s^w = \frac{\epsilon^w}{1 - \epsilon^s}, \quad \epsilon^g = 1 - \epsilon^s - \epsilon^w, \quad s^g = 1 - s^w, \quad \text{and } \epsilon^{ss} = \epsilon^{ws} + \epsilon^{gs},$$

can be used to determine s^w, ϵ^g, s^g, and ϵ^{ss}. In [89] constitutive relationships for the average macroscale interface velocity normal to the interface were proposed and are applicable to the system of interest here, such that

$$(3.90) \qquad \mathbf{w}^{\overline{\overline{wg}}} \approx \mathbf{G}^{wg} \cdot \left(\hat{A}^w \mathbf{v}^{\overline{w}} + \hat{A}^g \mathbf{v}^{\overline{g}} \right)$$

and

$$(3.91) \qquad \mathbf{w}^{\overline{\overline{wgs}}} \approx (\mathbf{G}^{wgs} - \mathbf{G}^{ss}) \cdot \left(\hat{B}^w \mathbf{v}^{\overline{w}} + \hat{B}^g \mathbf{v}^{\overline{g}} \right),$$

where $\hat{A}$ and $\hat{B}$ are parameters that will depend on the ratio of the wetting fluid to gas viscosities, the saturations, and interfacial area densities. We can also note that for the system of interest the velocity of the interface is primarily due to the movement of the interface rather than movement within the interface and thus we can make the approximations

$$\mathbf{v}^{\overline{wg}} \approx \mathbf{w}^{\overline{\overline{wg}}}, \quad \mathbf{v}^{\overline{ws}} \approx \mathbf{w}^{\overline{\overline{ws}}}, \quad \mathbf{v}^{\overline{gs}} \approx \mathbf{w}^{\overline{\overline{gs}}}, \quad \text{and} \quad \mathbf{v}^{\overline{wgs}} \approx \mathbf{w}^{\overline{\overline{wgs}}}.$$

We can use the derivation of [92] for a closure relationship for the solid stress on the system. For a non-deformable system, this relationship is given as

$$(3.92) \quad \epsilon^s \mathbf{t}^{\backslash \overline{\overline{s}}} = -\chi_{ws}^{ss} \left(p_w^{ws} + \gamma^{ws} J_s^{ws} \right) \mathbf{I}^{\backslash} - (1 - \chi_{ws}^{ss}) \left(p_g^{gs} + \gamma^{gs} J_s^{gs} \right) \mathbf{I}^{\backslash}$$

$$+ \frac{\epsilon^{wgs}}{\epsilon^{ss}} \gamma_{wg}^{wgs} \sin \varphi^{\overline{ws,wg}} \mathbf{I}^{\backslash} + (\epsilon^w p^w + \epsilon^g p^g) \mathbf{I}^{\backslash} - \epsilon^{wg} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash wg} \right) \gamma^{wg}$$

$$- \epsilon^{ws} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash ws} \right) \gamma^{ws} - \epsilon^{gs} \left(\mathbf{I}^{\backslash} - \mathbf{G}^{\backslash gs} \right) \gamma^{gs}.$$

Equations of state, formulated through averaging of known microscale equations of state to the macroscale, will provide the remaining constitutive equations necessary to create a closed system. We can write these equations in functional form. For the densities,

$$(3.93) \qquad\qquad \rho^\iota = \rho^\iota \left(\theta^{\overline{\iota}}, p^\iota \right) \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{f}}.$$

The pressures used in these relationships are the volume averaged macroscale pressures. The other unknown pressures, the surface averaged pressures can be approximated by the volume averages such that

$$(3.94) \qquad\qquad p_w^{ws} \approx p_w^{wg} \approx p^w \quad \text{and} \quad p_g^{gs} \approx p_g^{wg} \approx p^g.$$

Similarly to the pressures, the surface averaged chemical potentials and velocities can be approximated by the mass averaged chemical potentials and velocities, respectively, such that

$$(3.95) \qquad \mu_{iw}^{\overline{wg}} \approx \mu^{\overline{iw}}, \quad \mu_{ig}^{\overline{wg}} \approx \mu^{\overline{ig}}, \quad \mathbf{v}_w^{\overline{wg}} \approx \mathbf{v}^{\overline{w}}, \quad \text{and} \quad \mathbf{v}_g^{\overline{wg}} \approx \mathbf{v}^{\overline{g}}.$$

The bulk compressibility or bulk modulus, $\hat{\alpha}^{\mathrm{b}}$, relates the change in porosity with pressure [85] and is defined by

$$(3.96) \qquad\qquad \hat{\alpha}^{\mathrm{b}} = -\frac{1}{(1-\epsilon)\rho^s} \left(\frac{\partial [(1-\epsilon)\rho^s]}{\partial \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss}, \Omega_{ss}}} \right)_{\theta^{\overline{\overline{s}}}}.$$

In considering massless interfaces and common curves, the tensions associated with these entities can be approximated to be constant. We also say that

$$(3.97) \qquad \gamma_{wg}^{wgs} \approx \gamma^{wg}, \quad \gamma_{ws}^{wgs} \approx \gamma^{ws}, \quad \text{and} \quad \gamma_{gs}^{wgs} \approx \gamma^{gs}.$$

The remaining unknowns will be expressed as equations of state written in functional form given by:

$$(3.98) \qquad E^{\overline{\overline{\iota}}} = E^{\overline{\overline{\iota}}}\left(\theta^{\overline{\overline{\iota}}}, p^{\iota}, \rho^{\iota}\right) \quad \text{for } \iota \in \mathfrak{I},$$

$$(3.99) \qquad \mu^{\overline{\overline{i\iota}}} = \mu^{\overline{\overline{i\iota}}}\left(\theta^{\overline{\overline{\iota}}}, p^{\iota}, \rho^{\iota}\omega^{i\iota}\right) \quad \text{for } \iota \in \{w, g, s\},$$

$$(3.100) \qquad J_w^{wg} = J_w^{wg}\left(s^w, \epsilon^{wg}, \chi_{ws}^{ss}\right),$$

and

$$(3.101) \qquad \varphi^{\overline{ws,wg}} = \varphi^{\overline{ws,wg}}\left(s^w, \epsilon^{wg}, \chi_{ws}^{ss}\right).$$

The system equations in section §3.8.2, together with the restrictions and approximations on the system, the geometric evolution equations in section §3.8.3, and the approximations, identities, and equations of state in section §3.8.4 form a closed model.

3.9. Discussion

The interaction of two domains with differing entity sets appears routinely in environmental settings (e.g., flows in fractured rocks and evaporation from soils), industrial applications (e.g., filters, fuel cells, thermal insulation, drying processes), and biological processes (e.g., flows in blood vessels and tissue, transport of drugs and nutrients). The governing equations for individual domains have been widely investigated, but a challenge arises in describing the coupling between the models at the interface. In general, either a single-domain or two-domain approach is adopted [44, 74]. The single-domain

approach is very sensitive to parameters that are not readily available, the two-domain approach considers only sharp interfaces with no thermodynamic properties, and neither approach is capable, in its current state, to account for multi-component, multiple fluid systems.

In this work, we have developed transition region models that are capable of coupling two-fluid-phase, multi-component systems in which at least one of the domains adjacent to the transition region is a porous medium. To accomplish this goal, the TCAT approach is extended from previous model formulations to consider both two-fluid-phase flow and multi-component transport, and is averaged in the direction that is typically chosen approximately normal at the megascale to the intersection of the different regions to be joined. We note that the averaging theorems applied to achieve this formulation for the conservation equations causes a loss of some information in the normal direction, transforming spatial derivatives into boundary terms. However, the result of this process is a model for a domain, which unlike the interfaces for typical two-domain approaches, is capable of containing and evolving mass, momentum, and energy. A closed model for the transition region is given.

While the foundational theoretical framework for modeling transition regions has been developed in this work and a closed model has been specified that can be used to model a variety of common applications of concern, follow-up work would be of use. This work can be divided into applications and extensions. The applications work that should be considered includes the joining of the transition region model specified herein with a porous medium model and a free-flow model to produce a complete model formulation. Once such a complete model is formulated, it should be solved numerically, validated, and verified by comparing to experimental data. The case of water evaporation from a porous medium would seem to be an especially important and accessible application. Other applications are possible for the formulation developed in this work as well.

Many extensions to this work are possible as well, such as transition regions that vary in thickness or curvature, non-dilute systems, deformable solid systems, and in general

any system for which the secondary restrictions and approximations, and closure approximations made in this work are not appropriate. A convenient aspect about the approach taken in this work is that the conservation equations and constrained entropy inequality would apply to many additional conditions; only certain aspects of the derivation of the simplified entropy inequality and model closure would need to be revisited to model other systems. This would make such extensions to this work relatively straightforward in many cases. Certainly, extensions to the theory should match the sophistician needed to model accurately a given system of concern and model-experiment comparisons are important. These experiments may be laboratory or field based, or they may be the result of higly resolved microscale simulations over a sufficiently large domain to test the averaged model.

CHAPTER 4

Summary and Discussion

Current modeling of porous medium systems is beset with inconsistencies and ill-defined variables. The application of the classic experimental work of Darcy for the simplest of single-fluid-phase porous media to more complex systems and the absence of careful transformation of all microscale quantities to the scale of interest has contributed to these problems. The purpose of this work on the TCAT approach is to lay the foundation for rigorous model building for a variety of porous medium systems, while producing well-defined variables, connecting scales, providing thermodynamic consistency, and including the evolution of interfaces and common curves as mechanisms for modeling physically observable phenomena. The approach that has evolved to accomplish this goal is to present the components of the machinery needed to formulate models and to apply the components in order to create frameworks that support a hierarchy of models. Thus the intent of these works is not just to present solutions for a single problem, but to establish a series of frameworks that can be applied to entire families of problems.

This work outlined the shortcomings of traditional models as well as the elements of the TCAT approach needed for constructing macroscale models for two-fluid-phase porous medium systems. A clear separation of exact results from approximations, which are both needed to produced closed models, was detailed for each system. Novel aspects of this work include the application to two-fluid-phase flow systems and two-fluid-phase flow and species transport in transition regions. The manuscripts presented here built upon the TCAT foundation, which includes papers that outline the TCAT approach [84] and that provide the mathematical tools necessary [136, 137] for model formulation.

In Chapter 2, the class of problem considered was two-fluid-phase flow through a porous medium. The TCAT approach combined with the detailed set of restrictions and approximations was used to produce a hierarchy of three models. One strength of the TCAT approach is that a complete, explicit list of restrictions and approximations needed to produce all three model instances is provided, as are the means to produce alternative models based upon a different or relaxed set of restrictions and approximations. The simplest model was derived in an effort to recover a formulation similar to traditional two-fluid-phase flow models. While conceptually satisfying to show that with careful mathematical manipulations and the correct choice of restrictions and approximations, a form similar to traditional models can be achieved, it was not the overall goal of the formulation. Nonetheless, even this seemingly similar formulation boasts the benefit of having well-defined variables and consistency across scales. The two additional models presented each included interface dynamics and the most complex formulation also included the effects of the common curve. It has been observed that interfacial area in particular can play an important role in the physics of the system. Thus, models including mechanisms for understanding the physics are appealing.

In Chapter 3, transition region equations were sought to couple a free flow domain and two-fluid-phase porous medium domain. Again a two-fluid-phase flow system was considered with the additional complexity of species transport. The general model was derived to be macroscale in the dimensions of the transition region surface and megascale in the direction normal to the boundary between the two domains being coupled. The necessary theorems to accomplish this averaging were provided and a closed model was developed. The transition region model can be used to couple a single-phase free flow domain and a two-fluid-phase porous medium and is sufficiently general to be applied to wide array of applications. One such specific application is evaporation of water from and unsaturated ground source into the atmosphere. The transition region model can be coupled at its top boundary with the free flow domain and at the bottom boundary with the porous media domain. Coupling conditions necessary for linking these two domains

via the transition region must be determined. Additional applications for the transition region model are possible. For example, setting all the temperatures equal and looking at an isothermal system would allow for the removal of the energy equation from the system of equations to be solved. The resulting model could be applied to such systems as high humidity evaporation systems, in which temperature changes can be neglected, or the transport of CO_2 from the subsurface to the free flow regime. The transition region model is novel in that no macroscale coupling approach is available for coupling of flow systems with chemical species and more than one fluid-phase. Thus, while specific examples can be highlighted, the general formulation itself is a basis for a plethora of new and useful models.

An important element in each application of the TCAT approach is that the model formulation process proceeds in a series of formal, well-defined intermediate steps that provide convenient starting points for new model aspects without requiring the substantial foundational efforts needed to derive such elements as the CEI or the SEI.

Given the primary restrictions on the class of problem of concern and the applicability of CIT as an appropriate thermodynamic theory, the CEI that are derived are exact expressions. The CEI however, is not strictly in the desired form of a set of forces multiplying a set fluxes, which is needed to guide model closure. Because of this, a series of approximations and restrictions are applied to reduce the CEI to the SEI, which is strictly written in force-flux form. Alternative sets of restrictions and approximations to achieve force-flux forms can be used starting from the CEI to produce alternative forms of the SEI if such efforts are deemed necessary. For instance, if a different set of secondary restrictions is needed to adequately describe the porous medium of concern or if improved approximations become available. It should be noted that reducing the CEI to the SEI is much less effort than deriving the CEI, which requires a substantial series of manipulations. The sort of manipulations required to derive the CEI have been detailed in previous papers in the TCAT series [85, 87, 136, 137].

The SEI is used to guide the formulation of closure relations. A linear form of these closure relations is detailed, which are deemed a reasonable first approximation, but are neither unique nor of high complexity. The closure relations are in turn used to produce a complete set of closed equations for conservation of mass, momentum, and energy as needed for the system of concern. These closed equations can be applied to model a range of physical systems.

Still, the preceding should not be construed to suggest that all porous medium formulation problems are within reach. While the TCAT approach makes great strides toward correcting many deficiencies in traditional models and sheds some insight into the open research issues discussed in the introduction, there is still a tremendous amount of work to be done. Many unresolved issues exist that will require substantial, creative effort to produce a mature level of understanding. As an example, significant work remains to be done in looking at the effect of different thermodynamic approaches as well as the inclusion of stochastic models. Alternative thermodynamic approaches exist, and some of these approaches were reviewed previously [83]. For cases in which CIT must be extended such that thermodynamics are consistent with observations, that extended thermodynamic approach can be incorporated into the present framework at the microscale and then averaged to the macroscale. The averaging of such a framework to the macroscale would follow a similar approach to that used here. Determining the optimal thermodynamic theory, if one such choice exists for all systems, remains an open issue. In addition, all the models derived in this work require a clear separation of length scales that may not exist for many natural systems [155]. As an alternative to this, the single REV assumption could be relaxed to include REV's that vary as a function of quantity being considered or even to the stochastic case where averaging from the microscale is considered in a stochastic sense. Both of these approaches warrant additional consideration. Finally, the approximations used for both simplification to the SEI's and for formulating the closure relationships are subject to improvements. One way to accomplish this goal, would be the use of microscale simulations to examine the constitutive relationships for

such things as the evolution of the geometric densities, capillary pressure, permeabilities, and dynamic force balances.

Microscale and macroscale experimentation and simulation are necessary for successful application of the hierarchy of models presented in this work. The models developed must be tested via simulation. Unfortunately, pore-scale simulations of multiphase systems at REV scales remain a challenge. In addition, parameter estimation is crucial for implementation purposes, but experimentation methods can be timely and expensive for those parameters that are measurable. With the advancement of theoretical models for two-fluid-phase flow and transport therefore, comes the need for advancements in numerical simulation tools and experimentation techniques.

The hierarchy of models presented here, while novel and capable of tackling several of the shortcomings of traditional models, are just the first step toward a complete and physically consistent means of modeling multiphase flow phenomena in porous medium systems. The main challenge for the future is the validation of the hierarchy of models and the resolution of the open issues highlighted in this work.

APPENDIX A

TCAT6: Two-Fluid Phase Flow Details and Calculations

A.1. Conservation Equations

Conservation and balance equations can be derived at the macroscale by applying the averaging operator defined by

$$(A.1) \qquad \langle \mathcal{P}_i \rangle_{\Omega_j, \Omega_k, W} = \frac{\int\limits_{\Omega_j} W \mathcal{P}_i \, \mathrm{d}\mathfrak{r}}{\int\limits_{\Omega_k} W \, \mathrm{d}\mathfrak{r}} \qquad \text{for } \dim \Omega_j > 0, \ \dim \Omega_k > 0,$$

where $\mathcal{P}_i$ is a microscale quantity to be averaged, and W is a weighting function. If W is not specified, it is assumed to be 1. For the common case when $\Omega_k = \Omega$ the averaged quantity is normalized by an integral over the entire REV. Common forms of the averaging operator have been detailed previously [136].

A.1.1. Conservation Equations for a Phase. Consider the overall conservation of total energy for a phase at the microscale, which may be written as

$$(A.2) \quad \frac{\partial}{\partial t} \left[E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right] + \nabla \cdot \left\{ \left[E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right] \mathbf{v}_\iota \right\}$$
$$- \nabla \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota) - h_\iota - \rho_\iota \frac{\partial \psi_\iota}{\partial t} = 0 \qquad \text{for } \iota \in \mathcal{I}_\mathrm{P},$$

where ι is an entity qualifier that is subscripted for microscale quantities, $\mathcal{I}_\mathrm{P}$ is the index set of phases, E_ι is the internal energy density, ρ_ι is the mass density, $\mathbf{v}_\iota$ is the velocity vector for entity ι, ψ_ι is the body force potential, $\mathbf{t}_\iota$ is the stress tensor, $\mathbf{q}_\iota$ is the non-advective heat flux density vector, and h_ι is the heat source density.

Applying the averaging operator given by Eq. (A.1) to Eq. (A.2) yields

$$(A.3) \quad \left\langle \frac{\partial}{\partial t} \left[E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right] \right\rangle_{\Omega_\iota, \Omega} + \left\langle \nabla \cdot \left\{ \left[E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right] \mathbf{v}_\iota \right\} \right\rangle_{\Omega_\iota, \Omega}$$

$$-\langle \nabla \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota) \rangle_{\Omega_\iota, \Omega} - \langle h_\iota \rangle_{\Omega_\iota, \Omega} - \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}.$$

Eq. (A.3) contains averages of terms involving differential operators, and we wish to transform these to differential operators applied to averages. Applying the Divergence Theorem D[3,(3,0),0] and the Transport Theorem T[3,(3,0),0] to Eq. (A.3) and rearranging terms yields

$$(A.4) \quad \frac{\partial}{\partial t} \left\langle E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right\rangle_{\Omega_\iota, \Omega} + \nabla \cdot \left\langle \left[E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right] \mathbf{v}_\iota \right\rangle_{\Omega_\iota, \Omega}$$

$$-\nabla \cdot \langle \mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota \rangle_{\Omega_\iota, \Omega} - \langle h_\iota \rangle_{\Omega_\iota, \Omega} - \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\kappa \in \mathfrak{I}_{c\iota}} \left\langle \left[E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right] \mathbf{n}_\iota \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \right\rangle_{\Omega_\kappa, \Omega}$$

$$- \sum_{\kappa \in \mathfrak{I}_{c\iota}} \langle \mathbf{n}_\iota \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota) \rangle_{\Omega_\kappa, \Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}.$$

Considering Eq. (A.4) term by term to evaluate the averaging operators gives for the time derivative term

$$(A.5) \quad \frac{\partial}{\partial t} \left\langle E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right\rangle_{\Omega_\iota, \Omega} = \frac{\partial}{\partial t} \left[E^{\bar{\iota}} + \epsilon^\iota \rho^\iota \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} + \psi^{\bar{\iota}} \right) \right],$$

or

$$(A.6) \quad \frac{\partial}{\partial t} \langle E_{T\iota} \rangle_{\Omega_\iota, \Omega} = \frac{\partial}{\partial t} E_T^{\bar{\bar{\iota}}},$$

where

$$(A.7) \quad E_{T\iota} = E_\iota + \rho_\iota \left(\frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right),$$

$$(A.8) \quad E^{\bar{\iota}} = \langle E_\iota \rangle_{\Omega_\iota, \Omega},$$

$$(A.9) \quad \epsilon^\iota \rho^\iota K_E^{\bar{\bar{\iota}}} = \left\langle \rho_\iota \frac{(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}) \cdot (\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}})}{2} \right\rangle_{\Omega_\iota, \Omega},$$

$$(A.10) \quad \epsilon^\iota \rho^\iota \psi^{\bar{\iota}} = \langle \rho_\iota \psi_\iota \rangle_{\Omega_\iota, \Omega},$$

$$\text{(A.11)} \qquad E_T^{\bar{\bar{\iota}}} = E^{\bar{\iota}} + \epsilon^\iota \rho^\iota \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} + \psi^{\bar{\iota}} \right), \quad \text{and}$$

$$\text{(A.12)} \qquad E_T^{\bar{\bar{\iota}}} = \langle E_{T\iota} \rangle_{\Omega_\iota, \Omega}.$$

For the first divergence term in Eq. (A.4) things are a bit more complicated by the existence of the product of the internal and kinetic energy terms with the velocity. This term can be written as

$$\text{(A.13)} \qquad \nabla \cdot \langle E_{T\iota} \mathbf{v}_\iota \rangle_{\Omega_\iota, \Omega} = \nabla \cdot \left\langle \left[\frac{E_T^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota} + \left(\frac{E_{T\iota}}{\rho_\iota} - \frac{E_T^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota} \right) \right] \rho_\iota \left[\mathbf{v}^{\bar{\iota}} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right] \right\rangle_{\Omega_\iota, \Omega},$$

or

$$\text{(A.14)} \qquad \nabla \cdot \langle E_{T\iota} \mathbf{v}_\iota \rangle_{\Omega_\iota, \Omega} = \nabla \cdot \left(E_T^{\bar{\bar{\iota}}} \mathbf{v}^{\bar{\iota}} \right) + \nabla \cdot \left\langle E_{T\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega}.$$

Evaluating the last term in Eq. (A.13) gives

$$\text{(A.15)} \quad \nabla \cdot \left\langle E_{T\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega} = \nabla \cdot \left\langle \left(E_\iota + \rho_\iota \psi_\iota \right) \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \nabla \cdot \left\langle \left[\mathbf{v}^{\bar{\iota}} \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) + \frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right)}{2} \right] \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega}.$$

The second divergence term in Eq. (A.4) may be written as

$$\text{(A.16)} \qquad \nabla \cdot \langle \mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota \rangle_{\Omega_\iota, \Omega} = \nabla \cdot \left\langle \mathbf{t}_\iota \cdot \mathbf{v}^{\bar{\iota}} + \mathbf{t}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) + \mathbf{q}_\iota \right\rangle_{\Omega_\iota, \Omega}.$$

Combining terms from Eqs. (A.15) and (A.16) and dropping the divergence operator, which is applied to all terms, gives

$$\text{(A.17)} \quad \epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} + \epsilon^\iota \mathbf{q}^{\bar{\bar{\iota}}} = \left\langle \left[\mathbf{t}_\iota - \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right] \cdot \mathbf{v}^{\bar{\iota}} \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \left\langle \mathbf{q}_\iota - \left[E_\iota + \rho_\iota \left(\frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right)}{2} + \psi_\iota \right) \right] \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \left\langle \mathbf{t}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega},$$

where the first term on the right hand side (RHS) is the dot product of the macroscale stress tensor and macroscale velocity and the second two terms on the RHS sum to the macroscale heat source vector.

The remaining terms to be evaluated in Eq. (A.4) involve the transfer of energy at internal boundaries to interfaces. The inter-entity transfer of energy can be written as

$$
\begin{aligned}
\text{(A.18)} \quad -&\sum_{\kappa \in \mathcal{J}_{c\iota}} \langle E_{T\iota} \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) + \mathbf{n}_\iota \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota) \rangle_{\Omega_\kappa, \Omega} = \\
-&\sum_{\kappa \in \mathcal{J}_{c\iota}} \left\langle \left[\frac{E_T^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota} + \left(\frac{E_{T\iota}}{\rho_\iota} - \frac{E_T^{\bar{\iota}}}{\epsilon^\iota \rho^\iota} \right) \right] \rho_\iota \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \right\rangle_{\Omega_\kappa, \Omega} \\
-&\sum_{\kappa \in \mathcal{J}_{c\iota}} \left\langle \mathbf{n}_\iota \cdot \left\{ \mathbf{t}_\iota \cdot \left[\mathbf{v}^{\bar{\iota}} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right] + \mathbf{q}_\iota \right\} \right\rangle_{\Omega_\kappa, \Omega}, \\
= -&\sum_{\kappa \in \mathcal{J}_{c\iota}} \frac{E_T^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota} \langle \rho_\iota \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \rangle_{\Omega_\kappa, \Omega} \\
-&\sum_{\kappa \in \mathcal{J}_{c\iota}} \left\langle \mathbf{n}_\iota \cdot \left\{ \mathbf{t}_\iota \cdot \left[\mathbf{v}^{\bar{\iota}} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right] + \mathbf{q}_\iota \right\} \right\rangle_{\Omega_\kappa, \Omega} \\
-&\sum_{\kappa \in \mathcal{J}_{c\iota}} \left\langle \left(\frac{E_\iota}{\rho_\iota} - \frac{E^{\bar{\iota}}}{\epsilon^\iota \rho^\iota} - K_E^{\bar{\bar{\iota}}} + \psi_\iota - \psi^{\bar{\iota}} \right) \rho_\iota \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \right\rangle_{\Omega_\kappa, \Omega} \\
-&\sum_{\kappa \in \mathcal{J}_{c\iota}} \left\langle \left(\mathbf{v}^{\bar{\iota}} \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) + \frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right)}{2} \right) \rho_\iota \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \right\rangle_{\Omega_\kappa, \Omega}.
\end{aligned}
$$

Eq. (A.18) can be written as

$$
\begin{aligned}
\text{(A.19)} \quad &\sum_{\kappa \in \mathcal{J}_{c\iota}} \langle E_{T\iota} \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) + \mathbf{n}_\iota \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota) \rangle_{\Omega_\kappa, \Omega} \\
&= \sum_{\kappa \in \mathcal{J}_{c\iota}} \left[\overset{\kappa \to \iota}{M_E} + \left(\overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) \right],
\end{aligned}
$$

where the transfer terms are defined as

$$
(A.20) \qquad \overset{\kappa\to\iota}{M_E} = \begin{cases} \left(\dfrac{E_T^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota}\right) \overset{\kappa\to\iota}{M} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] -\left(\dfrac{E_T^{\bar{\bar{\kappa}}}}{\epsilon^\kappa \rho^\kappa}\right) \overset{\iota\to\kappa}{M} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(A.21) \qquad \overset{\kappa\to\iota}{T_v} = \begin{cases} \bar{\mathbf{v}^\iota}\cdot \overset{\kappa\to\iota}{\mathbf{T}} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] -\bar{\mathbf{v}^\kappa}\cdot \overset{\iota\to\kappa}{\mathbf{T}} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(A.22) \qquad \overset{\kappa\to\iota}{M} = \begin{cases} \langle \rho_\iota \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \rangle_{\Omega_\kappa,\Omega} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] -\langle \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \rangle_{\Omega_\iota,\Omega} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(A.23) \qquad \overset{\kappa\to\iota}{\mathbf{T}} = \begin{cases} \langle \mathbf{n}_\iota \cdot \mathbf{t}_\iota \rangle_{\Omega_\kappa,\Omega} + \left\langle \mathbf{n}_\iota \cdot \left[\rho_\iota (\mathbf{v}_\kappa - \mathbf{v}_\iota)(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}) \right] \right\rangle_{\Omega_\kappa,\Omega} \\[1ex] \qquad \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] -\langle \mathbf{n}_\kappa \cdot \mathbf{t}_\kappa \rangle_{\Omega_\iota,\Omega} - \left\langle \mathbf{n}_\kappa \cdot \left[\rho_\kappa (\mathbf{v}_\iota - \mathbf{v}_\kappa)(\mathbf{v}_\kappa - \mathbf{v}^{\bar{\kappa}}) \right] \right\rangle_{\Omega_\iota,\Omega} \\[1ex] \qquad \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(A.24) \qquad \overset{\kappa\to\iota}{Q} = \langle \mathbf{n}_\iota \cdot \mathbf{q}_\iota \rangle_{\Omega_\kappa,\Omega} + \left\langle \mathbf{n}_\iota \cdot \mathbf{t}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\kappa,\Omega}
$$
$$
+ \left\langle \rho_\iota \left(\frac{E_\iota}{\rho_\iota} - \frac{E^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho_\iota} + \psi_\iota - \psi^{\bar{\iota}} \right) \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \right\rangle_{\Omega_\kappa,\Omega}
$$
$$
+ \left\langle \rho_\iota \omega_{i\iota} \left(\frac{(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}})\cdot(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}})}{2} - K_E^{\bar{\bar{\iota}}} \right) \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \right\rangle_{\Omega_\kappa,\Omega}
$$
$$
\text{for } \dim\Omega_\iota > \dim\Omega_\kappa,
$$

and

$$
(A.25) \qquad \overset{\kappa\to\iota}{Q} = -\langle \mathbf{n}_\kappa \cdot \mathbf{q}_\kappa \rangle_{\Omega_\iota,\Omega} - \left\langle \mathbf{n}_\kappa \cdot \mathbf{t}_\kappa \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\bar{\kappa}} \right) \right\rangle_{\Omega_\iota,\Omega}
$$
$$
- \left\langle \left(\frac{E_\kappa}{\rho_\kappa} - \frac{E^{\bar{\bar{\kappa}}}}{\epsilon^\kappa \rho^\kappa} + \psi_\kappa - \psi^{\bar{\kappa}} \right) \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \right\rangle_{\Omega_\iota,\Omega}
$$

$$-\left\langle \left(\frac{\left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{\kappa}} \right) \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{\kappa}} \right)}{2} - K_E^{\overline{\overline{\kappa}}} \right) \rho_\kappa \mathbf{n}_\kappa \cdot \left(\mathbf{v}_\iota - \mathbf{v}_\kappa \right) \right\rangle_{\Omega_\iota, \Omega}$$

for $\dim \Omega_\kappa > \dim \Omega_\iota$.

Here $\overset{\kappa \to \iota}{M}$ represents transfer of mass from the κ entity to the ι entity per unit volume per unit time, $\overset{\kappa \to \iota}{\mathbf{T}}$ represents momentum transfer from the κ entity to the ι entity due to stress and deviation from mean processes per unit volume per unit time, and $\overset{\kappa \to \iota}{Q}$ represents transfer of energy from the κ entity to the ι entity resulting from heat transfer and deviation from mean processes per unit volume per unit time.

Combining Eqns.(A.4), (A.5), (A.14), (A.17), and (A.19) gives the conservation of energy equation for a phase

$$(A.26) \quad \mathcal{E}^\iota = \frac{\mathrm{D}^{\overline{\iota}} E_T^{\overline{\overline{\iota}}}}{\mathrm{D}t} + E_T^{\overline{\overline{\iota}}} \mathbf{I} : \mathbf{d}^{\overline{\overline{\iota}}} - \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\overline{\overline{\iota}}} \cdot \mathbf{v}^{\overline{\iota}} + \epsilon^\iota \mathbf{q}^{\overline{\iota}} \right) - \epsilon^\iota h^{\overline{\iota}}$$
$$- \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in \mathfrak{I}_{c\iota}} \left(\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) = 0 \qquad \text{for } \iota \in \mathfrak{I}_\mathrm{P},$$

where the rate of strain tensor is defined as

$$\mathbf{d}^{\overline{\overline{\iota}}} = \frac{1}{2} \left[\nabla \mathbf{v}^{\overline{\iota}} + \left(\nabla \mathbf{v}^{\overline{\iota}} \right)^{\mathrm{T}} \right].$$

Continuum mechanical equations must satisfy the axiom of objectivity, which means that all velocities must be referenced to a common frame of reference. Conservation equations must remain valid under a change in the reference velocity. Here we develop the macroscale mass and momentum conservation equations for a phase volume following the approach in [114] that was applied to microscale equations. If we adjust all velocities in Eq. (A.26) by subtracting a constant reference velocity $\mathbf{V}$ then we obtain

$$(A.27) \quad \frac{\mathrm{D}^{\overline{\iota}} \left[E^{\overline{\overline{\iota}}} + \epsilon^\iota \rho^\iota \left(\frac{\left(\mathbf{v}^{\overline{\iota}} - \mathbf{V} \right) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{V} \right)}{2} + K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}} \right) \right]}{\mathrm{D}t}$$
$$+ \left[E^{\overline{\overline{\iota}}} + \epsilon^\iota \rho^\iota \left(\frac{\left(\mathbf{v}^{\overline{\iota}} - \mathbf{V} \right) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{V} \right)}{2} + K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}} \right) \right] \mathbf{I} : \mathbf{d}^{\overline{\overline{\iota}}}$$

$$-\nabla\cdot\left(\epsilon^\iota\mathbf{t}^{\bar{\bar{\iota}}}\cdot\left(\mathbf{v}^{\bar{\iota}}-\mathbf{V}\right)+\epsilon^\iota\mathbf{q}^{\bar{\iota}}\right)-\epsilon^\iota h^{\bar{\bar{\iota}}}$$

$$+\left\langle\rho_\iota\frac{\partial\psi_\iota}{\partial t}-\rho_\iota\nabla\psi_{\iota\iota}\cdot\mathbf{V}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in\mathcal{J}_{c\iota}}\left(\frac{E^{\bar{\bar{\iota}}}}{\epsilon^\iota\rho^\iota}+\frac{\left(\mathbf{v}^{\bar{\iota}}-\mathbf{V}\right)\cdot\left(\mathbf{v}^{\bar{\iota}}-\mathbf{V}\right)}{2}+K_E^{\bar{\bar{\iota}}}+\psi^{\bar{\iota}}\right)\overset{\kappa\to\iota}{M}$$

$$-\sum_{\kappa\in\mathcal{J}_{c\iota}}\left[\overset{\kappa\to\iota}{\mathbf{T}}\cdot\left(\mathbf{v}^{\bar{\iota}}-\mathbf{V}\right)+\overset{\kappa\to\iota}{Q}\right]=0,\qquad\text{for }\iota\in\mathcal{J}_\mathrm{P}.$$

Expanding terms and combining quantities such that terms as they originally appeared in Eq. (A.26) are evident gives

(A.28)
$$\frac{\mathrm{D}^{\bar{\iota}}\left[E^{\bar{\bar{\iota}}}+\epsilon^\iota\rho^\iota\left(\frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2}+K_E^{\bar{\bar{\iota}}}+\psi^{\bar{\iota}}\right)\right]}{\mathrm{D}t}-\mathbf{V}\cdot\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\mathbf{v}^{\bar{\iota}}\right)}{\mathrm{D}t}+\frac{\mathbf{V}\cdot\mathbf{V}}{2}\frac{\mathrm{D}^{\bar{\iota}}\epsilon^\iota\rho^\iota}{\mathrm{D}t}$$

$$+\left[E^{\bar{\bar{\iota}}}+\epsilon^\iota\rho^\iota\left(\frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2}+K_E^{\bar{\bar{\iota}}}+\psi^{\bar{\iota}}\right)\right]\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}}-\epsilon^\iota\rho^\iota\mathbf{V}\cdot\mathbf{v}^{\bar{\iota}}\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}}$$

$$+\frac{\mathbf{V}\cdot\mathbf{V}}{2}\epsilon^\iota\rho^\iota\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}}-\nabla\cdot\left(\epsilon^\iota\mathbf{t}^{\bar{\bar{\iota}}}\cdot\mathbf{v}^{\bar{\iota}}+\epsilon^\iota\mathbf{q}^{\bar{\iota}}\right)+\nabla\cdot\left(\epsilon^\iota\mathbf{t}^{\bar{\bar{\iota}}}\cdot\mathbf{V}\right)-\epsilon^\iota h^{\bar{\bar{\iota}}}$$

$$-\mathbf{V}\cdot\langle\rho_\iota\nabla\psi_\iota\rangle_{\Omega_\iota,\Omega}+\left\langle\rho_\iota\frac{\partial\psi_\iota}{\partial t}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in\mathcal{J}_{c\iota}}\left(\frac{E^{\bar{\bar{\iota}}}}{\epsilon^\iota\rho^\iota}+\frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2}+K_E^{\bar{\bar{\iota}}}+\psi^{\bar{\iota}}\right)\overset{\kappa\to\iota}{M}-\sum_{\kappa\in\mathcal{J}_{c\iota}}\mathbf{V}\cdot\mathbf{v}^{\bar{\iota}}\overset{\kappa\to\iota}{M}$$

$$+\frac{\mathbf{V}\cdot\mathbf{V}}{2}\sum_{\kappa\in\mathcal{J}_{c\iota}}\overset{\kappa\to\iota}{M}-\sum_{\kappa\in\mathcal{J}_{c\iota}}\left(\overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{v}^{\bar{\iota}}+\overset{\kappa\to\iota}{Q}\right)+\sum_{\kappa\in\mathcal{J}_{c\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{V}=0\qquad\text{for }\iota\in\mathcal{J}_\mathrm{P}.$$

Here we should take into account the connection between the microscale acceleration vector, $\mathbf{g}_\iota$, and the microscale body force potential, ψ_ι, expressed as $\rho_\iota\mathbf{g}_\iota\cdot\mathbf{v}_\iota=-\rho_\iota\nabla\psi_\iota\cdot\mathbf{v}_\iota$.

The vector $\mathbf{V}$ can be made a factor in collecting terms such that Eq. (A.28) can be written in the form

(A.29)
$$\mathcal{E}^\iota-\mathbf{V}\cdot\boldsymbol{\mathcal{P}}^\iota+\frac{\mathbf{V}\cdot\mathbf{V}}{2}\mathcal{M}^\iota=0$$

where $\mathcal{E}^\iota$, $\boldsymbol{\mathcal{P}}^\iota$, and $\mathcal{M}^\iota$ are each independent of $\mathbf{V}$. Since $\mathbf{V}$ is an arbitrary constant vector, the null vector is a valid choice. This implies $\mathcal{E}^\iota=0$, which we also know to

be the case because this condition is identical to the conservation of energy equation as given by Eq. (A.26). With this condition imposed, Eq. (A.29) reduces to

$$(A.30) \qquad -\mathbf{V} \cdot \left(\boldsymbol{\mathcal{P}}^\iota - \frac{\mathbf{V}}{2} \mathcal{M}^\iota \right) = 0$$

Since $\mathbf{V}$ is an arbitrary vector, it can be chosen to be non-zero and orthogonal to $\boldsymbol{\mathcal{P}}^\iota$. Satisfaction of Eq. (A.30) then requires $\mathcal{M}^\iota = 0$. Making use of this constraint, we see that since $\mathbf{V}$ need not be orthogonal to $\boldsymbol{\mathcal{P}}^\iota$, $\boldsymbol{\mathcal{P}}^\iota$ itself must also equal $\mathbf{0}$.

These considerations imply a conservation of momentum equation for phases of the form

$$(A.31) \quad \boldsymbol{\mathcal{P}}^\iota = \frac{\mathrm{D}^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\bar{\iota}} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{v}^{\bar{\iota}} \mathbf{l} : \mathbf{d}^{\bar{\bar{\iota}}} - \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\iota}} \right)$$
$$- \epsilon^\iota \rho^\iota \mathbf{g}^{\bar{\iota}} - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \left(\overset{\kappa \to \iota}{\mathbf{M}_v} + \overset{\kappa \to \iota}{\mathbf{T}} \right) = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}}$$

and a conservation of mass equation for phases of the form

$$(A.32) \qquad \mathcal{M}^\iota = \frac{\mathrm{D}^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{l} : \mathbf{d}^{\bar{\bar{\iota}}} - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \overset{\kappa \to \iota}{M} = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{P}},$$

where

$$(A.33) \qquad \overset{\kappa \to \iota}{\mathbf{M}_v} = \begin{cases} \mathbf{v}^{\bar{\iota}} \overset{\kappa \to \iota}{M} & \text{for } \dim \Omega_\iota > \dim \Omega_\kappa, \\ -\mathbf{v}^{\bar{\kappa}} \overset{\iota \to \kappa}{M} & \text{for } \dim \Omega_\kappa > \dim \Omega_\iota. \end{cases}$$

A similar process can be carried out for interfaces and common curves.

A.1.2. Conservation Equations for an Interface. The microscale conservation of energy equation for an interface ι is

$$(A.34) \quad \frac{\partial' E_{T\iota}}{\partial t} + \nabla' \cdot (E_{T\iota} \mathbf{v}_\iota) - \nabla' \cdot \left(\mathbf{t}'_\iota \cdot \mathbf{v}_\iota + \mathbf{q}'_\iota \right) - h_\iota$$
$$- \rho_\iota \frac{\partial' \psi_\iota}{\partial t} + \sum_{\kappa \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{P}})} E_{T\kappa} (\mathbf{v}_\iota - \mathbf{v}_\kappa) \cdot \mathbf{n}_\kappa \bigg|_{\Omega_\iota}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{P})} \mathbf{n}_{\kappa} \cdot (\mathbf{t}_{\kappa} \cdot \mathbf{v}_{\kappa} + \mathbf{q}_{\kappa}) \Big|_{\Omega_{\iota}} = 0 \quad \text{for } \iota \in \mathfrak{I}_{I}.$$

Integrating Eq. (A.34) over the interfacial area, Ω_{ι}, we have

$$(A.35) \quad \left\langle \frac{\partial' E_{T\iota}}{\partial t} \right\rangle_{\Omega_{\iota}, \Omega} + \left\langle \nabla' \cdot (E_{T\iota} \mathbf{v}_{\iota}) \right\rangle_{\Omega_{\iota}, \Omega} - \left\langle \nabla' \cdot (\mathbf{t}_{\iota}' \cdot \mathbf{v}_{\iota} + \mathbf{q}_{\iota}') \right\rangle_{\Omega_{\iota}, \Omega}$$

$$- \langle h_{\iota} \rangle_{\Omega_{\iota}, \Omega} - \left\langle \rho_{\iota} \frac{\partial' \psi_{\iota}}{\partial t} \right\rangle_{\Omega_{\iota}, \Omega} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{P})} \langle E_{T\kappa} \mathbf{n}_{\kappa} \cdot (\mathbf{v}_{\iota} - \mathbf{v}_{\kappa}) \rangle_{\Omega_{\iota}, \Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{P})} \langle \mathbf{n}_{\kappa} \cdot (\mathbf{t}_{\kappa} \cdot \mathbf{v}_{\kappa} + \mathbf{q}_{\kappa}) \rangle_{\Omega_{\iota}, \Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_{I}.$$

Applying T[2,(3,0),0] to the first term in Eq. (A.35) yields

$$(A.36) \quad \left\langle \frac{\partial' E_{T\iota}}{\partial t} \right\rangle_{\Omega_{\iota}, \Omega} = \frac{\partial}{\partial t} \langle E_{T\iota} \rangle_{\Omega_{\iota}, \Omega} + \nabla \cdot \langle \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \cdot \mathbf{v}_{\iota} E_{T\iota} \rangle_{\Omega_{\iota}, \Omega}$$

$$- \langle (\nabla' \cdot \mathbf{n}_{\alpha}) \, \mathbf{n}_{\alpha} \cdot \mathbf{v}_{\iota} E_{T\iota} \rangle_{\Omega_{\iota}, \Omega} - \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{C})} \langle \mathbf{n}_{\iota} \cdot \mathbf{v}_{\kappa} E_{T\iota} \rangle_{\Omega_{\kappa}, \Omega}.$$

Applying D[2,(3,0),0] to the divergence terms in Eq. (A.35) provides

$$(A.37) \quad \langle \nabla' \cdot (E_{T\iota} \mathbf{v}_{\iota}) \rangle_{\Omega_{\iota}, \Omega} = \nabla \cdot \langle E_{T\iota} (\mathbf{v}_{\iota} - \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \cdot \mathbf{v}_{\iota}) \rangle_{\Omega_{\iota}, \Omega}$$

$$+ \langle (\nabla' \cdot \mathbf{n}_{\alpha}) \, \mathbf{n}_{\alpha} \cdot E_{T\iota} \mathbf{v}_{\iota} \rangle_{\Omega_{\iota}, \Omega} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{C})} \langle \mathbf{n}_{\iota} \cdot E_{T\iota} \mathbf{v}_{\iota} \rangle_{\Omega_{\kappa}, \Omega}$$

and

$$(A.38) \quad \langle \nabla' \cdot (\mathbf{t}_{\iota}' \cdot \mathbf{v}_{\iota} + \mathbf{q}_{\iota}') \rangle_{\Omega_{\iota}, \Omega} = \nabla \cdot \langle \mathbf{t}_{\iota}' \cdot \mathbf{v}_{\iota} + \mathbf{q}_{\iota}' \rangle_{\Omega_{\iota}, \Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{C})} \langle \mathbf{n}_{\iota} \cdot (\mathbf{t}_{\iota}' \cdot \mathbf{v}_{\iota} + \mathbf{q}_{\iota}') \rangle_{\Omega_{\kappa}, \Omega}.$$

Substituting these into Eq. (A.35) and canceling like terms we get

$$(A.39) \quad \frac{\partial}{\partial t} \langle E_{T\iota} \rangle_{\Omega_{\iota}, \Omega} + \nabla \cdot \langle E_{T\iota} \mathbf{v}_{\iota} \rangle_{\Omega_{\iota}, \Omega} - \nabla \cdot \langle \mathbf{t}_{\iota}' \cdot \mathbf{v}_{\iota} + \mathbf{q}_{\iota}' \rangle_{\Omega_{\iota}, \Omega}$$

$$-\langle h_\iota \rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota \frac{\partial' \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) E_{T\kappa} \rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_C)} \langle \mathbf{n}_\iota \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) E_{T\iota} \rangle_{\Omega_\kappa,\Omega} + \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{t}_\kappa \cdot \mathbf{v}_\kappa + \mathbf{q}_\kappa) \rangle_{\Omega_\iota,\Omega}$$

$$- \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_C)} \langle \mathbf{n}_\iota \cdot \mathbf{t}'_\iota \cdot \mathbf{v}_\iota \rangle_{\Omega_\kappa,\Omega} - \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_C)} \langle \mathbf{n}_\iota \cdot \mathbf{q}'_\iota \rangle_{\Omega_\kappa,\Omega}.$$

Considering Eq. (A.39) term by term to evaluate the averaging operators gives for the time derivative term

(A.40) $\quad \dfrac{\partial}{\partial t} \left\langle E_\iota + \rho_\iota \left(\dfrac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \psi_\iota \right) \right\rangle_{\Omega_\iota,\Omega}$

$$= \frac{\partial}{\partial t} \left[E^{\bar{\bar{\iota}}} + \epsilon^\iota \rho^\iota \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} + \psi^{\bar{\iota}} \right) \right].$$

Evaluating divergence terms in the same way as for phases provides

(A.41) $\quad \nabla \cdot \langle E_{T\iota} \mathbf{v}_\iota \rangle_{\Omega_\iota,\Omega} = \nabla \cdot \left(E_T^{\bar{\bar{\iota}}} \mathbf{v}^{\bar{\iota}} \right) + \nabla \cdot \left\langle (E_\iota + \rho_\iota \psi_\iota) \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota,\Omega}$

$$+ \nabla \cdot \left\langle \left(\mathbf{v}^{\bar{\iota}} \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) + \frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right)}{2} \right) \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota,\Omega}.$$

The second divergence term in Eq. (A.39) may be written as

(A.42) $\quad \nabla \cdot \langle \mathbf{t}'_\iota \cdot \mathbf{v}_\iota + \mathbf{q}'_\iota \rangle_{\Omega_\iota,\Omega} = \nabla \cdot \left\langle \mathbf{t}'_\iota \cdot \mathbf{v}^{\bar{\iota}} + \mathbf{t}'_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) + \mathbf{q}'_\iota \right\rangle_{\Omega_\iota,\Omega}.$

Combining Eqs. (A.41) and (A.42) gives

(A.43) $\quad \epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} + \epsilon^\iota \mathbf{q}^{\bar{\bar{\iota}}} = \left\langle \left[\mathbf{t}'_\iota - \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right] \cdot \mathbf{v}^{\bar{\iota}} \right\rangle_{\Omega_\iota,\Omega}$

$$+ \left\langle \mathbf{q}'_\iota - \left[E_\iota + \rho_\iota \left(\frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right)}{2} + \psi_\iota \right) \right] \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \mathbf{t}'_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}} \right) \right\rangle_{\Omega_\iota,\Omega},$$

where the first term on the RHS is the macroscale stress tensor for an interface and the second two terms on the RHS sum to the macroscale heat source vector for an interface.

The inter-entity transfer of energy from the phases that form the interface to the interface can be written as

$$(A.44) \quad -\sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) E_{T\kappa} \rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{t}_\kappa \cdot \mathbf{v}_\kappa + \mathbf{q}_\kappa) \rangle_{\Omega_\iota, \Omega}$$

$$= -\sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \frac{E_T^{\overline{\overline{\kappa}}}}{\epsilon^\kappa \rho^\kappa} \langle \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \rangle_{\Omega_\iota, \Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \left\langle \left(\frac{E_\kappa}{\rho_\kappa} - \frac{E^{\overline{\overline{\kappa}}}}{\epsilon^\kappa \rho^\kappa} - K_E^{\overline{\overline{\kappa}}} \right) \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \right\rangle_{\Omega_\iota, \Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \left\langle \left[\psi_\kappa - \psi^{\overline{\kappa}} + \mathbf{v}^{\overline{\kappa}} \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{\kappa}} \right) \right] \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \right\rangle_{\Omega_\iota, \Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \left\langle \frac{\left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{\kappa}} \right) \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{\kappa}} \right)}{2} \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \right\rangle_{\Omega_\iota, \Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \left\langle \mathbf{n}_\kappa \cdot \left(\mathbf{t}_\kappa \cdot \left[\mathbf{v}^{\overline{\kappa}} + \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{\kappa}} \right) \right] + \mathbf{q}_\kappa \right) \right\rangle_{\Omega_\iota, \Omega}.$$

Using notation from Eqs. (A.22)–(A.25), Eq. (A.44) can be written as

$$(A.45) \quad \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) E_{T\kappa} \rangle_{\Omega_\iota, \Omega} + \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{t}_\kappa \cdot \mathbf{v}_\kappa + \mathbf{q}_\kappa) \rangle_{\Omega_\iota, \Omega}$$

$$= -\sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \left[\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right].$$

The transfer of energy from a commom curve to an interface is simplified analogously to the case of the transfer of energy from a phase to an interface, where integration is performed over the lower dimensional entity and the transfer terms are written with respect to the higher dimensional entity, resulting in the short-hand expression

(A.46) $\quad - \displaystyle\sum_{\kappa \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{C}})} \langle E_{T\iota} \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) + \mathbf{n}_\iota \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota) \rangle_{\Omega_\kappa, \Omega} =$

$$- \sum_{\kappa \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{C}})} \left[\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right].$$

Collecting results, Eq. (A.39) can be written in final form for the conservation of energy in an interface as

$$
\begin{aligned}
\text{(A.47)} \quad \mathcal{E}^\iota = {} & \frac{\mathrm{D}^{\bar\iota} E_T^{\bar{\bar\iota}}}{\mathrm{D}t} + E_T^{\bar{\bar\iota}} \mathbf{I}{:}\mathbf{d}^{\bar{\bar\iota}} - \nabla\cdot\left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}}\cdot\mathbf{v}^{\bar\iota} + \epsilon^\iota \mathbf{q}^{\bar\iota} \right) - \epsilon^\iota h^{\overline{\overline{\iota\iota}}} \\
& - \left\langle \rho_\iota \frac{\partial' \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \left(\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) = 0 \qquad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}.
\end{aligned}
$$

The continuum mechanical principle of Galilean invariance can be applied to the macroscale conservation of energy equations for an interface to derive the conservation of momentum and conservation of mass equations for the interface. The results are

$$
\begin{aligned}
\text{(A.48)} \quad \boldsymbol{\mathcal{P}}^\iota = {} & \frac{\mathrm{D}^{\bar\iota}\left(\epsilon^\iota \rho^\iota \mathbf{v}^{\bar\iota} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{v}^{\bar\iota} \mathbf{I}{:}\mathbf{d}^{\bar{\bar\iota}} - \nabla\cdot\left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}} \right) \\
& - \epsilon^\iota \rho^\iota \mathbf{g}^{\bar\iota} - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \left(\overset{\kappa \to \iota}{\mathbf{M}_v} + \overset{\kappa \to \iota}{\mathbf{T}} \right) = 0 \qquad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}},
\end{aligned}
$$

where $\overset{\kappa \to \iota}{\mathbf{M}_v}$ is defined as in Eq. (A.33), $\overset{\kappa \to \iota}{\mathbf{T}}$ is defined in Eq. (A.23), and the general macroscale conservation of mass equation for an interface ι can be written

$$
\text{(A.49)} \qquad \mathcal{M}^\iota = \frac{\mathrm{D}^{\bar\iota}\left(\epsilon^\iota \rho^\iota \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{I}{:}\mathbf{d}^{\bar{\bar\iota}} - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \overset{\kappa \to \iota}{M} = 0 \qquad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}},
$$

where $\overset{\kappa \to \iota}{M}$ is defined in Eq. (A.22).

A.1.3. Conservation Equations for a Common Curve.
The microscale conservation of energy equation for a common curve ι is

$$
\text{(A.50)} \qquad \frac{\partial'' E_{T\iota}}{\partial t} + \nabla''\cdot\left(E_{T\iota} \mathbf{v}_\iota \right) - \nabla''\cdot\left(\mathbf{t}_\iota'' \cdot \mathbf{v}_\iota + \mathbf{q}_\iota'' \right) - h_\iota
$$

$$-\rho_\iota \frac{\partial'' \psi_\iota}{\partial t} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{I}})} E_{T\kappa} \left(\mathbf{v}_\iota - \mathbf{v}_\kappa \right) \cdot \mathbf{n}_\kappa \bigg|_{\Omega_\iota}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{I}})} \mathbf{n}_\kappa \cdot \left(\mathbf{t}_\kappa \cdot \mathbf{v}_\kappa + \mathbf{q}_\kappa \right) \bigg|_{\Omega_\iota} = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{C}}.$$

Integrating Eq. (A.50) over the ι common curve, we have

$$\text{(A.51)} \quad \left\langle \frac{\partial'' E_{T\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} + \left\langle \nabla'' \cdot (E_{T\iota} \mathbf{v}_\iota) \right\rangle_{\Omega_\iota,\Omega} - \left\langle \nabla'' \cdot \left(\mathbf{t}_\iota'' \cdot \mathbf{v}_\iota + \mathbf{q}_\iota'' \right) \right\rangle_{\Omega_\iota,\Omega}$$

$$- \langle h_\iota \rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota \frac{\partial'' \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{I}})} \langle E_{T\kappa} \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{I}})} \langle \mathbf{n}_\kappa \cdot (\mathbf{t}_\kappa \cdot \mathbf{v}_\kappa + \mathbf{q}_\kappa) \rangle_{\Omega_\iota,\Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{C}}.$$

Applying T[1,(3,0),0] to the first term in Eq. (A.51) yields

$$\text{(A.52)} \quad \left\langle \frac{\partial'' E_{T\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \frac{\partial}{\partial t} \langle E_{T\iota} \rangle_{\Omega_\iota,\Omega} + \nabla \cdot \langle (\mathbf{v}_\iota - \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_\iota) E_{T\iota} \rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot \mathbf{v}_\iota E_{T\iota} \right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{Pt}})} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa E_{T\iota} \rangle_{\Omega_\kappa,\Omega}.$$

Applying D[1,(3,0),0] to the first divergence term in Eq. (A.51)

$$\text{(A.53)} \quad \left\langle \nabla'' \cdot (E_{T\iota} \mathbf{v}_\iota) \right\rangle_{\Omega_\iota,\Omega} = \nabla \cdot \langle E_{T\iota} \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_\iota \rangle_{\Omega_\iota,\Omega}$$

$$- \left\langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot E_{T\iota} \mathbf{v}_\iota \right\rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{Pt}})} \langle \mathbf{n}_\iota \cdot E_{T\iota} \mathbf{v}_\iota \rangle_{\Omega_\kappa,\Omega},$$

and similarly for the second divergence term

$$\text{(A.54)} \quad \left\langle \nabla'' \cdot \left(\mathbf{t}_\iota'' \cdot \mathbf{v}_\iota + \mathbf{q}_\iota'' \right) \right\rangle_{\Omega_\iota,\Omega} = \nabla \cdot \left\langle \mathbf{t}_\iota'' \cdot \mathbf{v}_\iota + \mathbf{q}_\iota'' \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{Pt}})} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{t}_\iota'' \cdot \mathbf{v}_\iota + \mathbf{q}_\iota'' \right) \right\rangle_{\Omega_\kappa,\Omega}.$$

Substituting these into Eq. (A.51) and canceling like terms we get

(A.55) $\dfrac{\partial}{\partial t}\langle E_{T\iota}\rangle_{\Omega_\iota,\Omega} + \nabla\cdot\langle E_{T\iota}\mathbf{v}_\iota\rangle_{\Omega_\iota,\Omega} - \nabla\cdot\langle \mathbf{t}_\iota''\cdot\mathbf{v}_\iota + \mathbf{q}_\iota''\rangle_{\Omega_\iota,\Omega}$

$\qquad -\langle h_\iota\rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota\dfrac{\partial''\psi_\iota}{\partial t}\right\rangle_{\Omega_\iota,\Omega} + \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{I}})}\langle \mathbf{n}_\kappa\cdot(\mathbf{v}_\iota-\mathbf{v}_\kappa)\,E_{T\kappa}\rangle_{\Omega_\iota,\Omega}$

$\qquad + \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\langle \mathbf{n}_\iota\cdot(\mathbf{v}_\iota-\mathbf{v}_\kappa)\,E_{T\iota}\rangle_{\Omega_\kappa,\Omega} + \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{I}})}\langle \mathbf{n}_\kappa\cdot(\mathbf{t}_\kappa\cdot\mathbf{v}_\kappa+\mathbf{q}_\kappa)\rangle_{\Omega_\iota,\Omega}$

$\qquad - \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\langle \mathbf{n}_\iota\cdot\mathbf{t}_\iota''\cdot\mathbf{v}_\iota\rangle_{\Omega_\kappa,\Omega} - \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\langle \mathbf{n}_\iota\cdot\mathbf{q}_\iota''\rangle_{\Omega_\kappa,\Omega}.$

Considering Eq. (A.55) term by term to evaluate the averaging operators gives for the time derivative term

(A.56) $\dfrac{\partial}{\partial t}\left\langle E_\iota + \rho_\iota\left(\dfrac{\mathbf{v}_\iota\cdot\mathbf{v}_\iota}{2}+\psi_\iota\right)\right\rangle_{\Omega_\iota,\Omega} = \dfrac{\partial}{\partial t}\left[E^{\bar{\bar{\iota}}} + \epsilon^\iota\rho^\iota\left(\dfrac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2}+K_E^{\bar{\bar{\iota}}}+\psi^{\bar{\iota}}\right)\right].$

Evaluating divergence terms in the same way as for phases and interfaces provides

(A.57) $\nabla\cdot\langle E_{T\iota}\mathbf{v}_\iota\rangle_{\Omega_\iota,\Omega} = \nabla\cdot\left(E_T^{\bar{\bar{\iota}}}\mathbf{v}^{\bar{\iota}}\right) + \nabla\cdot\left\langle (E_\iota+\rho_\iota\psi_\iota)\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}$

$\qquad + \nabla\cdot\left\langle\left(\mathbf{v}^{\bar{\iota}}\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)+\dfrac{\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)}{2}\right)\rho_\iota\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}.$

The second divergence term in Eq. (A.55) may be written as

(A.58) $\nabla\cdot\langle \mathbf{t}_\iota''\cdot\mathbf{v}_\iota + \mathbf{q}_\iota''\rangle_{\Omega_\iota,\Omega} = \nabla\cdot\left\langle \mathbf{t}_\iota''\cdot\mathbf{v}^{\bar{\iota}} + \mathbf{t}_\iota''\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right) + \mathbf{q}_\iota''\right\rangle_{\Omega_\iota,\Omega}.$

Combining Eqs. (A.57) and (A.58) gives

(A.59) $\epsilon^\iota\mathbf{t}^{\bar{\bar{\iota}}}\cdot\mathbf{v}^{\bar{\iota}} + \epsilon^\iota\mathbf{q}^{\bar{\bar{\iota}}} = \left\langle\left[\mathbf{t}_\iota'' - \rho_\iota\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\right]\cdot\mathbf{v}^{\bar{\iota}}\right\rangle_{\Omega_\iota,\Omega}$

$\qquad + \left\langle \mathbf{q}_\iota'' - \left[E_\iota + \rho_\iota\left(\dfrac{\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)}{2}+\psi_\iota\right)\right]\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}$

$\qquad + \left\langle \mathbf{t}_\iota''\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\right\rangle_{\Omega_\iota,\Omega},$

where the first term on the RHS is the macroscale stress tensor for a common curve and the second two terms on the RHS sum to the macroscale heat source vector for a common curve.

Using the exchange term definitions, Eqs. (A.22)–(A.25), and Eq. (A.59), Eq. (A.55) can be written in final form for the conservation of energy of a common curve as

$$
\text{(A.60)} \quad \mathcal{E}^\iota = \frac{\mathrm{D}^{\bar{\iota}} E_T^{\bar{\bar{\iota}}}}{\mathrm{D}t} + E_T^{\bar{\bar{\iota}}} \mathbf{l} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}} - \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} + \epsilon^\iota \mathbf{q}^{\bar{\iota}} \right) - \epsilon^\iota h^{\overline{\overline{\iota\iota}}}
$$
$$
- \left\langle \rho_\iota \frac{\partial'' \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) = 0 \qquad \text{for } \iota \in \mathcal{I}_C.
$$

The continuum mechanical principle of Galilean invariance can be applied to the macroscale conservation of energy equations for an interface to derive the conservation of momentum and conservation of mass equations for the interface. The results are

$$
\text{(A.61)} \quad \boldsymbol{\mathcal{P}}^\iota = \frac{\mathrm{D}^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\bar{\iota}} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{v}^{\bar{\iota}} \mathbf{l} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}} - \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \right)
$$
$$
- \epsilon^\iota \rho^\iota \mathbf{g}^{\bar{\iota}} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\overset{\kappa \to \iota}{\mathbf{M}_v} + \overset{\kappa \to \iota}{\mathbf{T}} \right) = 0 \qquad \text{for } \iota \in \mathcal{I}_I,
$$

where $\overset{\kappa \to \iota}{\mathbf{M}_v}$ is defined as in Eq. (A.33), $\overset{\kappa \to \iota}{\mathbf{T}}$ is defined in Eq. (A.23), and the general macroscale conservation of mass equation for an interface ι can be written

$$
\text{(A.62)} \qquad \mathcal{M}^\iota = \frac{\mathrm{D}^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{l} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \overset{\kappa \to \iota}{M} = 0 \qquad \text{for } \iota \in \mathcal{I}_I,
$$

where $\overset{\kappa \to \iota}{M}$ is defined in Eq. (A.22).

A.1.4. Conservation Equations for General Entities. Looking at the final form of the energy, momentum, and mass equations for phases, interfaces, and common curves, the forms are very similar. In fact, if we state that when $\iota \in \mathcal{I}_I$

$$
\text{(A.63)} \qquad\qquad\qquad \frac{\partial \psi_\iota}{\partial t} = \frac{\partial' \psi_\iota}{\partial t},
$$

and when $\iota \in \mathcal{I}_C$

$$(\text{A.64}) \qquad \frac{\partial \psi_\iota}{\partial t} = \frac{\partial'' \psi_\iota}{\partial t},$$

then we can write a generalized form for all entities $\iota \in \mathcal{I}$. Thus the conservation of energy equation can be written as

$$
(\text{A.65}) \quad \mathcal{E}^\iota = \frac{\mathrm{D}^{\bar\iota} \left[E^{\bar{\bar\iota}} + \epsilon^\iota \rho^\iota \left(\frac{1}{2} \mathbf{v}^{\bar\iota} \cdot \mathbf{v}^{\bar\iota} + K_E^{\bar{\bar\iota}} + \psi^{\bar\iota} \right) \right]}{\mathrm{D}t}
$$

$$
+ \left[E^{\bar{\bar\iota}} + \epsilon^\iota \rho^\iota \left(\frac{1}{2} \mathbf{v}^{\bar\iota} \cdot \mathbf{v}^{\bar\iota} + K_E^{\bar{\bar\iota}} + \psi^{\bar\iota} \right) \right] \mathbf{I}{:}\mathbf{d}^{\bar{\bar\iota}} - \nabla{\cdot} \left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}} \cdot \mathbf{v}^{\bar\iota} + \epsilon^\iota \mathbf{q}^{\bar{\bar\iota}} \right)
$$

$$
- \epsilon^\iota h^{\bar{\bar\iota}} - \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\overset{\kappa \to \iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) = 0 \quad \text{for } \iota \in \mathcal{I},
$$

the conservation of momentum equation is

$$
(\text{A.66}) \quad \boldsymbol{\mathcal{P}}^\iota = \frac{\mathrm{D}^{\bar\iota} \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\bar\iota} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{v}^{\bar\iota} \mathbf{I}{:}\mathbf{d}^{\bar{\bar\iota}} - \nabla{\cdot} \left(\epsilon^\iota \mathbf{t}^{\bar{\bar\iota}} \right) - \epsilon^\iota \rho^\iota \mathbf{g}^{\bar\iota}
$$

$$
- \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\overset{\kappa \to \iota}{\mathbf{M}_v} + \overset{\kappa \to \iota}{\mathbf{T}} \right) = 0 \quad \text{for } \iota \in \mathcal{I},
$$

and the conservation of mass equation is

$$
(\text{A.67}) \qquad \mathcal{M}^\iota = \frac{\mathrm{D}^{\bar\iota} \left(\epsilon^\iota \rho^\iota \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \mathbf{I}{:}\mathbf{d}^{\bar{\bar\iota}} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \overset{\kappa \to \iota}{M} = 0 \quad \text{for } \iota \in \mathcal{I}.
$$

A.2. Entropy Balance Equations

The microscale entropy balance equations for phases, interfaces, and common curves can be averaged to the macroscale and summed over all entities to represent the entropy of the entire system of interest. According to the Second Law of Thermodynamics, we know that the entropy of the system must be greater than or equal to zero. We can use this information along with the previously developed conservation equations and the thermodynamic relationships to constrain the entropy inequality. The resulting inequality

can be used to guide closure relationships. To accomplish this goal we must formulate the needed entropy equations.

A.2.1. Entropy Balance Equations for Phases. The microscale balance of entropy equation for phase entity ι is

$$(A.68) \qquad \qquad \mathcal{S}_\iota = \frac{D_\iota \eta_\iota}{Dt} + \eta_\iota \mathbf{I}{:}\mathbf{d}_\iota - \nabla{\cdot}\boldsymbol{\varphi}_\iota - b_\iota = \Lambda_\iota,$$

where η_ι is the entropy density of entity ι, $\boldsymbol{\varphi}_\iota$ is the non-advective entropy density flux vector, b_ι is the entropy source density, and Λ_ι is the entropy production rate density. Applying the averaging operator Eq. (A.1) and transport and divergence theorems, T[3,(3,0),0] and D[3,(3,0),0], to Eq. (A.68) gives

$$(A.69) \quad \mathcal{S}^\iota = \frac{D^{\bar{\iota}}\eta^{\bar{\bar{\iota}}}}{Dt} + \eta^{\bar{\bar{\iota}}}\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}} - \nabla{\cdot}\left(\epsilon^\iota \boldsymbol{\varphi}^{\bar{\bar{\iota}}}\right) - \epsilon^\iota b^\iota - \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\overset{\kappa \to \iota}{M_\eta} + \overset{\kappa \to \iota}{\overset{*}{\Phi}}\right) = \Lambda^{\bar{\bar{\iota}}} \quad \text{for } \iota \in \mathcal{I}_{\mathrm{P}},$$

where

$$(A.70) \qquad \eta^{\bar{\bar{\iota}}} = \langle \eta_\iota \rangle_{\Omega_\iota,\Omega}, \qquad \epsilon^\iota b^\iota = \langle b_\iota \rangle_{\Omega_\iota,\Omega}, \qquad \Lambda^{\bar{\bar{\iota}}} = \langle \Lambda_\iota \rangle_{\Omega_\iota,\Omega},$$

$$(A.71) \qquad \qquad \epsilon^\iota \boldsymbol{\varphi}^{\bar{\bar{\iota}}} = \left\langle \boldsymbol{\varphi}_\iota - \eta_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}\right) \right\rangle_{\Omega_\iota,\Omega},$$

$$(A.72) \qquad \overset{\kappa \to \iota}{M_\eta} = \begin{cases} \left(\dfrac{\eta^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota}\right) \overset{\kappa \to \iota}{M} & \text{for } \dim \Omega_\iota > \dim \Omega_\kappa, \\[2ex] \left(\dfrac{\eta^{\bar{\bar{\kappa}}}}{\epsilon^\kappa \rho^\kappa}\right) \overset{\kappa \to \iota}{M} & \text{for } \dim \Omega_\kappa > \dim \Omega_\iota, \end{cases}$$

$$(A.73) \quad \overset{\kappa \to \iota}{\overset{*}{\Phi}} = \langle \mathbf{n}_\iota \cdot \boldsymbol{\varphi}_\iota \rangle_{\Omega_\kappa,\Omega} + \left\langle \rho_\iota \left(\frac{\eta_\iota}{\rho_\iota} - \frac{\eta^{\bar{\bar{\iota}}}}{\epsilon^\iota \rho^\iota}\right) \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \right\rangle_{\Omega_\kappa,\Omega}$$

$$\text{for } \dim \Omega_\iota > \dim \Omega_\kappa,$$

and

(A.74) $\quad \overset{\kappa \to \iota}{\Phi} = -\langle \mathbf{n}_\kappa \cdot \boldsymbol{\varphi}_\kappa \rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\kappa \left(\dfrac{\eta_\kappa}{\rho_\kappa} - \dfrac{\eta^{\overline{\overline{\kappa}}}}{\epsilon^\kappa \rho^\kappa} \right) \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \right\rangle_{\Omega_\iota,\Omega}$

$\qquad$ for $\dim \Omega_\kappa > \dim \Omega_\iota$,

where the quantity $\overset{\kappa \to \iota}{\Phi}$ represents the transfer of entropy from the κ entity to the ι entity due to processes other than phase change per unit volume per unit time.

A.2.2. Entropy Balance Equations for an Interfaces. The microscale balance of entropy for interface entity ι is

(A.75) $\quad \mathcal{S}_\iota = \dfrac{\partial' \eta_\iota}{\partial t} + \nabla' \cdot (\eta_\iota \mathbf{v}_\iota) - \nabla' \cdot \boldsymbol{\varphi}'_\iota - b_\iota$

$\qquad - \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_P)} \left. (-\boldsymbol{\varphi}_\kappa + \eta_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\iota)) \cdot \mathbf{n}_\kappa \right|_{\Omega_\iota} = \Lambda_\iota \quad \text{for } \iota \in \mathfrak{I}_I.$

Integrating Eq. (A.75) over the interface surface Ω_ι and applying T[2,(3,0),0] and D[2,(3,0),0] yields

(A.76) $\quad \dfrac{\partial}{\partial t} \langle \eta_\iota \rangle_{\Omega_\iota,\Omega} + \nabla \cdot \langle \eta_\iota \mathbf{v}_\iota \rangle_{\Omega_\iota,\Omega} - \nabla \cdot \langle \boldsymbol{\varphi}'_\iota \rangle_{\Omega_\iota,\Omega} - \langle b_\iota \rangle_{\Omega_\iota,\Omega}$

$\qquad - \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_P)} \langle \mathbf{n}_\kappa \cdot (-\boldsymbol{\varphi}_\kappa + \eta_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\iota)) \rangle_{\Omega_\iota,\Omega}$

$\qquad + \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_C)} \langle \mathbf{n}_\iota \cdot [-\boldsymbol{\varphi}_\iota + \eta_\iota (\mathbf{v}_\iota - \mathbf{v}_\kappa)] \rangle_{\Omega_\kappa,\Omega} = \langle \Lambda_\iota \rangle_{\Omega_\iota,\Omega}.$

Setting $\mathbf{v}_\iota = \mathbf{v}^{\overline{\iota}} + \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right)$ in the second term and averaging to the macroscale we get

(A.77) $\quad \dfrac{\partial \eta^{\overline{\overline{\iota}}}}{\partial t} + \nabla \cdot \left(\eta^{\overline{\overline{\iota}}} \mathbf{v}^{\overline{\iota}} \right) - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} \right) - \epsilon^\iota b^\iota$

$\qquad - \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_P)} \langle \mathbf{n}_\kappa \cdot (-\boldsymbol{\varphi}_\kappa + \eta_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\iota)) \rangle_{\Omega_\iota,\Omega}$

$$+ \sum_{\kappa \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{C}})} \langle \mathbf{n}_\iota \cdot [-\boldsymbol{\varphi}_\iota + \eta_\iota (\mathbf{v}_\iota - \mathbf{v}_\kappa)] \rangle_{\Omega_\kappa, \Omega} = \Lambda^{\overline{\overline{\iota\iota}}} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}},$$

where

$$(\text{A.78}) \qquad \qquad \epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} = \left\langle \boldsymbol{\varphi}'_\iota - \eta_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega}.$$

For the connected entities we can add in and subtract out the terms

$$(\text{A.79}) \qquad \qquad \frac{\eta^{\overline{\overline{\kappa}}}}{\epsilon^\kappa \rho^\kappa} \langle \rho_\kappa \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_\kappa) \rangle_{\Omega_\iota, \Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}, \kappa \in \mathfrak{I}_{\mathrm{P}}$$

and

$$(\text{A.80}) \qquad \qquad \frac{\eta^{\overline{\overline{\iota}}}}{\epsilon^\iota \rho^\iota} \langle \rho_\iota \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_\iota) \rangle_{\Omega_\kappa, \Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}, \kappa \in \mathfrak{I}_{\mathrm{C}}$$

such that

$$(\text{A.81}) \quad - \sum_{\kappa \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{P}})} \langle \mathbf{n}_\kappa \cdot (-\boldsymbol{\varphi}_\kappa + \eta_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\iota)) \rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{C}})} \langle \mathbf{n}_\iota \cdot [-\boldsymbol{\varphi}_\iota + \eta_\iota (\mathbf{v}_\iota - \mathbf{v}_\kappa)] \rangle_{\Omega_\kappa, \Omega}$$

$$= - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \left(\overset{\kappa \to \iota}{M_\eta} + \overset{\kappa \to \iota}{\Phi} \right),$$

where use is made of the definitions in Eqs. (A.72)–(A.74).

Thus the macroscopic entropy equation for entity ι can be written

$$(\text{A.82}) \qquad \mathcal{S}^\iota = \frac{\partial \eta^{\overline{\iota}}}{\partial t} + \nabla \cdot \left(\eta^{\overline{\iota}} \mathbf{v}^{\overline{\iota}} \right) - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} \right) - \epsilon^\iota b^\iota - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \left(\overset{\kappa \to \iota}{M_\eta} + \overset{\kappa \to \iota}{\Phi} \right) = \Lambda^{\overline{\overline{\iota}}},$$

which putting into material derivative form gives us

$$(\text{A.83}) \quad \mathcal{S}^\iota = \frac{\mathrm{D}^{\overline{\iota}} \eta^{\overline{\iota}}}{\mathrm{D} t} + \eta^{\overline{\iota}} \mathbf{I} : \mathbf{d}^{\overline{\iota}} - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} \right) - \epsilon^\iota b^\iota - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\iota}} \left(\overset{\kappa \to \iota}{M_\eta} + \overset{\kappa \to \iota}{\Phi} \right) = \Lambda^{\overline{\overline{\iota}}} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}},$$

where $\overset{\kappa \to \iota}{M_\eta}$ and $\overset{\kappa \to \iota}{\Phi}$ are defined in Eqs. (A.72)–(A.74).

A.2.3. Entropy Balance Equations for Common Curves. The same process can be applied to the microscale entropy equation for a common curve. The microscale balance of entropy equation for common curve ι can be written as

$$(A.84) \quad \mathcal{S}_\iota = \frac{\partial'' \eta_\iota}{\partial t} + \nabla'' \cdot (\eta_\iota \mathbf{v}_\iota) - \nabla'' \cdot \boldsymbol{\varphi}_\iota'' - b_\iota - \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_I)} \mathbf{n}_\kappa \cdot [-\boldsymbol{\varphi}_\kappa + \eta_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\iota)]$$

$$= \Lambda_\iota \qquad \text{for } \iota \in \mathcal{I}_C.$$

Integrating Eq. (A.84) over the ι common curve and applying Theorems D[1,(3,0),0] and T[1,(3,0),0] yields

$$(A.85) \quad \frac{\partial}{\partial t} \langle \eta_\iota \rangle_{\Omega_\iota, \Omega} + \nabla \cdot \langle \eta_\iota \mathbf{v}_\iota \rangle_{\Omega_\iota, \Omega} - \nabla \cdot \langle \boldsymbol{\varphi}_\iota'' \rangle_{\Omega_\iota, \Omega} - \langle b_\iota \rangle_{\Omega_\iota, \Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_I)} \langle \mathbf{n}_\kappa \cdot [(\mathbf{v}_\kappa - \mathbf{v}_\iota) \eta_\kappa - \boldsymbol{\varphi}_\kappa] \rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_{Pt})} \langle \mathbf{n}_\iota \cdot [(\mathbf{v}_\iota - \mathbf{v}_\kappa) \eta_\iota - \boldsymbol{\varphi}_\iota] \rangle_{\Omega_\kappa, \Omega} = \langle \Lambda_\iota \rangle_{\Omega_\iota, \Omega}.$$

Setting $\mathbf{v}_\iota = \mathbf{v}^{\overline{\iota}} + \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right)$ in the second term, averaging to the macroscale, adding in and subtracting out terms for the connected entity summations and defining

$$(A.86) \qquad \qquad \epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} = \left\langle \boldsymbol{\varphi}_\iota'' - \eta_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right) \right\rangle_{\Omega_\iota, \Omega},$$

the macroscopic entropy equation for entity ι can be written

$$(A.87) \quad \mathcal{S}^\iota = \frac{\partial \eta^{\overline{\overline{\iota}}}}{\partial t} + \nabla \cdot \left(\eta^{\overline{\overline{\iota}}} \mathbf{v}^{\overline{\iota}} \right) - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} \right) - \epsilon^\iota b^\iota - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\overset{\kappa \to \iota}{M_\eta} + \overset{\kappa \to \iota}{\Phi} \right) = \Lambda^{\overline{\overline{\iota}}} \quad \text{for } \iota \in \mathcal{I}_C,$$

which putting into material derivative form gives us

$$(A.88)$$

$$\mathcal{S}^\iota = \frac{D^\iota \eta^{\overline{\overline{\iota}}}}{Dt} + \eta^{\overline{\overline{\iota}}} \mathbf{I} : \mathbf{d}^{\overline{\overline{\iota}}} - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{\iota}}} \right) - \epsilon^\iota b^\iota - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left(\overset{\kappa \to \iota}{M_\eta} + \overset{\kappa \to \iota}{\Phi} \right) = \Lambda^{\overline{\overline{\iota}}} \quad \text{for } \iota \in \mathcal{I}_C.$$

A.2.4. System Entropy Balance Equation. Noting that the final form of the entropy balance equations is the same for phases, interfaces, and common curves, we can write

$$(A.89) \quad \mathcal{S}^\iota = \frac{D^{\bar\iota}\eta^{\bar\iota}}{Dt} + \eta^{\bar\iota}\mathbf{I}:\mathbf{d}^{\bar{\bar\iota}} - \nabla\cdot\left(\epsilon^\iota\boldsymbol{\varphi}^{\bar\iota}\right) - \epsilon^\iota b^\iota - \sum_{\kappa\in\mathcal{I}_{c\iota}} \left(\overset{\kappa\to\iota}{M_\eta} + \overset{\kappa\to\iota}{\Phi}\right) = \Lambda^{\bar\iota} \quad \text{for } \iota\in\mathcal{I}.$$

Then the sum over all entities produces the entropy inequality of the entire system, which by the Second Law of Thermodynamics must be greater than or equal to zero. Thus we have

$$(A.90) \quad \sum_{\iota\in\mathcal{I}} \mathcal{S}^\iota = \sum_{\iota\in\mathcal{I}} \left(\frac{D^{\bar\iota}\eta^{\bar\iota}}{Dt} + \eta^{\bar\iota}\mathbf{I}:\mathbf{d}^{\bar\iota} - \nabla\cdot\left(\epsilon^\iota\boldsymbol{\varphi}^{\bar\iota}\right) - \epsilon^\iota b^\iota\right) = \Lambda \geq 0 \quad \text{for } \iota\in\mathcal{I}.$$

A.3. Thermodynamics

Thermodynamic manipulations for phases and the interface are presented in the main text of the paper; we present the details for the common curve here. A similar process to that used to simplify the interface thermodynamics can be applied to the case of common curves. At the microscale, it is necessary to restrict the material derivative to the common curve, which is accomplished using

$$(A.91) \qquad \frac{D''^{\bar\iota}}{Dt} = \frac{\partial''}{\partial t} + \mathbf{v}^{\bar\iota}\cdot\nabla'',$$

and

$$(A.92) \qquad \frac{D''^{\bar\iota}}{Dt} = \frac{D''^{\bar s}}{Dt} + \mathbf{v}^{\bar\iota,\bar s}\cdot\nabla'',$$

where

$$(A.93) \qquad \frac{\partial''}{\partial t} = \frac{\partial}{\partial t} + \mathbf{v}_\iota\cdot(\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota)\cdot\nabla$$

$$(A.94) \qquad \nabla'' = \mathbf{l}_\iota\mathbf{l}_\iota\cdot\nabla$$

$\iota \in \mathcal{I}_C$, and $\mathbf{n}_\iota$ is a vector tangent to the common curve. Eq. (2.47) can be written in terms of material derivatives restricted to the common curve and referenced to the macroscale velocity of the solid phase giving

$$(A.95) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{D''^{\overline{s}}\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)}{Dt} + \rho_\iota \frac{D''^{\overline{s}}\left(\mu_\iota - \mu^{\overline{\iota}}\right)}{Dt} - \frac{D''^{\overline{s}}\left(\gamma_\iota - \gamma^\iota\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left[\eta_\iota \nabla''\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right) + \rho_\iota \nabla''\left(\mu_\iota - \mu^{\overline{\iota}}\right) - \nabla''\left(\gamma_\iota - \gamma^\iota\right) \right] \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla\theta^{\overline{\overline{\iota}}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota\right)\eta_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla\mu^{\overline{\iota}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota\right)\rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \nabla\gamma^\iota \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota\right) \right\rangle_{\Omega_\iota,\Omega} + \gamma^\iota \frac{D^{\overline{s}}\epsilon^\iota}{Dt} + \gamma^\iota \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \nabla\epsilon^\iota.$$

The microscale Gibbs-Duhem equation for common curves can be used to deduce

$$(A.96) \qquad \left\langle \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left(\eta_\iota\nabla''\theta_\iota + \rho_\iota\nabla''\mu_\iota - \nabla''\gamma_\iota\right) \right\rangle_{\Omega_\iota,\Omega} = 0 \qquad \iota \in \mathcal{I}_C,$$

which may be used to simplify Eq. (A.95) to

$$(A.97) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{D''^{\overline{s}}\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)}{Dt} + \rho_\iota \frac{D''^{\overline{s}}\left(\mu_\iota - \mu^{\overline{\iota}}\right)}{Dt} - \frac{D''^{\overline{s}}\left(\gamma_\iota - \gamma^\iota\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega}$$

$$- \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_\iota\nabla''\theta^{\overline{\overline{\iota}}} + \rho_\iota\nabla''\mu^{\overline{\iota}} - \nabla''\gamma^\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla\theta^{\overline{\overline{\iota}}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota\right)\eta_\iota \right\rangle_{\Omega_\iota,\Omega} - \nabla\mu^{\overline{\iota}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota\right)\rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \nabla\gamma^\iota \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota\right) \right\rangle_{\Omega_\iota,\Omega} + \gamma^\iota \frac{D^{\overline{s}}\epsilon^\iota}{Dt} + \gamma^\iota \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \nabla\epsilon^\iota.$$

Theorem MC[1,(3,0),0] [136] can be applied to write the material derivative of lineal tension term from Eq. (A.97) as

$$(A.98) \quad \left\langle \frac{D''^{\overline{s}}\left(\gamma_\iota - \gamma^\iota\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} = \nabla \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}}\right)\left(\gamma_\iota - \gamma^\iota\right) \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle (\mathbf{l}_\iota \cdot \nabla''\mathbf{l}_\iota) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}}\right)\left(\gamma_\iota - \gamma^\iota\right) \right\rangle_{\Omega_\iota,\Omega} + \left\langle (\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota)\left(\gamma_\iota - \gamma^\iota\right) \right\rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}}.$$

Theorem G[1,(3,0),0]

$$(A.99) \qquad \langle \nabla'' f_\iota \rangle_{\Omega_\iota,\Omega} = \nabla \langle f_\iota \rangle_{\Omega_\iota,\Omega} - \nabla \cdot \langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) f_\iota \rangle_{\Omega_\iota,\Omega} - \langle \mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota f_\iota \rangle_{\Omega_\iota,\Omega},$$

and Theorem T[1,(3,0),0] [82]

$$(A.100) \quad \left\langle \frac{\partial'' f_\iota}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \frac{\partial}{\partial t} \langle f_\iota \rangle_{\Omega_\iota,\Omega} + \nabla \cdot \langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \mathbf{v}_\iota f_\iota \rangle_{\Omega_\iota,\Omega} + \langle \mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota \cdot \mathbf{v}_\iota f_\iota \rangle_{\Omega_\iota,\Omega},$$

can be combined taking $f_\iota = 1$ and multiplying by $\gamma^\iota \mathbf{v}^{\overline{s}}\cdot$ and γ^ι, respectively, to obtain

$$(A.101) \quad \gamma^\iota \frac{\mathrm{D}^{\overline{s}} \epsilon^\iota}{\mathrm{D}t} = -\nabla \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma^\iota \right\rangle_{\Omega_\iota,\Omega} - \langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \gamma^\iota \rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \nabla \gamma^\iota \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\iota,\Omega} - \left\langle \mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma^\iota \right\rangle_{\Omega_\iota,\Omega}.$$

Combining Eqs. (A.97), (A.98), and (A.101) yields

$$(A.102) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}''^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\iota}} \right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}''^{\overline{s}} \left(\mu_\iota - \mu^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} - \langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \gamma_\iota \rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}}$$

$$- \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_\iota \nabla'' \theta^{\overline{\iota}} + \rho_\iota \nabla'' \mu^{\overline{\iota}} - \nabla'' \gamma^\iota \right\rangle_{\Omega_\iota,\Omega} + \nabla \gamma^\iota \cdot \langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \rangle_{\Omega_\iota,\Omega} \cdot \mathbf{v}^{\overline{\iota},\overline{s}}$$

$$+ \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \gamma^\iota \nabla \epsilon^\iota - \nabla \theta^{\overline{\iota}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota \right) \eta_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla \mu^{\overline{\iota}} \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \left(\mathbf{v}^{\overline{\iota}} - \mathbf{v}_\iota \right) \rho_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$- \nabla \cdot \left\langle (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega} - \left\langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota,\Omega}.$$

Eq. (A.94) and the product rule can be used to show

$$(A.103) \quad - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_\iota \nabla'' \theta^{\overline{\iota}} + \rho_\iota \nabla'' \mu^{\overline{\iota}} - \nabla'' \gamma^\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$= - \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \left\langle \eta_\iota (\mathbf{l}_\iota \mathbf{l}_\iota) \cdot \nabla \theta^{\overline{\iota}} + \rho_\iota (\mathbf{l}_\iota \mathbf{l}_\iota) \cdot \nabla \mu^{\overline{\iota}} - (\mathbf{l}_\iota \mathbf{l}_\iota) \cdot \nabla \gamma^\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$= - \nabla \theta^{\overline{\iota}} \cdot \left\langle \eta_\iota (\mathbf{l}_\iota \mathbf{l}_\iota) \cdot \mathbf{v}^{\overline{\iota},\overline{s}} \right\rangle_{\Omega_\iota,\Omega} - \nabla \mu^{\overline{\iota}} \cdot \left\langle \rho_\iota (\mathbf{l}_\iota \mathbf{l}_\iota) \cdot \mathbf{v}^{\overline{\iota},\overline{s}} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \nabla \gamma^\iota \cdot \left\langle (\mathbf{l}_\iota \mathbf{l}_\iota) \cdot \mathbf{v}^{\overline{\iota},\overline{s}} \right\rangle_{\Omega_\iota,\Omega}$$

$$= \nabla \theta^{\bar{\bar{\iota}}} \cdot \left\langle \eta_\iota \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \mathbf{v}^{\bar{\iota}, \bar{s}} \right\rangle_{\Omega_\iota, \Omega} + \nabla \mu^{\bar{\iota}} \cdot \left\langle \rho_\iota \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \mathbf{v}^{\bar{\iota}, \bar{s}} \right\rangle_{\Omega_\iota, \Omega}$$

$$- \nabla \gamma^\iota \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \mathbf{v}^{\bar{\iota}, \bar{s}} \right\rangle_{\Omega_\iota, \Omega} - \mathbf{v}^{\bar{\iota}, \bar{s}} \cdot \eta^{\bar{\iota}} \nabla \theta^{\bar{\bar{\iota}}} - \mathbf{v}^{\bar{\iota}, \bar{s}} \cdot \epsilon^\iota \rho^\iota \nabla \mu^{\bar{\iota}}$$

$$+ \epsilon^\iota \nabla \gamma^\iota \cdot \mathbf{v}^{\bar{\iota}, \bar{s}}.$$

Eq. (A.103) can be combined with Eq. (A.102) to write a final form of the residual term for common curve thermodynamics

$$(A.104) \quad \mathcal{T}_r^\iota = \left\langle \eta_\iota \frac{\mathrm{D}''^{\bar{s}} \left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right)}{\mathrm{D}t} + \rho_\iota \frac{\mathrm{D}''^{\bar{s}} \left(\mu_\iota - \mu^{\bar{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega}$$

$$- \mathbf{v}^{\bar{\iota}, \bar{s}} \cdot \left[\eta^{\bar{\iota}} \nabla \theta^{\bar{\bar{\iota}}} + \epsilon^\iota \rho^\iota \nabla \mu^{\bar{\iota}} - \nabla \left(\epsilon^\iota \gamma^\iota \right) \right] - \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega} : \mathbf{d}^{\bar{\bar{s}}}$$

$$+ \nabla \theta^{\bar{\bar{\iota}}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}} \right) \eta_\iota \right\rangle_{\Omega_\iota, \Omega} + \nabla \mu^{\bar{\iota}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}} \right) \rho_\iota \right\rangle_{\Omega_\iota, \Omega}$$

$$- \nabla \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega} - \left\langle \left(\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega}.$$

A.4. Constrained Entropy Inequality

The AEI given by Eq. (2.34) provides a connection between the system EI and the conservation equations using the thermodynamic relations. The Lagrange multipliers, Eq. (2.50), are choosen in a way to eliminate some of material derivatives to arrive at a final form of the CEI, which will be used to guide the formulation of the closed models. Once these material derivatives are removed, the resultant expression is referenced to a common frame of reference to satisfy the continuum mechanical axiom of objectivity and the resultant terms are placed into the force-flux pairs according to the entropy production postulate.

Substituting Eq. (2.50) into Eq. (2.34) and simplifying by cancelling out material derivatives gives Eq. (2.51). Expanding the shorthand expressions for $\mathcal{S}_r^\iota, \mathcal{E}_r^\iota, \mathcal{P}_r^\iota, \mathcal{M}_r^{i\iota},$ and $\mathcal{T}_r^\iota$ and canceling terms gives

$$(\text{A.105}) \quad \sum_{\iota\in\mathcal{J}} \left[\eta^{\overline{\overline{\iota}}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \nabla{\cdot}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{\iota}}}\right) - \epsilon^{\iota}b^{\iota} \right]$$

$$+\sum_{\iota\in\mathcal{J}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\mu^{\overline{\iota}}\epsilon^{\iota}\rho^{\iota}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{\iota}} + \psi^{\overline{\iota}} - \frac{\left(\mathbf{v}^{\overline{\iota}}{\cdot}\mathbf{v}^{\overline{\iota}}\right)}{2} \right) \sum_{\kappa\in\mathcal{J}_{c\iota}} \overset{\kappa\to\iota}{M} \right]$$

$$-\sum_{\iota\in\mathcal{J}} \frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}{\cdot}\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}} + \sum_{\kappa\in\mathcal{J}_{c\iota}} \left(\overset{\kappa\to\iota}{\mathbf{M}_v} + \overset{\kappa\to\iota}{\mathbf{T}} \right) \right]$$

$$-\sum_{\iota\in\mathcal{J}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\epsilon^{\iota}\rho^{\iota}\frac{\mathrm{D}^{\overline{s}}\left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}}\right)}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\nabla\left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}}\right) \right]$$

$$-\sum_{\iota\in\mathcal{J}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[E^{\overline{\overline{\iota}}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \epsilon^{\iota}\mathbf{t}^{\overline{\overline{\iota}}}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \theta^{\overline{\iota}}\nabla{\cdot}\left(\frac{\epsilon^{\iota}\mathbf{q}^{\overline{\overline{\iota}}}}{\theta^{\overline{\overline{\iota}}}}\right) - \theta^{\overline{\iota}}\frac{\epsilon^{\iota}\mathbf{q}^{\overline{\overline{\iota}}}}{\left(\theta^{\overline{\overline{\iota}}}\right)^2}{\cdot}\nabla\theta^{\overline{\iota}} \right]$$

$$+\sum_{\iota\in\mathcal{J}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\epsilon^{\iota}h^{\overline{\overline{\iota}}} + \left\langle \rho_{\iota}\frac{\partial\psi_{\iota}}{\partial t} \right\rangle_{\Omega_{\iota},\Omega} + \sum_{\kappa\in\mathcal{J}_{c\iota}} \left(\overset{\kappa\to\iota}{M_E} + \overset{\kappa\to\iota}{T_v} + \overset{\kappa\to\iota}{Q} \right) \right]$$

$$+\sum_{\iota\in\mathcal{J}_f} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \eta_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)}{\mathrm{D}t} + \rho_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\iota} - \mu^{\overline{\iota}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_f} \frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}{\cdot}\left\{ \left[-\eta^{\overline{\overline{\iota}}}\nabla\theta^{\overline{\iota}} - \epsilon^{\iota}\rho^{\iota}\nabla\mu^{\overline{\iota}} + \nabla\left(\epsilon^{\iota}p^{\iota}\right) \right] + \sum_{\kappa\in\mathcal{J}_{c\iota}} \left\langle p_{\iota}\left(\mathbf{v}_{\kappa} - \mathbf{v}^{\overline{s}}\right){\cdot}\mathbf{n}_{\iota} \right\rangle_{\Omega_{\kappa},\Omega} \right\}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \eta_s\frac{\mathrm{D}^{\overline{s}}\left(\theta_s - \theta^{\overline{\overline{s}}}\right)}{\mathrm{D}t} + \rho_s\frac{\mathrm{D}^{\overline{s}}\left(\mu_s - \mu^{\overline{s}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\iota\in\mathcal{J}_{cs}} \left\langle \left(\frac{\mathbf{C}_s}{j_s}{:}\boldsymbol{\sigma}_s\right)\left(\mathbf{v}_{\iota} - \mathbf{v}_s\right){\cdot}\mathbf{n}_s \right\rangle_{\Omega_{\iota},\Omega} - \frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{n}_s\mathbf{n}_s{\cdot}\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{I}'{\cdot}\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{ss},\Omega} + \frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \left(\nabla{\cdot}\mathbf{t}_s - \nabla\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right){\cdot}\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_s,\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\epsilon^s\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\frac{\mathbf{C}^s}{j^s}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{t}_s \right\rangle_{\Omega_s,\Omega}{:}\mathbf{d}^{\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla{\cdot}\left\langle \left(\mathbf{t}_s - \boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right){\cdot}\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_s,\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_I} \frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle \eta_{\iota}\frac{\mathrm{D}'^{\overline{s}}\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)}{\mathrm{D}t} + \rho_{\iota}\frac{\mathrm{D}'^{\overline{s}}\left(\mu_{\iota} - \mu^{\overline{\iota}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega}$$

$$
-\sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}} \cdot \left[\eta^{\overline{\overline{\iota}}} \nabla \theta^{\overline{\overline{\iota}}} + \epsilon^{\iota} \rho^{\iota} \nabla \mu^{\overline{\iota}} + \nabla \left(\epsilon^{\iota} \gamma^{\iota} \right) \right]
$$

$$
+\sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\nabla \theta^{\overline{\overline{\iota}}} \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \eta_{\iota} \right\rangle_{\Omega_{\iota},\Omega} + \nabla \mu^{\overline{\iota}} \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \rho_{\iota} \right\rangle_{\Omega_{\iota},\Omega} \right]
$$

$$
+\sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\nabla \cdot \left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{\iota},\Omega} - \left\langle \left(\nabla' \cdot \mathbf{n}_{\kappa} \right) \mathbf{n}_{\kappa} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{\iota},\Omega} \right]
$$

$$
+\sum_{\iota \in \mathfrak{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\left\langle \mathbf{n}_{\kappa} \mathbf{n}_{\kappa} \cdot \gamma_{\iota} \right\rangle_{\Omega_{\iota},\Omega} : \mathbf{d}^{\overline{\overline{s}}} - \left\langle \mathbf{n}_{\iota} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{wns},\Omega} \right]
$$

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \eta_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\theta_{wns} - \theta^{\overline{\overline{wns}}} \right)}{\mathrm{D}t} + \rho_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\mu_{wns} - \mu^{\overline{wns}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns},\Omega}
$$

$$
-\frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \left(\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns} \right) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega} : \mathbf{d}^{\overline{\overline{s}}}
$$

$$
-\frac{\mathbf{v}^{\overline{wns},\overline{s}}}{\theta^{\overline{\overline{wns}}}} \cdot \left(\eta^{\overline{\overline{wns}}} \nabla \theta^{\overline{\overline{wns}}} + \epsilon^{wns} \rho^{wns} \nabla \mu^{\overline{wns}} - \epsilon^{wns} \gamma^{wns} \right)
$$

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}} \nabla \theta^{\overline{\overline{wns}}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns} \right) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \eta_{wns} \right\rangle_{\Omega_{wns},\Omega}
$$

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}} \nabla \mu^{\overline{wns}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns} \right) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \rho_{wns} \right\rangle_{\Omega_{wns},\Omega}
$$

$$
-\frac{1}{\theta^{\overline{\overline{wns}}}} \nabla \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns} \right) \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{\iota} \right\rangle_{\Omega_{wns},\Omega}
$$

$$
-\frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \left(\mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} \right) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega} = \Lambda \geq 0
$$

where $\mathbf{n}_{\kappa}$ is the outward unit normal vector to phase κ, where $\kappa \in \left(\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{P}} \right)$ when $\iota \in \mathfrak{I}_{\mathrm{I}}$.

Further extensive but routine manipulations of Eq. (A.105) are required to arrive at the final form of the CEI, including applying the product rule, algebraic rearrangements, and regrouping the terms in the equation into force-flux pairs in order to recover equilibrium conditions. The details of these manipulations follow.

There exists terms arising from the product of a velocity in non-objective form with a term involving the gravitational acceleration body force $\mathbf{g}^{\overline{\iota}}$, which can be put into the

objective form for phase entities

$$(A.106) \quad -\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \cdot \mathbf{g}^{\overline{\iota}} + \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} = -\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{g}^{\overline{\iota}} + \left\langle \rho_\iota \frac{\mathrm{D}^{\overline{s}} \psi_\iota}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} \quad \text{for } \iota \in \mathfrak{I}_\mathrm{P},$$

for interface entities

$$(A.107) \quad \begin{aligned} &- \epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \cdot \mathbf{g}^{\overline{\iota}} + \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} = -\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{g}^{\overline{\iota}} + \left\langle \rho_\iota \frac{\mathrm{D}'^{\overline{s}} \psi_\iota}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} \\ &\quad + \left\langle \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_\kappa \mathbf{n}_\kappa \cdot \mathbf{g}_\iota \right\rangle_{\Omega_\iota, \Omega} \quad \text{for } \iota \in \mathfrak{I}_\mathrm{I}, \end{aligned}$$

and for common curves

$$(A.108) \quad \begin{aligned} &- \epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \cdot \mathbf{g}^{\overline{\iota}} + \left\langle \rho_\iota \frac{\partial \psi_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} = -\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{g}^{\overline{\iota}} + \left\langle \rho_\iota \frac{\mathrm{D}''^{\overline{s}} \psi_\iota}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega} \\ &\quad + \left\langle \rho_\iota \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \mathbf{g}_\iota \right\rangle_{\Omega_\iota, \Omega} \quad \text{for } \iota \in \mathfrak{I}_\mathrm{C}, \end{aligned}$$

where $\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_\mathrm{P})$ for $\iota \in \mathfrak{I}_\mathrm{I}$,

$$(A.109) \qquad \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} = \frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t} - \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_k \mathbf{n}_k \cdot \nabla \quad \text{and}$$

$$(A.110) \qquad \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} = \frac{\mathrm{D}''^{\overline{s}}}{\mathrm{D}t} - \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{I} - \mathbf{l}_{wns} \mathbf{l}_{wns} \right) \cdot \nabla.$$

The macroscale Euler equations for internal energy for phases, interfaces, and common curves can be used to deduce

$$(A.111) \qquad \epsilon^\iota p^\iota = \eta^{\overline{\overline{\iota}}} \theta^{\overline{\overline{\iota}}} + \mu^{\overline{\iota}} \epsilon^\iota \rho^\iota - E^{\overline{\overline{\iota}}} \quad \text{for } \iota \in \mathfrak{I}_\mathrm{f},$$

$$(A.112) \qquad 0 = \eta^{\overline{\overline{s}}} \theta^{\overline{\overline{s}}} + \mu^{\overline{s}} \epsilon^s \rho^s + \epsilon^s \boldsymbol{\sigma}^{\overline{\overline{s}}} : \frac{\mathbf{C}^s}{j_s} - E^{\overline{\overline{s}}},$$

$$(A.113) \qquad -\epsilon^\iota \gamma^\iota = \eta^{\overline{\overline{\iota}}} \theta^{\overline{\overline{\iota}}} + \mu^{\overline{\iota}} \epsilon^\iota \rho^\iota - E^{\overline{\overline{\iota}}} \quad \text{for } \iota \in \mathfrak{I}_\mathrm{I},$$

and

$$(A.114) \qquad \epsilon^{wns} \gamma^{wns} = \eta^{\overline{\overline{wns}}} \theta^{\overline{\overline{wns}}} + \mu^{\overline{\overline{wns}}} \epsilon^{wns} \rho^{wns} - E^{\overline{\overline{wns}}}.$$

Eqs. (A.106)–(A.114) can be used to write Eq. (A.105) as

$$
\text{(A.115)} \quad -\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \nabla\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\bar{\iota}} - \frac{\epsilon^{\iota}\mathbf{q}^{\bar{\bar{\iota}}}}{\theta^{\bar{\bar{\iota}}}}\right)
$$

$$
-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \left\{ \epsilon^{\iota}b^{\iota} - \frac{1}{\theta^{\bar{\bar{\iota}}}}\left[\epsilon^{\iota}h^{\bar{\bar{\iota}}} + \left\langle \eta_{\iota}\frac{\mathrm{D}^{\bar{s}}\left(\theta_{\iota} - \theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]\right.
$$

$$
\left. -\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle \rho_{\iota}\frac{\mathrm{D}^{\bar{s}}\left(\mu_{\iota} - \mu^{\bar{\iota}} + \psi_{\iota} - \psi^{\bar{\iota}} - K_{E}^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right\}
$$

$$
+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{\epsilon^{\iota}}{\theta^{\bar{\bar{\iota}}}}\left(\mathbf{t}^{\bar{\bar{\iota}}} + p^{\iota}\mathbf{I}\right):\mathbf{d}^{\bar{\bar{\iota}}} - \sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta^{\bar{\bar{\iota}}}}\cdot\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\bar{\iota}} + \epsilon^{\iota}\rho^{\iota}\nabla\left(K_{E}^{\bar{\bar{\iota}}} + \psi^{\bar{\iota}}\right)\right]
$$

$$
-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta^{\bar{\bar{\iota}}}}\cdot\left[\eta^{\bar{\iota}}\nabla\theta^{\bar{\bar{\iota}}} + \epsilon^{\iota}\rho^{\iota}\nabla\mu^{\bar{\iota}} - \nabla\left(\epsilon^{\iota}p^{\iota}\right)\right]
$$

$$
+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \left[\frac{\epsilon^{\iota}\mathbf{q}^{\bar{\bar{\iota}}}}{\left(\theta^{\bar{\bar{\iota}}}\right)^{2}}\cdot\nabla\theta^{\bar{\bar{\iota}}} + \sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}} \frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle p_{\iota}\left(\mathbf{v}_{\kappa} - \mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}\right]
$$

$$
-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{1}{\theta^{\bar{\bar{\iota}}}}\left[K_{E}^{\bar{\bar{\iota}}} + \mu^{\bar{\iota}} + \psi^{\bar{\iota}} - \frac{\left(\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}\right)}{2}\right]\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}} \overset{\kappa\to\iota}{M}
$$

$$
-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{1}{\theta^{\bar{\bar{\iota}}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}} \left[\mathbf{v}^{\bar{\iota}}\cdot\left(\overset{\kappa\to\iota}{\mathbf{M}_{v}} + \overset{\kappa\to\iota}{\mathbf{T}}\right) - \left(\overset{\kappa\to\iota}{M_{E}} + \overset{\kappa\to\iota}{T_{v}} + \overset{\kappa\to\iota}{Q}\right)\right]
$$

$$
-\nabla\cdot\left\{\epsilon^{s}\boldsymbol{\varphi}^{\bar{\bar{s}}} - \frac{1}{\theta^{\bar{\bar{s}}}}\left[\epsilon^{s}\mathbf{q}^{\bar{\bar{s}}} - \left\langle\left(\mathbf{t}_{s} - \boldsymbol{\sigma}_{s}:\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{s},\Omega}\right]\right\}
$$

$$
-\epsilon^{s}b^{s} + \frac{1}{\theta^{\bar{\bar{s}}}}\left[\epsilon^{s}h^{\bar{\bar{s}}} + \left\langle\eta_{s}\frac{\mathrm{D}^{\bar{s}}\left(\theta_{s} - \theta^{\bar{\bar{s}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega}\right]
$$

$$
+\frac{1}{\theta^{\bar{\bar{s}}}}\left\langle\rho_{s}\frac{\mathrm{D}^{\bar{s}}\left(\mu_{s} - \mu^{\bar{s}} + \psi_{s} - \psi^{\bar{s}} - K_{E}^{\bar{\bar{s}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega}
$$

$$
+\frac{\epsilon^{s}}{\theta^{\bar{\bar{s}}}}\left(\mathbf{t}^{\bar{\bar{s}}} - \mathbf{t}^{s}\right):\mathbf{d}^{\bar{\bar{s}}} - \frac{1}{\theta^{\bar{\bar{s}}}}\left[K_{E}^{\bar{\bar{s}}} + \mu^{\bar{s}} + \psi^{\bar{s}} - \frac{\left(\mathbf{v}^{\bar{s}}\cdot\mathbf{v}^{\bar{s}}\right)}{2}\right]\sum_{\kappa\in\mathcal{I}_{\mathrm{c}s}} \overset{\kappa\to s}{M}
$$

168

$$-\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}}\cdot\sum_{\kappa\in\mathcal{I}_{\mathrm{c}s}}\left(\overset{\kappa\to s}{\mathbf{M}_v}+\overset{\kappa\to s}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{c}s}}\left(\overset{\kappa\to s}{M_E}+\overset{\kappa\to s}{T_v}+\overset{\kappa\to s}{Q}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{c}s}}\left\langle\frac{\mathbf{C}_s}{j_s}{:}\boldsymbol{\sigma}_s\left(\mathbf{v}_\kappa-\mathbf{v}_s\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\left(\theta^{\overline{\overline{s}}}\right)^2}\left[\epsilon^s\mathbf{q}^{\overline{\overline{s}}}-\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\cdot\nabla\theta^{\overline{\overline{s}}}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\nabla\cdot\left(\epsilon^\iota\boldsymbol{\varphi}^{\overline{\iota}}-\frac{\epsilon^\iota\mathbf{q}^{\overline{\overline{\iota}}}}{\theta^{\overline{\overline{\iota}}}}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left\{\epsilon^\iota b^\iota-\frac{1}{\theta^{\overline{\iota}}}\left[\epsilon^\iota h^{\overline{\iota}}+\left\langle\eta_\iota\frac{\mathrm{D}'^{\overline{s}}\left(\theta_\iota-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right]\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\rho_\iota\frac{\mathrm{D}'^{\overline{s}}\left(\mu_\iota-\mu^{\overline{\iota}}+\psi_\iota-\psi^{\overline{\iota}}-K_E^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right\}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\epsilon^\iota}{\theta^{\overline{\overline{\iota}}}}\left(\mathbf{t}^{\overline{\overline{\iota}}}-\gamma^\iota\mathbf{I}\right){:}\mathbf{d}^{\overline{\overline{\iota}}}-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left[\epsilon^\iota\rho^\iota\mathbf{g}^{\overline{\iota}}+\epsilon^\iota\rho^\iota\nabla\left(K_E^{\overline{\overline{\iota}}}+\psi^{\overline{\iota}}\right)\right]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left[\eta^{\overline{\overline{\iota}}}\nabla\theta^{\overline{\overline{\iota}}}+\epsilon^\iota\rho^\iota\nabla\mu^{\overline{\iota}}+\nabla\left(\epsilon^\iota\gamma^\iota\right)\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\epsilon^\iota\mathbf{q}^{\overline{\overline{\iota}}}}{\left(\theta^{\overline{\iota}}\right)^2}\cdot\nabla\theta^{\overline{\overline{\iota}}}-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[K_E^{\overline{\overline{\iota}}}+\mu^{\overline{\iota}}+\psi^{\overline{\iota}}-\frac{\left(\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}\right)}{2}\right]\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\overset{\kappa\to\iota}{M}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\left[\mathbf{v}^{\overline{\iota}}\cdot\left(\overset{\kappa\to\iota}{\mathbf{M}_v}+\overset{\kappa\to\iota}{\mathbf{T}}\right)-\left(\overset{\kappa\to\iota}{M_E}+\overset{\kappa\to\iota}{T_v}+\overset{\kappa\to\iota}{Q}\right)\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\rho_\iota\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\mathbf{g}_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left[\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\theta^{\overline{\overline{\iota}}}\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}+\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\mu^{\overline{\iota}}\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\rho_\iota\right\rangle_{\Omega_\iota,\Omega}\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left[\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}-\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\left(\nabla'\cdot\mathbf{n}_\kappa\right)\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left[\frac{1}{\theta^{\bar{\bar{\iota}}}}\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\gamma_\iota\rangle_{\Omega_\iota,\Omega}\mathbf{:d}^{\bar{\bar{s}}}-\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\gamma_\iota\right\rangle_{\Omega_{wns},\Omega}\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla\left(K_E^{\bar{\bar{\iota}}}+\psi^{\bar{\iota}}\right)\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{s}}\right)\rho_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$-\nabla\cdot\left(\epsilon^{wns}\boldsymbol{\varphi}^{\overline{\overline{wns}}}-\frac{\epsilon^{wns}\mathbf{q}^{\overline{\overline{wns}}}}{\theta^{\overline{\overline{wns}}}}\right)$$

$$-\epsilon^{wns}b^{wns}+\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\epsilon^{wns}h^{\overline{\overline{wns}}}+\left\langle\eta_{wns}\frac{\mathrm{D}''^{\bar{s}}\left(\theta_{wns}-\theta^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\rho_{wns}\frac{\mathrm{D}''^{\bar{s}}\left(\mu_{wns}-\mu^{\overline{wns}}+\psi_{wns}-\psi^{\overline{wns}}-K_E^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{t}^{\overline{\overline{wns}}}+\gamma^{wns}\mathbf{I}\right)\mathbf{:d}^{\overline{\overline{wns}}}+\frac{\epsilon^{wns}\mathbf{q}^{\overline{\overline{wns}}}}{\left(\theta^{\overline{\overline{wns}}}\right)^2}\cdot\nabla\theta^{\overline{\overline{wns}}}$$

$$-\frac{\mathbf{v}^{\overline{wns},\bar{s}}}{\theta^{\overline{\overline{wns}}}}\cdot\left[\epsilon^{wns}\rho^{wns}\mathbf{g}^{\overline{wns}}+\epsilon^{wns}\rho^{wns}\nabla\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right]$$

$$-\frac{\mathbf{v}^{\overline{wns},\bar{s}}}{\theta^{\overline{\overline{wns}}}}\cdot\left[\eta^{\overline{\overline{wns}}}\nabla\theta^{\overline{\overline{wns}}}+\epsilon^{wns}\rho^{wns}\nabla\mu^{\overline{wns}}-\nabla\left(\epsilon^{wns}\gamma^{wns}\right)\right]$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left[K_E^{\overline{\overline{wns}}}+\mu^{\overline{wns}}+\psi^{\overline{wns}}-\frac{\left(\mathbf{v}^{\overline{wns}}\cdot\mathbf{v}^{\overline{wns}}\right)}{2}\right]\sum_{\kappa\in\mathcal{I}_{cwns}}\overset{\kappa\to wns}{M}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\sum_{\kappa\in\mathcal{I}_{cwns}}\left[\mathbf{v}^{\overline{wns}}\cdot\left(\overset{\kappa\to wns}{\mathbf{M}_v}+\overset{\kappa\to wns}{\mathbf{T}}\right)-\left(\overset{\kappa\to wns}{M_E}+\overset{\kappa\to wns}{T_v}+\overset{\kappa\to wns}{Q}\right)\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\mathbf{g}_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\theta^{\overline{\overline{wns}}}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\eta_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\mu^{\overline{wns}}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\rho_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\left(\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\rho_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\mathbf{:}\mathbf{d}^{\overline{\overline{s}}}=\Lambda\geq0$$

Terms involving the inter-entity transfer of mass, momentum, and energy need to be rearranged into force-flux form. The straightforward, but somewhat lengthy, manipulations needed to derive this form are guided by the a priori knowledge of equilibrium conditions, which can be utilized to derive forms in which the forces are known to be zero at equilibrium. The needed rearrangement is accomplished by extracting all terms involving the transfer of momentum, mass, and energy from Eq. (A.115) and manipulating them to derive the desired form. These manipulations are detailed in turn. First, consider terms involving the interfacial transport of momentum, which may be written as

$$
\begin{aligned}
\text{(A.116)}\quad T ={}& -\sum_{\iota\in\mathfrak{I}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\cdot\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}+\sum_{\iota\in\mathfrak{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{T_v}\\[4pt]
={}& -\frac{\mathbf{v}^{\overline{w}}}{\theta^{\overline{\overline{w}}}}\cdot\left(\overset{wn\to w}{\mathbf{T}}+\overset{ws\to w}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mathbf{v}^{\overline{w}}\cdot\overset{wn\to w}{\mathbf{T}}+\mathbf{v}^{\overline{w}}\cdot\overset{ws\to w}{\mathbf{T}}\right)\\[4pt]
& -\frac{\mathbf{v}^{\overline{n}}}{\theta^{\overline{\overline{n}}}}\cdot\left(\overset{wn\to n}{\mathbf{T}}+\overset{ns\to n}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{n}}}}\left(\mathbf{v}^{\overline{n}}\cdot\overset{wn\to n}{\mathbf{T}}+\mathbf{v}^{\overline{n}}\cdot\overset{ns\to n}{\mathbf{T}}\right)\\[4pt]
& -\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}}\cdot\left(\overset{ws\to s}{\mathbf{T}}+\overset{ns\to s}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mathbf{v}^{\overline{s}}\cdot\overset{ws\to s}{\mathbf{T}}+\mathbf{v}^{\overline{s}}\cdot\overset{ns\to s}{\mathbf{T}}\right)\\[4pt]
& -\frac{\mathbf{v}^{\overline{wn}}}{\theta^{\overline{\overline{wn}}}}\cdot\left(-\overset{wn\to w}{\mathbf{T}}-\overset{wn\to n}{\mathbf{T}}+\overset{wns\to wn}{\mathbf{T}}\right)\\[4pt]
& +\frac{1}{\theta^{\overline{\overline{wn}}}}\left(-\mathbf{v}^{\overline{w}}\cdot\overset{wn\to w}{\mathbf{T}}-\mathbf{v}^{\overline{n}}\cdot\overset{wn\to n}{\mathbf{T}}+\mathbf{v}^{\overline{wn}}\cdot\overset{wns\to wn}{\mathbf{T}}\right)\\[4pt]
& -\frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}}\cdot\left(-\overset{ws\to w}{\mathbf{T}}-\overset{ws\to s}{\mathbf{T}}+\overset{wns\to ws}{\mathbf{T}}\right)\\[4pt]
& +\frac{1}{\theta^{\overline{\overline{ws}}}}\left(-\mathbf{v}^{\overline{w}}\cdot\overset{ws\to w}{\mathbf{T}}-\mathbf{v}^{\overline{s}}\cdot\overset{ws\to s}{\mathbf{T}}+\mathbf{v}^{\overline{ws}}\cdot\overset{wns\to ws}{\mathbf{T}}\right)\\[4pt]
& -\frac{\mathbf{v}^{\overline{ns}}}{\theta^{\overline{\overline{ns}}}}\cdot\left(-\overset{ns\to n}{\mathbf{T}}-\overset{ns\to s}{\mathbf{T}}+\overset{wns\to ns}{\mathbf{T}}\right)\\[4pt]
& +\frac{1}{\theta^{\overline{\overline{ns}}}}\left(-\mathbf{v}^{\overline{n}}\cdot\overset{ns\to n}{\mathbf{T}}-\mathbf{v}^{\overline{s}}\cdot\overset{ns\to s}{\mathbf{T}}+\mathbf{v}^{\overline{ns}}\cdot\overset{wns\to ns}{\mathbf{T}}\right)
\end{aligned}
$$

$$-\frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}}\cdot\left(-\overset{wns\to wn}{\mathbf{T}}-\overset{wns\to ws}{\mathbf{T}}-\overset{wns\to ns}{\mathbf{T}}\right)$$
$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\left(-\mathbf{v}^{\overline{wn}}\cdot\overset{wns\to wn}{\mathbf{T}}-\mathbf{v}^{\overline{ws}}\cdot\overset{wns\to ws}{\mathbf{T}}-\mathbf{v}^{\overline{ns}}\cdot\overset{wns\to ns}{\mathbf{T}}\right).$$

Noting that all terms multiplied by phase velocities cancel as well as the common curve terms that are multiplied by interface temperatures, leaves us with

$$(\text{A.117})\quad T=-\frac{\mathbf{v}^{\overline{wn}}}{\theta^{\overline{\overline{wn}}}}\cdot\left(-\overset{wn\to w}{\mathbf{T}}-\overset{wn\to n}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{wn}}}}\left(-\mathbf{v}^{\overline{w}}\cdot\overset{wn\to w}{\mathbf{T}}-\mathbf{v}^{\overline{n}}\cdot\overset{wn\to n}{\mathbf{T}}\right)$$
$$-\frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}}\cdot\left(-\overset{ws\to w}{\mathbf{T}}-\overset{ws\to s}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{ws}}}}\left(-\mathbf{v}^{\overline{w}}\cdot\overset{ws\to w}{\mathbf{T}}-\mathbf{v}^{\overline{s}}\cdot\overset{ws\to s}{\mathbf{T}}\right)$$
$$-\frac{\mathbf{v}^{\overline{ns}}}{\theta^{\overline{\overline{ns}}}}\cdot\left(-\overset{ns\to n}{\mathbf{T}}-\overset{ns\to s}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{ns}}}}\left(-\mathbf{v}^{\overline{n}}\cdot\overset{ns\to n}{\mathbf{T}}-\mathbf{v}^{\overline{s}}\cdot\overset{ns\to s}{\mathbf{T}}\right)$$
$$-\frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}}\cdot\left(-\overset{wns\to wn}{\mathbf{T}}-\overset{wns\to ws}{\mathbf{T}}-\overset{wns\to ns}{\mathbf{T}}\right)$$
$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\left(-\mathbf{v}^{\overline{wn}}\cdot\overset{wns\to wn}{\mathbf{T}}-\mathbf{v}^{\overline{ws}}\cdot\overset{wns\to ws}{\mathbf{T}}-\mathbf{v}^{\overline{ns}}\cdot\overset{wns\to ns}{\mathbf{T}}\right),$$

or putting in objective form by referencing all velocities to $\mathbf{v}^{\overline{s}}$

$$(\text{A.118})\quad T=\frac{1}{\theta^{\overline{\overline{wn}}}}\left[\mathbf{v}^{\overline{wn},\overline{s}}\cdot\left(\overset{wn\to w}{\mathbf{T}}+\overset{wn\to n}{\mathbf{T}}\right)-\left(\mathbf{v}^{\overline{w},\overline{s}}\cdot\overset{wn\to w}{\mathbf{T}}+\mathbf{v}^{\overline{n},\overline{s}}\cdot\overset{wn\to n}{\mathbf{T}}\right)\right]$$
$$+\frac{1}{\theta^{\overline{\overline{ws}}}}\left[\mathbf{v}^{\overline{ws},\overline{s}}\cdot\left(\overset{ws\to w}{\mathbf{T}}+\overset{ws\to s}{\mathbf{T}}\right)-\mathbf{v}^{\overline{w},\overline{s}}\cdot\overset{ws\to w}{\mathbf{T}}\right]$$
$$+\frac{1}{\theta^{\overline{\overline{ns}}}}\left[\mathbf{v}^{\overline{ns},\overline{s}}\cdot\left(\overset{ns\to n}{\mathbf{T}}+\overset{ns\to s}{\mathbf{T}}\right)-\mathbf{v}^{\overline{n},\overline{s}}\cdot\overset{ns\to n}{\mathbf{T}}\right]$$
$$+\frac{\mathbf{v}^{\overline{wns},\overline{s}}}{\theta^{\overline{\overline{wns}}}}\cdot\left(\overset{wns\to wn}{\mathbf{T}}+\overset{wns\to ws}{\mathbf{T}}+\overset{wns\to ns}{\mathbf{T}}\right)$$
$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{v}^{\overline{wn},\overline{s}}\cdot\overset{wns\to wn}{\mathbf{T}}+\mathbf{v}^{\overline{ws},\overline{s}}\cdot\overset{wns\to ws}{\mathbf{T}}+\mathbf{v}^{\overline{ns},\overline{s}}\cdot\overset{wns\to ns}{\mathbf{T}}\right).$$

Adding and subtracting like terms to put into force-flux pairs gives

$$(\text{A.119})\quad T=-\frac{\mathbf{v}^{\overline{w},\overline{s}}}{\theta^{\overline{\overline{w}}}}\cdot\overset{wn\to w}{\mathbf{T}}-\frac{\mathbf{v}^{\overline{n},\overline{s}}}{\theta^{\overline{\overline{n}}}}\cdot\overset{wn\to n}{\mathbf{T}}+\frac{\mathbf{v}^{\overline{wn},\overline{s}}}{\theta^{\overline{\overline{wn}}}}\cdot\left(\overset{wn\to w}{\mathbf{T}}+\overset{wn\to n}{\mathbf{T}}\right)$$
$$+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{wn}}}}\right)\mathbf{v}^{\overline{w},\overline{s}}\cdot\overset{wn\to w}{\mathbf{T}}+\left(\frac{1}{\theta^{\overline{\overline{n}}}}-\frac{1}{\theta^{\overline{\overline{wn}}}}\right)\mathbf{v}^{\overline{n},\overline{s}}\cdot\overset{wn\to n}{\mathbf{T}}$$

172

$$
-\frac{\mathbf{v}^{\overline{w},\overline{s}}}{\theta^{\overline{\overline{w}}}} \cdot \overset{ws\to w}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{\theta^{\overline{\overline{ws}}}} \cdot \left(\overset{ws\to w}{\mathbf{T}} + \overset{ws\to s}{\mathbf{T}}\right) + \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}}\right) \mathbf{v}^{\overline{w},\overline{s}} \cdot \overset{ws\to w}{\mathbf{T}}
$$

$$
-\frac{\mathbf{v}^{\overline{n},\overline{s}}}{\theta^{\overline{\overline{n}}}} \cdot \overset{ns\to n}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{ns},\overline{s}}}{\theta^{\overline{\overline{ns}}}} \cdot \left(\overset{ns\to n}{\mathbf{T}} + \overset{ns\to s}{\mathbf{T}}\right) + \left(\frac{1}{\theta^{\overline{\overline{n}}}} - \frac{1}{\theta^{\overline{\overline{ns}}}}\right) \mathbf{v}^{\overline{n},\overline{s}} \cdot \overset{ns\to n}{\mathbf{T}}
$$

$$
-\frac{\mathbf{v}^{\overline{wn},\overline{s}}}{\theta^{\overline{\overline{wn}}}} \cdot \overset{wns\to wn}{\mathbf{T}} - \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{\theta^{\overline{\overline{ws}}}} \cdot \overset{wns\to ws}{\mathbf{T}} - \frac{\mathbf{v}^{\overline{ns},\overline{s}}}{\theta^{\overline{\overline{ns}}}} \cdot \overset{wns\to ns}{\mathbf{T}}
$$

$$
+ \left(\frac{1}{\theta^{\overline{\overline{wn}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}}\right) \mathbf{v}^{\overline{wn},\overline{s}} \cdot \overset{wns\to wn}{\mathbf{T}} + \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}}\right) \mathbf{v}^{\overline{ws},\overline{s}} \cdot \overset{wns\to ws}{\mathbf{T}}
$$

$$
+ \left(\frac{1}{\theta^{\overline{\overline{ns}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}}\right) \mathbf{v}^{\overline{ns},\overline{s}} \cdot \overset{wns\to ns}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{wns},\overline{s}}}{\theta^{\overline{\overline{wns}}}} \left(\overset{wns\to wn}{\mathbf{T}} + \overset{wns\to ws}{\mathbf{T}} + \overset{wns\to ns}{\mathbf{T}}\right).
$$

This resultant form is convenient because forces consisting of referenced velocities and differences in the inverse of temperatures are known to be zero at equilibrium from a previously performed variational analysis.

The terms from Eq. (A.115) that involve the dot product of velocities and mass exchange between pairs of entities can be written as

$$
(A.120) \qquad M = \sum_{\iota\in\mathcal{I}} \frac{\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}}{2\theta^{\overline{\iota}}} \sum_{\kappa\in\mathcal{I}_{C\iota}} \overset{\kappa\to\iota}{M} - \sum_{\iota\in\mathcal{I}} \frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\iota}}} \cdot \sum_{\kappa\in\mathcal{I}_{C\iota}} \overset{\kappa\to\iota}{\mathbf{M}_v} + \sum_{\iota\in\mathcal{I}} \frac{1}{\theta^{\overline{\iota}}} \sum_{\kappa\in\mathcal{I}_{C\iota}} \overset{\kappa\to\iota}{M_{Ev}},
$$

where $\overset{\kappa\to\iota}{M_{Ev}}$ represents the inter-entity exchange of energy due to momentum exchange.

It may be observed that all terms in Eq. (A.120) for the cases in which $\iota = w, n, s$ sum to zero. Furthermore, for the cases in which $\iota = ws, wn, ns$ all terms associated with mass transfer from the common curve also sum to zero. Thus, the expanded form of Eq. (A.120) becomes

$$
(A.121) \quad M = -\frac{\mathbf{v}^{\overline{wn}}\cdot\mathbf{v}^{\overline{wn}}}{2\theta^{\overline{\overline{wn}}}} \left(\overset{wn\to w}{M} + \overset{wn\to n}{M}\right) + \frac{\mathbf{v}^{\overline{wn}}}{\theta^{\overline{\overline{wn}}}} \cdot \left(\mathbf{v}^{\overline{w}} \overset{wn\to w}{M} + \mathbf{v}^{\overline{n}} \overset{wn\to n}{M}\right)
$$

$$
-\frac{1}{2\theta^{\overline{\overline{wn}}}} \left(\mathbf{v}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}} \overset{wn\to w}{M} + \mathbf{v}^{\overline{n}}\cdot\mathbf{v}^{\overline{n}} \overset{wn\to n}{M}\right)
$$

$$
-\frac{\mathbf{v}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}}{2\theta^{\overline{\overline{ws}}}} \left(\overset{ws\to w}{M} + \overset{ws\to s}{M}\right) + \frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}} \cdot \left(\mathbf{v}^{\overline{w}} \overset{ws\to w}{M} + \mathbf{v}^{\overline{s}} \overset{ws\to s}{M}\right)
$$

$$
-\frac{1}{2\theta^{\overline{\overline{ws}}}} \left(\mathbf{v}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}} \overset{ws\to w}{M} + \mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}} \overset{ws\to s}{M}\right)
$$

$$-\frac{\mathbf{v}^{\overline{ns}}\cdot\mathbf{v}^{\overline{ns}}}{2\theta^{\overline{\overline{ns}}}}\left(\overset{ns\to n}{M}+\overset{ns\to s}{M}\right)+\frac{\mathbf{v}^{\overline{ns}}}{\theta^{\overline{\overline{ns}}}}\cdot\left(\mathbf{v}^{\overline{n}}\overset{ns\to n}{M}+\mathbf{v}^{\overline{s}}\overset{ns\to s}{M}\right)$$

$$-\frac{1}{2\theta^{\overline{\overline{ns}}}}\left(\mathbf{v}^{\overline{n}}\cdot\mathbf{v}^{\overline{n}}\overset{ns\to n}{M}+\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}\overset{ns\to s}{M}\right)$$

$$-\frac{\mathbf{v}^{\overline{wns}}\cdot\mathbf{v}^{\overline{wns}}}{2\theta^{\overline{\overline{wns}}}}\left(\overset{wns\to wn}{M}+\overset{wns\to ws}{M}+\overset{wns\to ns}{M}\right)$$

$$+\frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}}\cdot\left(\mathbf{v}^{\overline{wn}}\overset{wns\to wn}{M}+\mathbf{v}^{\overline{ws}}\overset{wns\to ws}{M}+\mathbf{v}^{\overline{ns}}\overset{wns\to ns}{M}\right)$$

$$-\frac{1}{2\theta^{\overline{\overline{wns}}}}\left(\mathbf{v}^{\overline{wn}}\cdot\mathbf{v}^{\overline{wn}}\overset{wns\to wn}{M}+\mathbf{v}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}\overset{wns\to ws}{M}+\mathbf{v}^{\overline{ns}}\cdot\mathbf{v}^{\overline{ns}}\overset{wns\to ns}{M}\right).$$

Putting in objective form by referencing velocities to the solid-phase velocity and canceling like terms yields

$$(A.122)\quad M=-\frac{\mathbf{v}^{\overline{wn,\overline{s}}}\cdot\mathbf{v}^{\overline{wn,\overline{s}}}}{2\theta^{\overline{\overline{wn}}}}\left(\overset{wn\to w}{M}+\overset{wn\to n}{M}\right)+\frac{\mathbf{v}^{\overline{wn,\overline{s}}}}{\theta^{\overline{\overline{wn}}}}\cdot\left(\mathbf{v}^{\overline{w,\overline{s}}}\overset{wn\to w}{M}+\mathbf{v}^{\overline{n,\overline{s}}}\overset{wn\to n}{M}\right)$$

$$-\frac{1}{2\theta^{\overline{\overline{wn}}}}\left(\mathbf{v}^{\overline{w,\overline{s}}}\cdot\mathbf{v}^{\overline{w,\overline{s}}}\overset{wn\to w}{M}+\mathbf{v}^{\overline{n,\overline{s}}}\cdot\mathbf{v}^{\overline{n,\overline{s}}}\overset{wn\to n}{M}\right)$$

$$-\frac{\mathbf{v}^{\overline{ws,\overline{s}}}\cdot\mathbf{v}^{\overline{ws,\overline{s}}}}{2\theta^{\overline{\overline{ws}}}}\left(\overset{ws\to w}{M}+\overset{ws\to s}{M}\right)+\frac{\mathbf{v}^{\overline{ws,\overline{s}}}}{\theta^{\overline{\overline{ws}}}}\cdot\mathbf{v}^{\overline{w,\overline{s}}}\overset{ws\to w}{M}-\frac{1}{2\theta^{\overline{\overline{ws}}}}\mathbf{v}^{\overline{w,\overline{s}}}\cdot\mathbf{v}^{\overline{w,\overline{s}}}\overset{ws\to w}{M}$$

$$-\frac{\mathbf{v}^{\overline{ns,\overline{s}}}\cdot\mathbf{v}^{\overline{ns,\overline{s}}}}{2\theta^{\overline{\overline{ns}}}}\left(\overset{ns\to n}{M}+\overset{ns\to s}{M}\right)+\frac{\mathbf{v}^{\overline{ns,\overline{s}}}}{\theta^{\overline{\overline{ns}}}}\cdot\mathbf{v}^{\overline{n,\overline{s}}}\overset{ns\to n}{M}-\frac{1}{2\theta^{\overline{\overline{ns}}}}\mathbf{v}^{\overline{n,\overline{s}}}\cdot\mathbf{v}^{\overline{n,\overline{s}}}\overset{ns\to n}{M}$$

$$-\frac{\mathbf{v}^{\overline{wns,\overline{s}}}\cdot\mathbf{v}^{\overline{wns,\overline{s}}}}{2\theta^{\overline{\overline{wns}}}}\left(\overset{wns\to wn}{M}+\overset{wns\to ws}{M}+\overset{wns\to ns}{M}\right)$$

$$+\frac{\mathbf{v}^{\overline{wns,\overline{s}}}}{\theta^{\overline{\overline{wns}}}}\cdot\left(\mathbf{v}^{\overline{wn,\overline{s}}}\overset{wns\to wn}{M}+\mathbf{v}^{\overline{ws,\overline{s}}}\overset{wns\to ws}{M}+\mathbf{v}^{\overline{ns,\overline{s}}}\overset{wns\to ns}{M}\right)$$

$$-\frac{1}{2\theta^{\overline{\overline{wns}}}}\left(\mathbf{v}^{\overline{wn,\overline{s}}}\cdot\mathbf{v}^{\overline{wn,\overline{s}}}\overset{wns\to wn}{M}+\mathbf{v}^{\overline{ws,\overline{s}}}\cdot\mathbf{v}^{\overline{ws,\overline{s}}}\overset{wns\to ws}{M}+\mathbf{v}^{\overline{ns,\overline{s}}}\cdot\mathbf{v}^{\overline{ns,\overline{s}}}\overset{wns\to ns}{M}\right).$$

Looking at just those terms involving $\theta^{\overline{\overline{wn}}}$. We can regroup the terms as well as add in and subtract out terms to get:

$$(A.123)$$

$$M=-\frac{\mathbf{v}^{\overline{w,\overline{s}}}}{2\theta^{\overline{\overline{w}}}}\cdot\mathbf{v}^{\overline{w,\overline{wn}}}\overset{wn\to w}{M}-\frac{\mathbf{v}^{\overline{n,\overline{s}}}}{2\theta^{\overline{\overline{n}}}}\cdot\mathbf{v}^{\overline{n,\overline{wn}}}\overset{wn\to n}{M}+\frac{\mathbf{v}^{\overline{wn,\overline{s}}}}{2\theta^{\overline{\overline{wn}}}}\cdot\left(\mathbf{v}^{\overline{w,\overline{wn}}}\overset{wn\to w}{M}+\mathbf{v}^{\overline{n,\overline{wn}}}\overset{wn\to n}{M}\right)$$

$$+ \left(\frac{1}{2\theta^{\overline{w}}} - \frac{1}{2\theta^{\overline{\overline{wn}}}} \right) \mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{w},\overline{wn}} \overset{wn \to w}{M} + \left(\frac{1}{2\theta^{\overline{n}}} - \frac{1}{2\theta^{\overline{\overline{wn}}}} \right) \mathbf{v}^{\overline{n},\overline{s}} \cdot \mathbf{v}^{\overline{n},\overline{wn}} \overset{wn \to n}{M}.$$

Similarly, this process can b repeated for all of the other terms, giving

(A.124)

$$M = -\frac{\mathbf{v}^{\overline{w},\overline{s}}}{2\theta^{\overline{\overline{w}}}} \cdot \mathbf{v}^{\overline{w},\overline{wn}} \overset{wn \to w}{M} - \frac{\mathbf{v}^{\overline{n},\overline{s}}}{2\theta^{\overline{\overline{n}}}} \cdot \mathbf{v}^{\overline{n},\overline{wn}} \overset{wn \to n}{M} + \frac{\mathbf{v}^{\overline{wn},\overline{s}}}{2\theta^{\overline{\overline{wn}}}} \cdot \left(\mathbf{v}^{\overline{w},\overline{wn}} \overset{wn \to w}{M} + \mathbf{v}^{\overline{n},\overline{wn}} \overset{wn \to n}{M} \right)$$

$$+ \left(\frac{1}{2\theta^{\overline{\overline{w}}}} - \frac{1}{2\theta^{\overline{\overline{wn}}}} \right) \mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{w},\overline{wn}} \overset{wn \to w}{M} + \left(\frac{1}{2\theta^{\overline{\overline{n}}}} - \frac{1}{2\theta^{\overline{\overline{wn}}}} \right) \mathbf{v}^{\overline{n},\overline{s}} \cdot \mathbf{v}^{\overline{n},\overline{wn}} \overset{wn \to n}{M}$$

$$- \frac{\mathbf{v}^{\overline{w},\overline{s}}}{2\theta^{\overline{\overline{w}}}} \cdot \mathbf{v}^{\overline{w},\overline{ws}} \overset{ws \to w}{M} + \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{2\theta^{\overline{\overline{ws}}}} \cdot \left(\mathbf{v}^{\overline{w},\overline{ws}} \overset{ws \to w}{M} + \mathbf{v}^{\overline{s},\overline{ws}} \overset{ws \to s}{M} \right)$$

$$+ \left(\frac{1}{2\theta^{\overline{\overline{w}}}} - \frac{1}{2\theta^{\overline{\overline{ws}}}} \right) \mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{w},\overline{ws}} \overset{ws \to w}{M}$$

$$- \frac{\mathbf{v}^{\overline{n},\overline{s}}}{2\theta^{\overline{\overline{n}}}} \cdot \mathbf{v}^{\overline{n},\overline{ns}} \overset{ns \to n}{M} + \frac{\mathbf{v}^{\overline{ns},\overline{s}}}{2\theta^{\overline{\overline{ns}}}} \cdot \left(\mathbf{v}^{\overline{n},\overline{ns}} \overset{ns \to n}{M} + \mathbf{v}^{\overline{s},\overline{ns}} \overset{ns \to s}{M} \right)$$

$$+ \left(\frac{1}{2\theta^{\overline{\overline{n}}}} - \frac{1}{2\theta^{\overline{\overline{ns}}}} \right) \mathbf{v}^{\overline{n},\overline{s}} \cdot \mathbf{v}^{\overline{n},\overline{ns}} \overset{ns \to n}{M}$$

$$- \frac{\mathbf{v}^{\overline{wn},\overline{s}}}{2\theta^{\overline{\overline{wn}}}} \cdot \mathbf{v}^{\overline{wn},\overline{wns}} \overset{wns \to wn}{M} + \left(\frac{1}{2\theta^{\overline{\overline{wn}}}} - \frac{1}{2\theta^{\overline{\overline{wns}}}} \right) \mathbf{v}^{\overline{wn},\overline{s}} \cdot \mathbf{v}^{\overline{wn},\overline{wns}} \overset{wns \to wn}{M}$$

$$- \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{2\theta^{\overline{\overline{ws}}}} \cdot \mathbf{v}^{\overline{ws},\overline{wns}} \overset{wns \to ws}{M} + \left(\frac{1}{2\theta^{\overline{\overline{ws}}}} - \frac{1}{2\theta^{\overline{\overline{wns}}}} \right) \mathbf{v}^{\overline{ws},\overline{s}} \cdot \mathbf{v}^{\overline{ws},\overline{wns}} \overset{wns \to ws}{M}$$

$$- \frac{\mathbf{v}^{\overline{ns},\overline{s}}}{2\theta^{\overline{\overline{ns}}}} \cdot \mathbf{v}^{\overline{ns},\overline{wns}} \overset{wns \to ns}{M} + \left(\frac{1}{2\theta^{\overline{\overline{ns}}}} - \frac{1}{2\theta^{\overline{\overline{wns}}}} \right) \mathbf{v}^{\overline{ns},\overline{s}} \cdot \mathbf{v}^{\overline{ns},\overline{wns}} \overset{wns \to ns}{M}$$

$$+ \frac{\mathbf{v}^{\overline{wns},\overline{s}}}{2\theta^{\overline{\overline{wns}}}} \cdot \left(\mathbf{v}^{\overline{wn},\overline{wns}} \overset{wns \to wn}{M} + \mathbf{v}^{\overline{ws},\overline{wns}} \overset{wns \to ws}{M} + \mathbf{v}^{\overline{ns},\overline{wns}} \overset{wns \to ns}{M} \right).$$

This form is attractive because each grouping of terms matches a flux-force pair.

Looking at the remaining energy transfer terms

(A.125)
$$Q = \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\overline{\iota}}} \sum_{\kappa \in \mathcal{I}_{C\iota}} \overset{\kappa \to \iota}{Q},$$

can be expanded as follows:

(A.126) $\quad Q = \dfrac{1}{\theta^{\overline{\overline{w}}}} \left(\overset{wn \to w}{Q} + \overset{ws \to w}{Q} \right) + \dfrac{1}{\theta^{\overline{\overline{n}}}} \left(\overset{wn \to n}{Q} + \overset{ns \to n}{Q} \right)$

$$
+\frac{1}{\theta^{\overline{\overline{s}}}}\left(\overset{ws\to s}{Q}+\overset{ns\to s}{Q}\right)+\frac{1}{\theta^{\overline{\overline{wn}}}}\left(\overset{wns\to wn}{Q}-\overset{wn\to w}{Q}-\overset{wn\to n}{Q}\right)
$$

$$
+\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\overset{wns\to ws}{Q}-\overset{ws\to w}{Q}-\overset{ws\to s}{Q}\right)+\frac{1}{\theta^{\overline{\overline{ns}}}}\left(\overset{wns\to ns}{Q}-\overset{ns\to n}{Q}-\overset{ns\to s}{Q}\right)
$$

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}}\left(-\overset{wns\to wn}{Q}-\overset{wns\to ws}{Q}-\overset{wns\to ns}{Q}\right).
$$

Which rewriting in flux-force form is

$$
\text{(A.127)}\quad Q=\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{wn}}}}\right)\overset{wn\to w}{Q}+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\overset{ws\to w}{Q}+\left(\frac{1}{\theta^{\overline{\overline{n}}}}-\frac{1}{\theta^{\overline{\overline{wn}}}}\right)\overset{wn\to n}{Q}
$$

$$
+\left(\frac{1}{\theta^{\overline{\overline{n}}}}-\frac{1}{\theta^{\overline{\overline{ns}}}}\right)\overset{ns\to n}{Q}+\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\overset{ws\to s}{Q}+\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ns}}}}\right)\overset{ns\to s}{Q}
$$

$$
+\left(\frac{1}{\theta^{\overline{\overline{wn}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)\overset{wns\to wn}{Q}+\left(\frac{1}{\theta^{\overline{\overline{ws}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)\overset{wns\to ws}{Q}+\left(\frac{1}{\theta^{\overline{\overline{ns}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)\overset{wns\to ns}{Q}.
$$

Using these new flux-force groupings for the exchange terms and grouping other force-flux pairs which already exist, the final CEI can be written as

(A.128)

$$
-\sum_{\iota\in\{\mathcal{I}_f\cup\mathcal{I}_I\cup\mathcal{I}_C\}}\nabla\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\iota}}-\frac{\epsilon^{\iota}\mathbf{q}^{\overline{\overline{\iota}}}}{\theta^{\overline{\iota}}}\right)
$$

$$
-\nabla\cdot\left\{\epsilon^{s}\boldsymbol{\varphi}^{\overline{\overline{s}}}-\frac{1}{\theta^{\overline{\overline{s}}}}\left[\epsilon^{s}\mathbf{q}^{\overline{\overline{s}}}-\left\langle\left(\mathbf{t}_{s}-\boldsymbol{\sigma}_{s}:\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}\right]\right\}
$$

$$
-\sum_{\iota\in\mathcal{I}_P}\left\{\epsilon^{\iota}b^{\iota}-\frac{1}{\theta^{\overline{\iota}}}\left[\epsilon^{\iota}h^{\overline{\iota}}+\left\langle\eta_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]\right.
$$

$$
\left.-\frac{1}{\theta^{\overline{\iota}}}\left\langle\rho_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_{E}^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right\}
$$

$$
-\sum_{\iota\in\mathcal{I}_I}\left\{\epsilon^{\iota}b^{\iota}-\frac{1}{\theta^{\overline{\iota}}}\left[\epsilon^{\iota}h^{\overline{\iota}}+\left\langle\eta_{\iota}\frac{\mathrm{D}^{\prime\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]\right.
$$

$$
\left.-\frac{1}{\theta^{\overline{\iota}}}\left\langle\rho_{\iota}\frac{\mathrm{D}^{\prime\overline{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_{E}^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right\}
$$

$$-\epsilon^{wns}b^{wns} + \frac{1}{\theta^{\overline{\overline{wns}}}}\left[\epsilon^{wns}h^{\overline{\overline{wns}}} + \left\langle \eta_{wns}\frac{\mathrm{D}''^{\overline{s}}\left(\theta_{wns} - \theta^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle \rho_{wns}\frac{\mathrm{D}''^{\overline{s}}\left(\mu_{wns} + \psi_{wns} - \mu^{\overline{wns}} - \psi^{\overline{wns}} - K_E^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{\epsilon^{\iota}}{\theta^{\overline{\overline{\iota}}}}\left(\mathbf{t}^{\overline{\overline{\iota}}} + p^{\iota}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\iota}}} + \frac{\epsilon^{s}}{\theta^{\overline{\overline{s}}}}\left(\mathbf{t}^{\overline{\overline{s}}} - \mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}} + \sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{\epsilon^{\iota}}{\theta^{\overline{\overline{\iota}}}}\left(\mathbf{t}^{\overline{\overline{\iota}}} - \gamma^{\iota}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\iota}}}$$

$$+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{t}^{\overline{\overline{wns}}} + \gamma^{wns}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{wns}}} + \sum_{\iota\in\{\mathfrak{I}_{\mathrm{f}}\cup\mathfrak{I}_{\mathrm{I}}\cup\mathfrak{I}_{\mathrm{C}}\}}\frac{\epsilon^{\iota}\mathbf{q}^{\overline{\overline{\iota}}}}{\left(\theta^{\overline{\overline{\iota}}}\right)^2}\cdot\nabla\theta^{\overline{\overline{\iota}}}$$

$$+\frac{1}{\left(\theta^{\overline{\overline{s}}}\right)^2}\left[\epsilon^{s}\mathbf{q}^{\overline{\overline{s}}} - \left\langle\left(\mathbf{t}_s - \boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\cdot\nabla\theta^{\overline{\overline{s}}}$$

$$-\sum_{\iota\in\mathfrak{I}_P}\sum_{\kappa\in\mathfrak{I}_{C\iota}}\frac{1}{\theta^{\overline{\overline{\kappa}}}}\overset{\kappa\to\iota}{M}\left[\left(K_E^{\overline{\overline{\iota}}} + \psi^{\iota} + \mu^{\iota}\right) - \left(K_E^{\overline{\overline{\kappa}}} + \psi^{\overline{\kappa}} + \mu^{\overline{\kappa}}\right)\right]$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\sum_{\kappa\in\mathfrak{I}_{cwns}}\overset{wns\to\kappa}{M}\left[\left(K_E^{\overline{\overline{\kappa}}} + \psi^{\overline{\kappa}} + \mu^{\overline{\kappa}}\right) - \left(K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}} + \mu^{\overline{wns}}\right)\right]$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{P}}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left[\overset{\kappa\to\iota}{Q} + \left(\frac{E^{\overline{\overline{\iota}}}}{\epsilon^{\iota}\rho^{\iota}} - \mu^{\iota}\right)\overset{\kappa\to\iota}{M} + \mathbf{v}^{\iota,\overline{s}}\cdot\left(\overset{\kappa\to\iota}{\mathbf{T}} + \frac{\mathbf{v}^{\iota,\overline{\kappa}}}{2}\overset{\kappa\to\iota}{M}\right)\right]\left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\left[\overset{wns\to\iota}{Q} + \left(\frac{E^{\overline{\overline{\iota}}}}{\epsilon^{\iota}\rho^{\iota}} - \mu^{\iota}\right)\overset{wns\to\iota}{M} + \mathbf{v}^{\iota,\overline{s}}\cdot\left(\overset{wns\to\iota}{\mathbf{T}} + \frac{\mathbf{v}^{\iota,\overline{wns}}}{2}\overset{wns\to\iota}{M}\right)\right]\left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}}\right)$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left\langle p_{\iota}\left(\mathbf{v}_{\kappa} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}} + \epsilon^{\iota}\rho^{\iota}\nabla\left(K_E^{\overline{\overline{\iota}}} + \psi^{\iota} + \mu^{\iota}\right) + \eta^{\overline{\overline{\iota}}}\nabla\theta^{\overline{\overline{\iota}}}\right.$$

$$\left. -\nabla\left(\epsilon^{\iota}p^{\iota}\right) + \sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left(\overset{\kappa\to\iota}{\mathbf{T}} + \frac{\mathbf{v}^{\iota,\overline{\kappa}}}{2}\overset{\kappa\to\iota}{M}\right)\right]\cdot\mathbf{v}^{\iota,\overline{s}}$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}} + \epsilon^{\iota}\rho^{\iota}\nabla\left(K_E^{\overline{\overline{\iota}}} + \psi^{\iota} + \mu^{\iota}\right) + \eta^{\overline{\overline{\iota}}}\nabla\theta^{\overline{\overline{\iota}}} + \nabla\left(\epsilon^{\iota}\gamma^{\iota}\right)\right.$$

$$\left. -\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}\cap\mathfrak{I}_{\mathrm{P}}}\left(\overset{\iota\to\kappa}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{\kappa},\iota}}{2}\overset{\iota\to\kappa}{M}\right) + \left(\overset{wns\to\iota}{\mathbf{T}} + \frac{\mathbf{v}^{\iota,\overline{wns}}}{2}\overset{wns\to\iota}{M}\right)\right]\cdot\mathbf{v}^{\iota,\overline{s}}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\epsilon^{wns}\rho^{wns}\mathbf{g}^{\overline{wns}}+\epsilon^{wns}\rho^{wns}\nabla\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}+\mu^{\overline{wns}}\right)+\eta^{\overline{\overline{wns}}}\nabla\theta^{\overline{wns}}\right.$$

$$\left.-\nabla\left(\epsilon^{wns}\gamma^{wns}\right)-\sum_{\kappa\in\mathcal{I}_{cwns}}\left(\overset{wns\to\kappa}{\mathbf{T}}+\frac{\mathbf{v}^{\kappa,\overline{wns}}}{2}\overset{wns\to\kappa}{M}\right)\right]\cdot\mathbf{v}^{\overline{wns},\overline{s}}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\frac{\mathbf{C}_s}{j_s}:\boldsymbol{\sigma}_s\left(\mathbf{v}_\kappa-\mathbf{v}_s\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\theta^{\overline{\iota}}\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\overline{\overline{s}}}-\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_{wns},\Omega}\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla\left(K_E^{\overline{\overline{\iota}}}+\psi^{\overline{\iota}}+\mu^{\overline{\iota}}\right)\cdot\left\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\rho_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wn}}}}\left\langle\left(p_w-p_n-\gamma_{wn}\nabla'\cdot\mathbf{n}_w+\rho_{wn}\mathbf{n}_w\cdot\mathbf{g}_{wn}\right)\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_w\right\rangle_{\Omega_{wn},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle\left(p_w+\gamma_{ws}\nabla'\cdot\mathbf{n}_s-\rho_{ws}\mathbf{n}_s\cdot\mathbf{g}_{ws}\right)\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{ns}}}}\left\langle\left(p_n+\gamma_{ns}\nabla'\cdot\mathbf{n}_s-\rho_{ns}\mathbf{n}_s\cdot\mathbf{g}_{ns}\right)\left(\mathbf{v}_{ns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ns},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\mathbf{g}_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\left(\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\theta^{\overline{wns}}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\eta_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}+\mu^{\overline{wns}}\right)\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\rho_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{s}}}=\Lambda\geq0.$$

A.5. Simplified Entropy Inequality

Starting from the CEI given in Eq. (2.77), the restrictions and approximations outlined in §2.6 can be applied to produce an SEI. To do this, we first restrict the system to be isothermal according to Secondary Restriction 1 and to have no mass exchange between phases according to Secondary Restriction 2. The condition of no mass exchange implies that for phase ι,

$$(A.129) \qquad (\mathbf{v}_\kappa - \mathbf{v}_\iota)\cdot\mathbf{n}_\iota = 0 \qquad \mathrm{on}\,\Omega_\kappa,$$

where $\iota \in \mathcal{I}_\mathrm{P}$ and $\kappa \in \mathcal{I}_{\mathrm{c}\iota}$. Consistent with Approximation 7, the terms involving deviation kinetic energy are assumed to be negligible since they are second order in velocity deviations. Also all terms that contain interface or common curve densities are eliminated based on Approximation 8. Applying these two restrictions to the CEI results in the following SEI:

$$(A.130) \quad -\sum_{\iota\in\{\mathcal{I}_\mathrm{f}\cup\mathcal{I}_\mathrm{I}\cup\mathcal{I}_\mathrm{C}\}} \nabla\cdot\left(\epsilon^\iota\boldsymbol{\varphi}^{\overline{\overline{\iota}}} - \frac{\epsilon^\iota\mathbf{q}^{\overline{\overline{\iota}}}}{\theta}\right)$$

$$-\nabla\cdot\left\{\epsilon^s\boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta}\left[\epsilon^s\mathbf{q}^{\overline{\overline{s}}} - \left\langle\left(\mathbf{t}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\colon\frac{\mathbf{C}^s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\right\}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{P}}\left[\epsilon^\iota b^\iota - \frac{1}{\theta}\left(\epsilon^\iota h^{\overline{\overline{\iota}}} + \left\langle\eta_\iota\frac{\mathrm{D}^{\overline{s}}(\theta - \theta)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right)\right.$$

$$\left. -\frac{1}{\theta}\left\langle\rho_\iota\frac{\mathrm{D}^{\overline{s}}\left(\mu_\iota + \psi_\iota - \mu^{\overline{\iota}} - \psi^{\overline{\iota}} - K_E^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right]$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{I}}\left[\epsilon^\iota b^\iota - \frac{1}{\theta}\left(\epsilon^\iota h^{\overline{\overline{\iota}}} + \left\langle\eta_\iota\frac{\mathrm{D}'^{\overline{s}}(\theta - \theta)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right)\right.$$

$$\left. -\frac{1}{\theta}\left\langle\rho_\iota\frac{\mathrm{D}'^{\overline{s}}\left(\mu_\iota + \psi_\iota - \mu^{\overline{\iota}} - \psi^{\overline{\iota}} - K_E^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right]$$

$$-\epsilon^{wns}b^{wns} + \frac{1}{\theta}\left(\epsilon^{wns}h^{\overline{\overline{wns}}} + \left\langle\eta_{wns}\frac{\mathrm{D}''^{\overline{s}}(\theta - \theta)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\right)$$

$$+\frac{1}{\theta}\left\langle \rho_{wns}\frac{\mathrm{D}''^{\overline{s}}\left(\mu_{wns}+\psi_{wns}-\mu^{\overline{wns}}-\psi^{\overline{wns}}-K_{E}^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{f}}}\frac{\epsilon^{\iota}}{\theta}\left(\mathbf{t}^{\overline{\overline{\iota}}}+p^{\iota}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\iota}}}+\frac{\epsilon^{s}}{\theta}\left(\mathbf{t}^{\overline{\overline{s}}}-\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}}+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{\epsilon^{\iota}}{\theta}\left(\mathbf{t}^{\overline{\overline{\iota}}}-\gamma^{\iota}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\iota}}}$$

$$+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{t}^{\overline{\overline{wns}}}+\gamma^{wns}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{wns}}}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta}\cdot\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}}+\epsilon^{\iota}\rho^{\iota}\nabla\left(\psi^{\overline{\iota}}+\mu^{\overline{\iota}}\right)+\nabla\left(\epsilon^{\iota}p^{\iota}\right)+\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right]$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta}\cdot\left[\nabla\left(\epsilon^{\iota}\gamma^{\iota}\right)+\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{wns},\overline{s}}}{\theta}\cdot\left[-\nabla\left(\epsilon^{wns}\gamma^{wns}\right)-\sum_{\kappa\in\mathcal{J}_{cwns}}\overset{wns\to\kappa}{\mathbf{T}}\right]$$

$$+\frac{1}{\theta}\left\langle\left(\nabla\cdot\mathbf{t}_{s}-\nabla\boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\mathbf{C}^{s}}{j_{s}}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}-\frac{1}{\theta}\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{I}'\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta}\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\mathbf{n}_{s}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta}\nabla\cdot\left\langle\mathbf{n}_{\kappa}\mathbf{n}_{\kappa}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta}\left[\langle\mathbf{n}_{\kappa}\mathbf{n}_{\kappa}\gamma_{\iota}\rangle_{\Omega_{\iota},\Omega}:\mathbf{d}^{\overline{\overline{s}}}-\left\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{wns},\Omega}\right]$$

$$+\frac{1}{\theta}\left\langle\left(p_{w}-p_{n}-\gamma_{wn}\nabla'\cdot\mathbf{n}_{w}\right)\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{w}\right\rangle_{\Omega_{wn},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(p_{w}+\gamma_{ws}\nabla'\cdot\mathbf{n}_{s}\right)\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(p_{n}+\gamma_{ns}\nabla'\cdot\mathbf{n}_{s}\right)\left(\mathbf{v}_{ns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{ns},\Omega}$$

$$-\frac{1}{\theta}\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta}\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\gamma_{wns}\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{s}}}=\Lambda\geq0.$$

Next, using the identities provided in Eqs. (2.15)–(2.22), the SEI can be rearranged to give

$$\text{(A.131)} \quad -\sum_{\iota\in\{\mathfrak{I}_{\mathrm{f}}\cup\mathfrak{I}_{\mathrm{I}}\cup\mathfrak{I}_{\mathrm{C}}\}} \nabla\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{\iota}}} - \frac{\epsilon^{\iota}\mathbf{q}^{\overline{\overline{\iota}}}}{\theta}\right)$$

$$-\nabla\cdot\left\{\epsilon^{s}\boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta}\left[\epsilon^{s}\mathbf{q}^{\overline{\overline{s}}} - \left\langle\left(\mathbf{t}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\mathpunct{:}\frac{\mathbf{C}^s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\right\}$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{P}}}\left[\epsilon^{\iota}b^{\iota} - \frac{1}{\theta}\left(\epsilon^{\iota}h^{\overline{\overline{\iota}}} + \left\langle\eta_{\iota}\frac{\mathrm{D}^{\overline{s}}(\theta-\theta)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right)\right.$$

$$\left.-\frac{1}{\theta}\left\langle\rho_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_E^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\left[\epsilon^{\iota}b^{\iota} - \frac{1}{\theta}\left(\epsilon^{\iota}h^{\overline{\overline{\iota}}} + \left\langle\eta_{\iota}\frac{\mathrm{D}'^{\overline{s}}(\theta-\theta)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right)\right.$$

$$\left.-\frac{1}{\theta}\left\langle\rho_{\iota}\frac{\mathrm{D}'^{\overline{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_E^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]$$

$$-\epsilon^{wns}b^{wns} + \frac{1}{\theta}\left(\epsilon^{wns}h^{\overline{\overline{wns}}} + \left\langle\eta_{wns}\frac{\mathrm{D}''^{\overline{s}}(\theta-\theta)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\right)$$

$$+\frac{1}{\theta}\left\langle\rho_{wns}\frac{\mathrm{D}''^{\overline{s}}\left(\mu_{wns}+\psi_{wns}-\mu^{\overline{wns}}-\psi^{\overline{wns}}-K_E^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{\epsilon^{\iota}}{\theta}\left(\mathbf{t}^{\overline{\overline{\iota}}}+p^{\iota}\mathbf{I}\right)\mathpunct{:}\mathbf{d}^{\overline{\overline{\iota}}} + \frac{\epsilon^s}{\theta}\left(\mathbf{t}^{\overline{\overline{s}}}-\mathbf{t}^s\right)\mathpunct{:}\mathbf{d}^{\overline{\overline{s}}} + \sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{\epsilon^{\iota}}{\theta}\left(\mathbf{t}^{\overline{\overline{\iota}}}-\gamma^{\iota}\mathbf{I}\right)\mathpunct{:}\mathbf{d}^{\overline{\overline{\iota}}}$$

$$+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{t}^{\overline{\overline{wns}}}+\gamma^{wns}\mathbf{I}\right)\mathpunct{:}\mathbf{d}^{\overline{\overline{wns}}}$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta}\cdot\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}} + \epsilon^{\iota}\rho^{\iota}\nabla\left(\psi^{\overline{\iota}}+\mu^{\overline{\iota}}\right) + \nabla\left(\epsilon^{\iota}p^{\iota}\right) + \sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right]$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta}\cdot\left[\nabla\left(\epsilon^{\iota}\gamma^{\iota}\right) + \sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{wns},\overline{s}}}{\theta}\cdot\left[-\nabla\left(\epsilon^{wns}\gamma^{wns}\right) - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}wns}}\overset{wns\to\kappa}{\mathbf{T}}\right]$$

$$+\frac{1}{\theta}\left\langle\left(\nabla\cdot\mathbf{t}_s - \nabla\boldsymbol{\sigma}^{\overline{\overline{s}}}\mathpunct{:}\frac{\mathbf{C}^s}{j_s}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega} - \frac{1}{\theta}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\nabla\cdot\left\langle \mathbf{n}_\kappa\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}+\langle\mathbf{n}_\kappa\mathbf{n}_\kappa\gamma_\iota\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\overline{\overline{s}}}\right]$$

$$+\frac{1}{\theta}\left\langle\left(p_w-p_n-\gamma_{wn}\nabla'\cdot\mathbf{n}_w\right)\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_w\right\rangle_{\Omega_{wn},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(p_w+\gamma_{ws}\nabla'\cdot\mathbf{n}_s\right)\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(p_n+\gamma_{ns}\nabla'\cdot\mathbf{n}_s\right)\left(\mathbf{v}_{ns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ns},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(\gamma_{wns}\kappa_N-\gamma_{wn}\sin(\varphi_{ws,wn})\right)\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(\gamma_{ws}+\gamma_{wn}\cos(\varphi_{ws,wn})-\gamma_{ns}+\gamma_{wns}\kappa_G\right)\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta}\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns}\right)\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta}\langle(\mathbf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns})\,\gamma_{wns}\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{s}}}=\Lambda\geq0.$$

Using the definitions for the geometric tensors, the approximations given by Eqs. (2.81)–(2.84), noting that

$$(\mathrm{A}.132)\qquad\begin{aligned}\nabla\cdot\left(\epsilon^\iota\mathbf{G}^\iota\cdot\mathbf{v}^{\overline{\iota},\overline{s}}\gamma^\iota\right)&=\nabla\cdot(\epsilon^\iota\mathbf{G}^\iota\gamma^\iota)\cdot\mathbf{v}^{\overline{\iota},\overline{s}}+\epsilon^\iota\mathbf{G}^\iota\gamma^\iota:\nabla\mathbf{v}^{\overline{\iota},\overline{s}}\\&=\nabla\cdot(\epsilon^\iota\mathbf{G}^\iota\gamma^\iota)\cdot\mathbf{v}^{\overline{\iota},\overline{s}}+\epsilon^\iota\mathbf{G}^\iota\gamma^\iota:\left(\mathbf{d}^{\overline{\iota}}-\mathbf{d}^{\overline{\overline{s}}}\right),\end{aligned}$$

and regrouping, the SEI becomes

$$(\mathrm{A}.133)\quad-\sum_{\iota\in\{\mathfrak{I}_{\mathrm{f}}\cup\mathfrak{I}_{\mathrm{I}}\cup\mathfrak{I}_{\mathrm{C}}\}}\nabla\cdot\left(\epsilon^\iota\boldsymbol{\varphi}^{\overline{\iota}}-\frac{\epsilon^\iota\mathbf{q}^{\overline{\overline{\iota}}}}{\theta}\right)$$

$$-\nabla\cdot\left\{\epsilon^s\boldsymbol{\varphi}^{\overline{\overline{s}}}-\frac{1}{\theta}\left[\epsilon^s\mathbf{q}^{\overline{\overline{s}}}-\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\mathbf{C}^s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\right\}$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{P}}}\left[\epsilon^\iota b^\iota-\frac{1}{\theta}\left(\epsilon^\iota h^{\overline{\overline{\iota}}}+\left\langle\eta_\iota\frac{\mathrm{D}^{\overline{s}}\left(\theta-\theta\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right)\right.$$

$$\left.-\frac{1}{\theta}\left\langle\rho_\iota\frac{\mathrm{D}^{\overline{s}}\left(\mu_\iota+\psi_\iota-\mu^{\overline{\iota}}-\psi^{\overline{\iota}}-K_E^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}\right]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left[\epsilon^{\iota}b^{\iota}-\frac{1}{\theta}\left(\epsilon^{\iota}h^{\bar{\bar{\iota}}}+\left\langle\eta_{\iota}\frac{\mathrm{D}'^{\bar{s}}\left(\theta-\theta\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right)\right.$$

$$\left.-\frac{1}{\theta}\left\langle\rho_{\iota}\frac{\mathrm{D}'^{\bar{s}}\left(\mu_{\iota}+\psi_{\iota}-\mu^{\bar{\iota}}-\psi^{\bar{\iota}}-K_{E}^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right]$$

$$-\epsilon^{wns}b^{wns}+\frac{1}{\theta}\left(\epsilon^{wns}h^{\overline{\overline{wns}}}+\left\langle\eta_{wns}\frac{\mathrm{D}''^{\bar{s}}\left(\theta-\theta\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\right)$$

$$+\frac{1}{\theta}\left\langle\rho_{wns}\frac{\mathrm{D}''^{\bar{s}}\left(\mu_{wns}+\psi_{wns}-\mu^{\overline{wns}}-\psi^{\overline{wns}}-K_{E}^{\overline{\overline{wns}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\epsilon^{\iota}}{\theta}\left(\mathbf{t}^{\bar{\bar{\iota}}}+p^{\iota}\mathbf{I}\right):\mathbf{d}^{\bar{\bar{\iota}}}+\frac{\epsilon^{s}}{\theta}\left(\mathbf{t}^{\bar{\bar{s}}}-\mathbf{t}^{s}\right):\mathbf{d}^{\bar{\bar{s}}}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\epsilon^{\iota}}{\theta}\left[\mathbf{t}^{\bar{\bar{\iota}}}-\gamma^{\iota}\left(\mathbf{I}-\mathbf{G}^{\iota}\right)\right]:\mathbf{d}^{\bar{\bar{\iota}}}+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}}\left[\mathbf{t}^{\overline{wns}}+\gamma^{wns}\left(\mathbf{I}-\mathbf{G}^{wns}\right)\right]:\mathbf{d}^{\overline{\overline{wns}}}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta}\cdot\left[\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\bar{\iota}}+\epsilon^{\iota}\rho^{\iota}\nabla\left(\psi^{\bar{\iota}}+\mu^{\bar{\iota}}\right)+\nabla\left(\epsilon^{\iota}p^{\iota}\right)+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta}\cdot\left[\nabla\cdot\left[\epsilon^{\iota}\gamma^{\iota}\left(\mathbf{I}-\mathbf{G}^{\iota}\right)\right]+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{wns},\bar{s}}}{\theta}\cdot\left[-\nabla\cdot\left[\epsilon^{wns}\gamma^{wns}\left(\mathbf{I}-\mathbf{G}^{wns}\right)\right]-\sum_{\kappa\in\mathcal{I}_{\mathrm{C}wns}}\overset{wns\to\kappa}{\mathbf{T}}\right]$$

$$+\frac{1}{\theta}\left\langle\left(\nabla\cdot\mathbf{t}_{s}-\nabla\boldsymbol{\sigma}^{\bar{\bar{s}}}:\frac{\mathbf{C}^{s}}{j_{s}}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{s},\Omega}-\frac{1}{\theta}\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{I}'\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$-\frac{1}{\theta}\left\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\mathbf{n}_{s}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\theta}\left\langle\left(p_{w}-p_{n}-\gamma_{wn}\nabla'\cdot\mathbf{n}_{w}\right)\left(\mathbf{v}_{wn}-\mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_{w}\right\rangle_{\Omega_{wn},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(p_{w}+\gamma_{ws}\nabla'\cdot\mathbf{n}_{s}\right)\left(\mathbf{v}_{ws}-\mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(p_{n}+\gamma_{ns}\nabla'\cdot\mathbf{n}_{s}\right)\left(\mathbf{v}_{ns}-\mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{ns},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(\gamma_{ws}+\gamma_{wn}\cos(\varphi_{ws,wn})-\gamma_{ns}+\gamma_{wns}\kappa_{G}\right)\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega}$$

$$-\frac{1}{\theta}\left\langle\left(\gamma_{wns}\kappa_{N}-\gamma_{wn}\sin(\varphi_{ws,wn})\right)\mathbf{n}_{s}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=\Lambda\geq0.$$

Geometric density approximations can be derived in the same manner for interfaces and common curves as they were for phases (Eqs. (2.95)–(2.97)). Starting from the gradient and transport theorems for interfaces, G[2,(3,0),0] and T[2,(3,0),0] respectively, and letting our integration be over the ws interface with function value of 1,

(A.134) $\qquad 0 = \nabla \epsilon^{ws} - \nabla \cdot \langle \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{ws},\Omega} + \langle (\nabla' \cdot \mathbf{n}_s) \mathbf{n}_s \rangle_{\Omega_{ws},\Omega} + \langle \mathbf{n}_{ws} \rangle_{\Omega_{wns},\Omega}$

and

(A.135)
$$0 = \frac{\partial \epsilon^{ws}}{\partial t} + \nabla \cdot \langle \mathbf{n}_s \mathbf{n}_s \cdot \mathbf{v}_{ws} \rangle_{\Omega_{ws},\Omega} - \langle (\nabla' \cdot \mathbf{n}_s) \, \mathbf{n}_s \cdot \mathbf{v}_{ws} \rangle_{\Omega_{ws},\Omega} - \langle \mathbf{n}_{ws} \cdot \mathbf{v}_{wns} \rangle_{\Omega_{wns},\Omega}.$$

Taking the vector product of Eq. (A.134) with the macroscale velocity of the solid phase, $\mathbf{v}^{\overline{s}}$, and adding the result to Eq. (A.135) yields:

(A.136) $\quad 0 = \dfrac{D^{\overline{s}} \epsilon^{ws}}{Dt} - \nabla \cdot \langle \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{ws},\Omega} \cdot \mathbf{v}^{\overline{s}} + \nabla \cdot \langle \mathbf{n}_s \mathbf{n}_s \cdot \mathbf{v}_{ws} \rangle_{\Omega_{ws},\Omega}$

$\qquad - \left\langle (\nabla' \cdot \mathbf{n}_s) \, \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} - \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega}.$

This means that

(A.137) $\quad \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} = \dfrac{D^{\overline{s}} \epsilon^{ws}}{Dt} - \nabla \cdot \langle \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{ws},\Omega} \cdot \mathbf{v}^{\overline{s}}$

$\qquad + \nabla \cdot \langle \mathbf{n}_s \mathbf{n}_s \cdot \mathbf{v}_{ws} \rangle_{\Omega_{ws},\Omega} - \left\langle (\nabla' \cdot \mathbf{n}_s) \, \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega}$

$\qquad \approx \dfrac{D^{\overline{s}} \epsilon^{ws}}{Dt} - \nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{s}} + \nabla \cdot \left[(\epsilon^{ws} \mathbf{G}^{ws}) \cdot \langle \mathbf{v}_{ws} \rangle_{\Omega_{ws},\Omega_{ws}} \right]$

$\qquad - J_s^{ws} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega}$

$\qquad \approx \dfrac{D^{\overline{s}} \epsilon^{ws}}{Dt} + \nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\overline{s}} + \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\overline{\overline{ws}}} - J_s^{ws} \chi_{ws}^{ss} \dfrac{D^{\overline{s}} \epsilon^s}{Dt}.$

Similarly, integrating over the ns interface yields

(A.138) $\quad \left\langle \mathbf{n}_{ns} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} \approx$

$$\frac{\mathrm{D}^{\bar{s}}\epsilon^{ns}}{\mathrm{D}t} + \nabla\boldsymbol{\cdot}(\epsilon^{ns}\mathbf{G}^{ns})\boldsymbol{\cdot}\mathbf{v}^{\overline{ns},\bar{s}} + \epsilon^{ns}\mathbf{G}^{ns}\boldsymbol{:}\mathbf{d}^{\overline{\overline{ns}}} - J_s^{ns}\chi_{ns}^{ss}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}.$$

Adding Eq. (A.137) and Eq. (A.138) produces

$$(\text{A.139}) \quad 0 \approx \frac{\mathrm{D}^{\bar{s}}\left(\epsilon^{ws} + \epsilon^{ns}\right)}{\mathrm{D}t} + \nabla\boldsymbol{\cdot}(\epsilon^{ws}\mathbf{G}^{ws})\boldsymbol{\cdot}\mathbf{v}^{\overline{ws},\bar{s}} + \nabla\boldsymbol{\cdot}(\epsilon^{ns}\mathbf{G}^{ns})\boldsymbol{\cdot}\mathbf{v}^{\overline{ns},\bar{s}}$$

$$+\epsilon^{ws}\mathbf{G}^{ws}\boldsymbol{:}\mathbf{d}^{\overline{\overline{ws}}} + \epsilon^{ns}\mathbf{G}^{ns}\boldsymbol{:}\mathbf{d}^{\overline{\overline{ns}}} - (J_s^{ws}\chi_{ws}^{ss} + J_s^{ns}\chi_{ns}^{ss})\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}.$$

We can also obtain directly by integrating over the entire solid surface

$$(\text{A.140}) \quad 0 \approx \frac{\mathrm{D}^{\bar{s}}\left(\epsilon^{ws} + \epsilon^{ns}\right)}{\mathrm{D}t} + \nabla\boldsymbol{\cdot}(\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{\cdot}\left(\chi_{ws}^{ss}\mathbf{v}^{\overline{ws},\bar{s}} + \chi_{ns}^{ss}\mathbf{v}^{\overline{ns},\bar{s}}\right)$$

$$+ (\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{:}\mathbf{d}^{\overline{\overline{ss}}} - (J_s^{ws}\chi_{ws}^{ss} + J_s^{ns}\chi_{ns}^{ss})\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}.$$

However, noting that $\mathbf{d}^{\overline{\overline{ss}}}$ is dotted with a symmetric tensor, this can be written as

$$(\text{A.141}) \qquad\qquad \mathbf{d}^{\overline{\overline{ss}}} = \chi_{ws}^{ss}\mathbf{d}^{\overline{\overline{ws}}} + \chi_{ns}^{ss}\mathbf{d}^{\overline{\overline{ns}}} + \mathbf{v}^{\overline{ws},\bar{s}}\nabla\chi_{ws}^{ss} + \mathbf{v}^{\overline{ns},\bar{s}}\nabla\chi_{ns}^{ss},$$

to obtain

$$(\text{A.142}) \quad 0 \approx \frac{\mathrm{D}^{\bar{s}}\left(\epsilon^{ws} + \epsilon^{ns}\right)}{\mathrm{D}t} + \nabla\boldsymbol{\cdot}(\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{\cdot}\left(\chi_{ws}^{ss}\mathbf{v}^{\overline{ws},\bar{s}} + \chi_{ns}^{ss}\mathbf{v}^{\overline{ns},\bar{s}}\right)$$

$$+\chi_{ws}^{ss}(\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{:}\mathbf{d}^{\overline{\overline{ws}}} + \chi_{ns}^{ss}(\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{:}\mathbf{d}^{\overline{\overline{ns}}}$$

$$+ (\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{:}\mathbf{v}^{\overline{ws},\bar{s}}\nabla\chi_{ws}^{ss} + (\epsilon^{ss}\mathbf{G}^{ss})\boldsymbol{:}\mathbf{v}^{\overline{ns},\bar{s}}\nabla\chi_{ns}^{ss}$$

$$- (J_s^{ws}\chi_{ws}^{ss} + J_s^{ns}\chi_{ns}^{ss})\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t},$$

which rearranges to

$$(\text{A.143}) \quad 0 \approx \frac{\mathrm{D}^{\bar{s}}\left(\epsilon^{ws} + \epsilon^{ns}\right)}{\mathrm{D}t} + \nabla\boldsymbol{\cdot}(\epsilon^{ws}\mathbf{G}^{ss})\boldsymbol{\cdot}\mathbf{v}^{\overline{ws},\bar{s}} + \nabla\boldsymbol{\cdot}(\epsilon^{ns}\mathbf{G}^{ss})\boldsymbol{\cdot}\mathbf{v}^{\overline{ns},\bar{s}}$$

$$+\epsilon^{ws}\mathbf{G}^{ss}\boldsymbol{:}\mathbf{d}^{\overline{\overline{ws}}} + \epsilon^{ns}\mathbf{G}^{ss}\boldsymbol{:}\mathbf{d}^{\overline{\overline{ns}}} - J_s^{ss}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t},$$

where

$$(A.144) \qquad J_s^{ss} = J_s^{ws}\chi_{ws}^{ss} + J_s^{ns}\chi_{ns}^{ss}.$$

Note that the difference between Eq. (A.139) and Eq. (A.143) resides in the use of $\mathbf{G}^{ss}$. Because independence of orientation for integration purposes has been assumed, this indeed means that

$$(A.145) \qquad \mathbf{G}^{ss} = \mathbf{G}^{ws} = \mathbf{G}^{ns}.$$

Now multiply Eq. (A.143) by χ_{ws}^{ss} and rearrange using the product rule

$$(A.146) \quad 0 \approx \frac{D^{\bar{s}}\epsilon^{ws}}{Dt} - (\epsilon^{ws} + \epsilon^{ns})\frac{D^{\bar{s}}\chi_{ws}^{ss}}{Dt} + \chi_{ws}^{ss}\nabla\cdot(\epsilon^{ws}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ws},\bar{s}}$$

$$+\chi_{ws}^{ss}\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ns},\bar{s}} + \chi_{ws}^{ss}\epsilon^{ws}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ws}}} + \chi_{ws}^{ss}\epsilon^{ns}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ns}}} - \chi_{ws}^{ss}J_s^{\overline{\overline{ss}}}\frac{D^{\bar{s}}\epsilon^s}{Dt}.$$

Since this is equal to zero, it may be subtracted from Eq. (A.137)

$$(A.147) \quad \left\langle \mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \approx$$

$$+\nabla\cdot(\epsilon^{ws}\mathbf{G}^{ws})\cdot\mathbf{v}^{\overline{ws},\bar{s}} + \epsilon^{ws}\mathbf{G}^{ws}:\mathbf{d}^{\overline{\overline{ws}}} - J_s^{ws}\chi_{ws}^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt}$$

$$+(\epsilon^{ws} + \epsilon^{ns})\frac{D^{\bar{s}}\chi_{ws}^{ss}}{Dt} - \chi_{ws}^{ss}\nabla\cdot(\epsilon^{ws}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ws},\bar{s}} - \chi_{ws}^{ss}\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ns},\bar{s}}$$

$$-\chi_{ws}^{ss}\epsilon^{ws}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ws}}} - \chi_{ws}^{ss}\epsilon^{ns}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ns}}} + \chi_{ws}^{ss}J_s^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt}.$$

Making use of Eq. (A.145) in this expression and collecting terms

$$(A.148) \quad \left\langle \mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \approx (\epsilon^{ws} + \epsilon^{ns})\frac{D^{\bar{s}}\chi_{ws}^{ss}}{Dt}$$

$$+\chi_{ns}^{ss}\nabla\cdot(\epsilon^{ws}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ws},\bar{s}} - \chi_{ws}^{ss}\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ns},\bar{s}}$$

$$+\chi_{ns}^{ss}\epsilon^{ws}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ws}}} - \chi_{ws}^{ss}\epsilon^{ns}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ns}}}.$$

In obtaining this equation, use has been made of Secondary Restriction 3 stipulating that the curvature of the solid grain surface is independent of the fluid phase it contacts. Applying Eqs. (2.22)–(2.33) to terms from Eq. (A.133) in addition to assuming independence between our geometric approximation terms and other quantities within our SEI results in the following approximations:

$$
\text{(A.149)} \quad \frac{1}{\theta}\left\langle \left(p_w - p_n - \gamma_{wn}\nabla'\cdot\mathbf{n}_w\right)\left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_w \right\rangle_{\Omega_{wn},\Omega}
$$

$$
\approx \frac{1}{\theta}\left\langle \left(p_w - p_n - \gamma_{wn}\nabla'\cdot\mathbf{n}_w\right)\right\rangle_{\Omega_{wn},\Omega_{wn}} \left(\frac{\mathrm{D}^{\bar{s}}\epsilon^w}{\mathrm{D}t} + \chi^{ss}_{ws}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}\right)
$$

$$
\approx \frac{1}{\theta}\left(p_w^{wn} - p_n^{wn} - \gamma^{wn}J_w^{wn}\right)\left(\frac{\mathrm{D}^{\bar{s}}\epsilon^w}{\mathrm{D}t} + \chi^{ss}_{ws}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}\right),
$$

$$
\text{(A.150)} \quad -\frac{1}{\theta}\left\langle \left(p_w + \gamma_{ws}\nabla'\cdot\mathbf{n}_s\right)\left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega}
$$

$$
\approx -\frac{1}{\theta}\left\langle \left(p_w + \gamma_{ws}\nabla'\cdot\mathbf{n}_s\right)\right\rangle_{\Omega_{ws},\Omega_{ws}}\chi^{ss}_{ws}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
\approx -\frac{1}{\theta}\left(p_w^{ws} + \gamma^{ws}J_s^{ws}\right)\chi^{ss}_{ws}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t},
$$

$$
\text{(A.151)} \quad -\frac{1}{\theta}\left\langle \left(p_n + \gamma_{ns}\nabla'\cdot\mathbf{n}_s\right)\left(\mathbf{v}_{ns} - \mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_s \right\rangle_{\Omega_{ns},\Omega}
$$

$$
\approx -\frac{1}{\theta}\left\langle \left(p_n + \gamma_{ns}\nabla'\cdot\mathbf{n}_s\right)\right\rangle_{\Omega_{ns},\Omega_{ns}}\chi^{ss}_{ns}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
\approx -\frac{1}{\theta}\left(p_n^{ns} + \gamma^{ns}J_s^{ns}\right)\chi^{ss}_{ns}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t},
$$

$$
\text{(A.152)} \quad -\frac{1}{\theta}\left\langle \left[\gamma_{wns}\kappa_{Nwns} - \gamma_{wn}\sin(\varphi_{ws,wn})\right]\mathbf{n}_s\cdot\left(\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega}
$$

$$
\approx -\frac{1}{\theta}\left\langle \left[\gamma_{wns}\kappa_{Nwns} - \gamma_{wn}\sin(\varphi_{ws,wn})\right]\right\rangle_{\Omega_{wns},\Omega_{wns}}\chi^{ss}_{wns}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
\approx -\frac{1}{\theta}\left[\gamma^{wns}\kappa_N^{\overline{wns}} - \gamma_{wn}^{wns}\sin(\varphi^{\overline{ws,wn}})\right]\frac{\epsilon^{wns}}{\epsilon^{ss}}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t},
$$

and

$$(A.153) \quad -\frac{1}{\theta} \Big\langle \big(\gamma_{ws} + \gamma_{wn} \cos \varphi_{ws,wn} - \gamma_{ns} + \gamma_{wns}\kappa_{Gwns}\big) \, \mathbf{n}_{ws}\cdot \Big(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\Big) \Big\rangle_{\Omega_{wns},\Omega}$$

$$\approx -\frac{1}{\theta} \big\langle \gamma_{ws} + \gamma_{wn} \cos \varphi_{ws,wn} - \gamma_{ns} + \gamma_{wns}\kappa_{Gwns} \big\rangle_{\Omega_{wns},\Omega_{wns}}$$

$$\times \Bigg[(\epsilon^{ws} + \epsilon^{ns}) \frac{\mathrm{D}^{\overline{s}}\chi^{ss}_{ws}}{\mathrm{D}t} + \chi^{ss}_{ns}\nabla\cdot (\epsilon^{ws}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ws},\overline{s}} - \chi^{ss}_{ws}\nabla\cdot (\epsilon^{ns}\mathbf{G}^{ss})\cdot\mathbf{v}^{\overline{ns},\overline{s}}$$

$$+ \chi^{ss}_{ns}\epsilon^{ws}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ws}}} - \chi^{ss}_{ws}\epsilon^{ns}\mathbf{G}^{ss}:\mathbf{d}^{\overline{\overline{ns}}} \Bigg].$$

Applying all of the above mentioned approximations along with the definitions for a macroscopically simple system, the SEI may be written as follows:

$$(A.154) \quad \sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{\epsilon^{\iota}}{\theta} \left(\mathbf{t}^{\overline{\overline{\iota}}} + p^{\iota}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\iota}}} + \frac{\epsilon^{s}}{\theta} \left(\mathbf{t}^{\overline{\overline{s}}} - \mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}} + \frac{\epsilon^{wn}}{\theta} \left[\mathbf{t}^{\overline{wn}} - \gamma^{wn}\left(\mathbf{I} - \mathbf{G}^{wn}\right)\right]:\mathbf{d}^{\overline{wn}}$$

$$+\frac{1}{\theta} \Big[\epsilon^{ws}\mathbf{t}^{\overline{\overline{ws}}} - \epsilon^{ws}\gamma^{ws}\left(\mathbf{I} - \mathbf{G}^{ws}\right)$$

$$-\chi^{ss}_{ns} \left(\gamma^{wns}_{ws} + \gamma^{wns}_{wn} \cos\varphi^{\overline{ws,wn}} - \gamma^{wns}_{ns} + \gamma^{wns}\kappa^{\overline{wns}}_{G}\right)\mathbf{G}^{ss}\Big]:\mathbf{d}^{\overline{\overline{ws}}}$$

$$+\frac{1}{\theta} \Big[\epsilon^{ns}\mathbf{t}^{\overline{\overline{ns}}} - \epsilon^{ns}\gamma^{ns}\left(\mathbf{I} - \mathbf{G}^{ns}\right)$$

$$+\chi^{ss}_{ws} \left(\gamma^{wns}_{ws} + \gamma^{wns}_{wn} \cos\varphi^{\overline{ws,wn}} - \gamma^{wns}_{ns} + \gamma^{wns}\kappa^{\overline{wns}}_{G}\right)\mathbf{G}^{ss}\Big]:\mathbf{d}^{\overline{\overline{ns}}}$$

$$+\frac{\epsilon^{wns}}{\theta^{\overline{\overline{wns}}}} \Big[\mathbf{t}^{\overline{wns}} + \gamma^{wns}\left(\mathbf{I} - \mathbf{G}^{wns}\right)\Big]:\mathbf{d}^{\overline{wns}}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{1}{\theta} \left(\epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}} + \epsilon^{\iota}\rho^{\iota}\nabla\left(\psi^{\overline{\iota}} + \mu^{\overline{\iota}}\right) - \nabla\left(\epsilon^{\iota}p^{\iota}\right) + \sum_{\kappa\in\mathcal{I}_{c\iota}} \overset{\kappa\to\iota}{\mathbf{T}}\right)\cdot\mathbf{v}^{\overline{\iota},\overline{s}}$$

$$-\frac{1}{\theta} \left(\nabla\cdot\left[\epsilon^{wn}\gamma^{wn}\left(\mathbf{I} - \mathbf{G}^{wn}\right)\right] + \sum_{\kappa\in\mathcal{I}_{cwn}} \overset{\kappa\to wn}{\mathbf{T}}\right)\cdot\mathbf{v}^{\overline{wn},\overline{s}}$$

$$-\frac{1}{\theta} \Bigg(\nabla\cdot\left[\epsilon^{ws}\gamma^{ws}\left(\mathbf{I} - \mathbf{G}^{ws}\right)\right] + \sum_{\kappa\in\mathcal{I}_{cws}} \overset{\kappa\to ws}{\mathbf{T}} + \chi^{ss}_{ns}\Big(\gamma^{wns}_{ws} + \gamma^{wns}_{wn} \cos\varphi^{\overline{ws,wn}}$$

$$-\gamma^{wns}_{ns} + \gamma^{wns}\kappa^{\overline{wns}}_{G}\Big)\nabla\cdot\left(\epsilon^{ws}\mathbf{G}^{ss}\right)\Bigg)\cdot\mathbf{v}^{\overline{ws},\overline{s}}$$

$$-\frac{1}{\theta} \Bigg(\nabla\cdot\left[\epsilon^{ns}\gamma^{ns}\left(\mathbf{I} - \mathbf{G}^{ns}\right)\right] + \sum_{\kappa\in\mathcal{I}_{cns}} \overset{\kappa\to ns}{\mathbf{T}} - \chi^{ss}_{ws}\Big(\gamma^{wns}_{ws} + \gamma^{wns}_{wn} \cos\varphi^{\overline{ws,wn}}$$

$$\left. \begin{array}{c} \left. -\gamma_{ns}^{wns} + \gamma^{wns} \kappa_G^{\overline{\overline{wns}}} \right) \nabla\cdot\left(\epsilon^{ns}\mathbf{G}^{ss}\right) \right) \cdot \mathbf{v}^{\overline{ns},\overline{s}} \end{array} \right.$$

$$-\frac{1}{\theta}\left(-\nabla\cdot\left[\epsilon^{wns}\gamma^{wns}\left(\mathbf{I}-\mathbf{G}^{wns}\right)\right] - \sum_{\kappa\in\mathfrak{I}_{cwns}} \overset{wns\to\kappa}{\mathbf{T}} \right)\cdot\mathbf{v}^{\overline{\overline{wns}},\overline{s}}$$

$$-\frac{1}{\theta}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\theta}\left(\frac{\mathrm{D}^{\overline{s}}\epsilon^w}{\mathrm{D}t} + \chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} \right)(p_w^{wn}-p_n^{wn}-\gamma^{wn}J_w^{wn})$$

$$-\frac{1}{\theta}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}\left[(p_w^{ws}+\gamma^{ws}J_s^{ws})\chi_{ws}^{ss} + (p_n^{ns}+\gamma^{ns}J_s^{ns})\chi_{ns}^{ss} + \langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}} \right.$$

$$\left. + \left(\gamma^{wns}\kappa_N^{\overline{\overline{wns}}} - \gamma_{wn}^{wns}\sin\varphi^{\overline{\overline{ws,wn}}}\right)\frac{\epsilon^{wns}}{\epsilon^{ss}} \right]$$

$$-\frac{1}{\theta}\epsilon^{ss}\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}\left(\gamma_{ws}^{wns} + \gamma_{wn}^{wns}\cos\varphi^{\overline{\overline{ws,wn}}} - \gamma_{ns}^{wns} + \gamma^{wns}\kappa_G^{\overline{\overline{wns}}} \right) = \Lambda \geq 0.$$

A.6. Dynamic Conditions

Approximate relations for the evolution of geometric variables have been obtained through the application of time and space averaging theorems [93]. The geometric equations are derived from G[2,(3,0),0] and T[2,(3,0),0] as follows. For the surface area of the fluid-fluid interface, relations may be obtained from using the same theorems applied to the *wn* interface. These equations are, respectively:

(A.155) $\qquad 0 = \nabla\epsilon^{wn} - \nabla\cdot\langle\mathbf{n}_w\mathbf{n}_w\rangle_{\Omega_{wn},\Omega} + \left\langle\left(\nabla'\cdot\mathbf{n}_w\right)\mathbf{n}_w\right\rangle_{\Omega_{wn},\Omega} + \langle\mathbf{n}_{wn}\rangle_{\Omega_{wns},\Omega}$

and

(A.156) $\quad 0 = \dfrac{\partial\epsilon^{wn}}{\partial t} + \nabla\cdot\langle\mathbf{n}_w\mathbf{n}_w\cdot\mathbf{v}_{wn}\rangle_{\Omega_{wn},\Omega} - \left\langle\left(\nabla'\cdot\mathbf{n}_w\right)\mathbf{n}_w\cdot\mathbf{v}_{wn}\right\rangle_{\Omega_{wn},\Omega}$

$\qquad -\langle\mathbf{n}_{wn}\cdot\mathbf{v}_{wns}\rangle_{\Omega_{wns},\Omega}.$

Taking the vector product of Eq. (A.155) with the macroscale velocity of the solid phase, $\mathbf{v}^{\overline{s}}$, and adding the result to Eq. (A.156),

$$\text{(A.157)} \quad 0 = \frac{D^{\bar{s}}\epsilon^{wn}}{Dt} + \nabla\cdot\langle\mathbf{n}_w\mathbf{n}_w\cdot\mathbf{v}_{wn}\rangle_{\Omega_{wn},\Omega} - \nabla\cdot\langle\mathbf{n}_w\mathbf{n}_w\rangle_{\Omega_{wn},\Omega}\cdot\mathbf{v}^{\bar{s}}$$

$$-\left\langle\left(\nabla'\cdot\mathbf{n}_w\right)\mathbf{n}_w\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wn},\Omega} - \left\langle\mathbf{n}_{wn}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega}.$$

This equation contains no approximations , however the presence of the normal vectors in the integrals makes these difficult to evaluate exactly. Making use of the geometric parameter definitions the integral terms may be approximated as

$$\text{(A.158)} \quad \frac{D^{\bar{s}}\epsilon^{wn}}{Dt} \approx -\nabla\cdot\left(\epsilon^{wn}\mathbf{G}^{wn}\right)\cdot\mathbf{v}^{\overline{wn,\bar{s}}} - \epsilon^{wn}\mathbf{G}^{wn}:\mathbf{d}^{\overline{\overline{wn}}} + J_w^{wn}\left(\frac{D^{\bar{s}}\epsilon^w}{Dt} + \chi_{ws}^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt}\right)$$

$$+\left\langle\mathbf{n}_{wn}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega}.$$

From geometric considerations, the unit vector $\mathbf{n}_{wn} = \mathbf{n}_{ws}\cos\varphi_{ws,wn} - \mathbf{n}_s\sin\varphi_{ws,wn}$. Now Eq. (A.158) may be written as

$$\text{(A.159)} \quad \frac{D^{\bar{s}}\epsilon^{wn}}{Dt} - J_w^{wn}\left(\frac{D^{\bar{s}}\epsilon^w}{Dt} + \chi_{ws}^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt}\right) \approx -\nabla\cdot\left(\epsilon^{wn}\mathbf{G}^{wn}\right)\cdot\mathbf{v}^{\overline{wn,\bar{s}}} - \epsilon^{wn}\mathbf{G}^{wn}:\mathbf{d}^{\overline{\overline{wn}}}$$

$$+\cos\varphi^{\overline{ws,wn}}\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega} - \sin\varphi^{\overline{ws,wn}}\frac{\epsilon^{wns}}{\epsilon^{ss}}\frac{D^{\bar{s}}\epsilon^s}{Dt}.$$

Similarly for the fluid-solid interfaces

$$\text{(A.160)} \quad \frac{D^{\bar{s}}\epsilon^{ws}}{Dt} - J_s^{ws}\chi_{ws}^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt} \approx -\nabla\cdot\left(\epsilon^{ws}\mathbf{G}^{ws}\right)\cdot\mathbf{v}^{\overline{ws,\bar{s}}} - \epsilon^{ws}\mathbf{G}^{ws}:\mathbf{d}^{\overline{\overline{ws}}}$$

$$+\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega},$$

and

$$\text{(A.161)} \quad \frac{D^{\bar{s}}\epsilon^{ns}}{Dt} - J_s^{ns}\chi_{ns}^{ss}\frac{D^{\bar{s}}\epsilon^s}{Dt} \approx -\nabla\cdot\left(\epsilon^{ns}\mathbf{G}^{ns}\right)\cdot\mathbf{v}^{\overline{ns,\bar{s}}} - \epsilon^{ns}\mathbf{G}^{ns}:\mathbf{d}^{\overline{\overline{ns}}}$$

$$-\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wns},\Omega}.$$

For the common curve, G[1,(3,0),0] and T[1,(3,0),0] are used for the wns domain to yield

$$\text{(A.162)} \quad \frac{D^{\bar{s}}\epsilon^{wns}}{Dt} = -\nabla\cdot\left(\epsilon^{wns}\mathbf{G}^{wns}\right)\cdot\mathbf{v}^{\overline{wns,\bar{s}}} - \epsilon^{wns}\mathbf{G}^{wns}:\mathbf{d}^{\overline{\overline{wns}}}$$

$$-\left\langle \mathbf{l}_{wns} \cdot \nabla \mathbf{l}_{wns} \cdot \left(\mathbf{w} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wns},\Omega},$$

and

(A.163) $\dfrac{D^{\bar{s}} \epsilon^{wns}}{Dt} = -\nabla \cdot (\epsilon^{wns} \mathbf{G}^{wns}) \cdot \mathbf{v}^{\overline{wns},\bar{s}} - \epsilon^{wns} \mathbf{G}^{wns} {:} \mathbf{d}^{\overline{\overline{wns}}}$

$\qquad -\kappa_N^{\overline{\overline{wns}}} \dfrac{\epsilon^{wns}}{\epsilon^{ss}} \dfrac{D^{\bar{s}} \epsilon^s}{Dt} - \kappa_G^{\overline{\overline{wns}}} \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wns},\Omega}.$

The objective now is to combine Eqs. (A.159)–(A.161) and Eq. (A.163) to eliminate the integrals that appear. Summing Eq. (A.160) and Eq. (A.161) gives us

(A.164) $\dfrac{D^{\bar{s}} (\epsilon^{ws} + \epsilon^{ns})}{Dt} - (J_s^{ws} \chi_{ws}^{ss} + J_s^{ns} \chi_{ns}^{ss}) \dfrac{D^{\bar{s}} \epsilon^s}{Dt}$

$\qquad \approx -\nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\bar{s}} - \epsilon^{ws} \mathbf{G}^{ws} {:} \mathbf{d}^{\overline{\overline{ws}}} - \nabla \cdot (\epsilon^{ns} \mathbf{G}^{ns}) \cdot \mathbf{v}^{\overline{ns},\bar{s}}$

$\qquad -\epsilon^{ns} \mathbf{G}^{ns} {:} \mathbf{d}^{\overline{\overline{ns}}},$

or

(A.165) $\dfrac{D^{\bar{s}} (\epsilon^{ws} + \epsilon^{ns})}{Dt} - J_s^{ss} \dfrac{D^{\bar{s}} \epsilon^s}{Dt} \approx -\nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\bar{s}} - \epsilon^{ws} \mathbf{G}^{ws} {:} \mathbf{d}^{\overline{\overline{ws}}}$

$\qquad -\nabla \cdot (\epsilon^{ns} \mathbf{G}^{ns}) \cdot \mathbf{v}^{\overline{ns},\bar{s}} - \epsilon^{ns} \mathbf{G}^{ns} {:} \mathbf{d}^{\overline{\overline{ns}}}.$

It is desirable to obtain an expression for the change in the fraction of the solid surface in contact with the non-wetting phase, χ_{ns}^{ss}. This can be done by substituting $\chi_{ns}^{ss} \epsilon^{ss}$ for ϵ^{ns} in Eq. (A.161)) and then using the equation for the entire solid surface, Eq. (A.143) to eliminate $\dfrac{D^{\bar{s}} \epsilon^{ss}}{Dt}$ from the result. The result of these manipulations is:

(A.166) $0 = \epsilon^{ss} \dfrac{D^{\bar{s}} \chi_{ns}^{ss}}{Dt} + (1 - \chi_{ns}^{ss}) \nabla \cdot (\epsilon^{ns} \mathbf{G}^{ns}) \cdot \mathbf{v}^{\overline{ns},\bar{s}} + (1 - \chi_{ns}^{ss}) \epsilon^{ns} \mathbf{G}^{ns} {:} \mathbf{d}^{\overline{\overline{ns}}}$

$\qquad -\chi_{ns}^{ss} (J_s^{ns} - J_s^{ss}) \dfrac{D^{\bar{s}} \epsilon^s}{Dt} - \chi_{ns}^{ss} \nabla \cdot (\epsilon^{ws} \mathbf{G}^{ws}) \cdot \mathbf{v}^{\overline{ws},\bar{s}} - \chi_{ns}^{ss} \epsilon^{ws} \mathbf{G}^{ws} {:} \mathbf{d}^{\overline{\overline{ws}}}$

$\qquad +\left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wns},\Omega}.$

Multiply this equation by $\cos\varphi^{\overline{\overline{ws,wn}}}$ and add to Eq. (A.159) to obtain

$$
\text{(A.167)} \quad 0 = \frac{\mathrm{D}^{\overline{s}}\epsilon^{wn}}{\mathrm{D}t} + \epsilon^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\chi^{ss}_{ns}}{\mathrm{D}t} - \cos\varphi^{\overline{\overline{ws,wn}}}\chi^{ss}_{ns}\left(J^{ns}_s - J^{ss}_s\right)\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
+\nabla\cdot(\epsilon^{wn}\mathbf{G}^{wn})\cdot\mathbf{v}^{\overline{wn,\overline{s}}} + \epsilon^{wn}\mathbf{G}^{wn}{:}\mathbf{d}^{\overline{\overline{wn}}} - J^{wn}_w\left(\frac{\mathrm{D}^{\overline{s}}\epsilon^w}{\mathrm{D}t} + \chi^{ss}_{ws}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}\right)
$$

$$
-\chi^{ss}_{ns}\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ns})\cdot\mathbf{v}^{\overline{ns,\overline{s}}} + \nabla\cdot(\epsilon^{ws}\mathbf{G}^{ws})\cdot\mathbf{v}^{\overline{ws,\overline{s}}}\right\}
$$

$$
-\chi^{ss}_{ns}\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\epsilon^{ns}\mathbf{G}^{ns}{:}\mathbf{d}^{\overline{\overline{ns}}} + \epsilon^{ws}\mathbf{G}^{ws}{:}\mathbf{d}^{\overline{\overline{ws}}}\right\}
$$

$$
+\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ns})\cdot\mathbf{v}^{\overline{ns,\overline{s}}} + \epsilon^{ns}\mathbf{G}^{ns}{:}\mathbf{d}^{\overline{\overline{ns}}}\right\}
$$

$$
+\frac{\epsilon^{wns}}{\epsilon^{ss}}\sin\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}.
$$

Now note that

$$
\text{(A.168)} \quad 0 = \frac{\mathrm{D}^{\overline{s}}\epsilon^n}{\mathrm{D}t} + \left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{ns} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ns},\Omega} + \left\langle\mathbf{n}_w\cdot\left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}
$$

$$
\approx \frac{\mathrm{D}^{\overline{s}}\epsilon^n}{\mathrm{D}t} + \chi^{ss}_{ns}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} + \frac{\mathrm{D}^{\overline{s}}\epsilon^w}{\mathrm{D}t} + \chi^{ss}_{ws}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t},
$$

which multiplying by J^{wn}_w and adding to Eq. (A.167)) gives us

$$
\text{(A.169)} \quad 0 \approx \frac{\mathrm{D}^{\overline{s}}\epsilon^{wn}}{\mathrm{D}t} + \epsilon^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\chi^{ss}_{ns}}{\mathrm{D}t} - \cos\varphi^{\overline{\overline{ws,wn}}}\chi^{ss}_{ns}\left(J^{ns}_s - J^{ss}_s\right)\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
+\nabla\cdot(\epsilon^{wn}\mathbf{G}^{wn})\cdot\mathbf{v}^{\overline{wn,\overline{s}}} + \epsilon^{wn}\mathbf{G}^{wn}{:}\mathbf{d}^{\overline{\overline{wn}}}
$$

$$
-\chi^{ss}_{ns}\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ns})\cdot\mathbf{v}^{\overline{ns,\overline{s}}} + \nabla\cdot(\epsilon^{ws}\mathbf{G}^{ws})\cdot\mathbf{v}^{\overline{ws,\overline{s}}}\right\}
$$

$$
-\chi^{ss}_{ns}\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\epsilon^{ns}\mathbf{G}^{ns}{:}\mathbf{d}^{\overline{\overline{ns}}} + \epsilon^{ws}\mathbf{G}^{ws}{:}\mathbf{d}^{\overline{\overline{ws}}}\right\}
$$

$$
+\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ns})\cdot\mathbf{v}^{\overline{ns,\overline{s}}} + \epsilon^{ns}\mathbf{G}^{ns}{:}\mathbf{d}^{\overline{\overline{ns}}}\right\}
$$

$$
+\chi^{ss}_{wns}\sin\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} + J^{wn}_w\frac{\mathrm{D}^{\overline{s}}\epsilon^n}{\mathrm{D}t} + J^{wn}_w\chi^{ss}_{ns}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
= \frac{\mathrm{D}^{\overline{s}}\epsilon^{wn}}{\mathrm{D}t} - \epsilon^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\chi^{ss}_{ws}}{\mathrm{D}t} - \cos\varphi^{\overline{\overline{ws,wn}}}\chi^{ss}_{ns}\left(J^{ns}_s - J^{ss}_s\right)\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}
$$

$$
+\nabla\cdot(\epsilon^{wn}\mathbf{G}^{wn})\cdot\mathbf{v}^{\overline{wn,\overline{s}}} + \epsilon^{wn}\mathbf{G}^{wn}{:}\mathbf{d}^{\overline{\overline{wn}}}
$$

$$
-\chi^{ss}_{ns}\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\nabla\cdot(\epsilon^{ns}\mathbf{G}^{ns})\cdot\mathbf{v}^{\overline{ns,\overline{s}}} + \nabla\cdot(\epsilon^{ws}\mathbf{G}^{ws})\cdot\mathbf{v}^{\overline{ws,\overline{s}}}\right\}
$$

$$-\chi_{ns}^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\epsilon^{ns}\mathbf{G}^{ns}\mathbf{:d}^{\overline{\overline{ns}}}+\epsilon^{ws}\mathbf{G}^{ws}\mathbf{:d}^{\overline{\overline{ws}}}\right\}$$

$$+\cos\varphi^{\overline{\overline{ws,wn}}}\left\{\nabla\mathbf{\cdot}(\epsilon^{ns}\mathbf{G}^{ns})\mathbf{\cdot v}^{\overline{ns,\overline{s}}}+\epsilon^{ns}\mathbf{G}^{ns}\mathbf{:d}^{\overline{\overline{ns}}}\right\}$$

$$+\frac{\epsilon^{wns}}{\epsilon^{ss}}\sin\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}-J_{w}^{wn}\frac{\mathrm{D}^{\overline{s}}\epsilon^{w}}{\mathrm{D}t}-J_{w}^{wn}\chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t},$$

or

$$(\text{A.170})\quad\frac{\mathrm{D}^{\overline{s}}\epsilon^{wn}}{\mathrm{D}t}-\epsilon^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}-J_{w}^{wn}\frac{\mathrm{D}^{\overline{s}}\epsilon^{w}}{\mathrm{D}t}$$

$$-\left(\chi_{ws}^{ss}J_{w}^{wn}-\chi_{wns}^{ss}\sin\varphi^{\overline{\overline{ws,wn}}}\right)\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}$$

$$\approx\chi_{ns}^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\left(\nabla\mathbf{\cdot}(\epsilon^{ws}\mathbf{G}^{ws})\mathbf{\cdot v}^{\overline{ws,\overline{s}}}+\epsilon^{ws}\mathbf{G}^{ws}\mathbf{:d}^{\overline{\overline{ws}}}\right)$$

$$-\chi_{ws}^{ss}\cos\varphi^{\overline{\overline{ws,wn}}}\left(\nabla\mathbf{\cdot}(\epsilon^{ns}\mathbf{G}^{ns})\mathbf{\cdot v}^{\overline{ns,\overline{s}}}+\epsilon^{ns}\mathbf{G}^{ns}\mathbf{:d}^{\overline{\overline{ns}}}\right)$$

$$-\nabla\mathbf{\cdot}(\epsilon^{wn}\mathbf{G}^{wn})\mathbf{\cdot v}^{\overline{wn,\overline{s}}}-\epsilon^{wn}\mathbf{G}^{wn}\mathbf{:d}^{\overline{\overline{wn}}}.$$

Multiplying Eq. (A.166) by $\kappa_{G}^{\overline{\overline{wns}}}$ and subtracting it from Eq. (A.163)

$$(\text{A.171})\quad0\approx\frac{\mathrm{D}^{\overline{s}}\epsilon^{wns}}{\mathrm{D}t}+\nabla\mathbf{\cdot}(\epsilon^{wns}\mathbf{G}^{wns})\mathbf{\cdot v}^{\overline{wns,\overline{s}}}+\epsilon^{wns}\mathbf{G}^{wns}\mathbf{:d}^{\overline{\overline{wns}}}$$

$$+\kappa_{N}^{\overline{\overline{wns}}}\chi_{wns}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}-\kappa_{G}^{\overline{\overline{wns}}}\epsilon^{ss}\frac{\mathrm{D}^{\overline{s}}\chi_{ns}^{ss}}{\mathrm{D}t}-\kappa_{G}^{\overline{\overline{wns}}}\chi_{ws}^{ss}\nabla\mathbf{\cdot}(\epsilon^{ns}\mathbf{G}^{ns})\mathbf{\cdot v}^{\overline{ns,\overline{s}}}$$

$$-\kappa_{G}^{\overline{\overline{wns}}}\chi_{ws}^{ss}\epsilon^{ns}\mathbf{G}^{ns}\mathbf{:d}^{\overline{\overline{ns}}}+\kappa_{G}^{\overline{\overline{wns}}}\chi_{ns}^{ss}\left(J_{s}^{ns}-J_{s}^{ss}\right)\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}$$

$$+\kappa_{G}^{\overline{\overline{wns}}}\chi_{ns}^{ss}\nabla\mathbf{\cdot}(\epsilon^{ws}\mathbf{G}^{ws})\mathbf{\cdot v}^{\overline{ws,\overline{s}}}+\kappa_{G}^{\overline{\overline{wns}}}\chi_{ns}^{ss}\epsilon^{ws}\mathbf{G}^{ws}\mathbf{:d}^{\overline{\overline{ws}}},$$

or

$$(\text{A.172})\quad\frac{\mathrm{D}^{\overline{s}}\epsilon^{wns}}{\mathrm{D}t}+\kappa_{G}^{\overline{\overline{wns}}}(\epsilon^{ws}+\epsilon^{ns})\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}+\chi_{wns}^{ss}\kappa_{N}^{\overline{\overline{wns}}}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}$$

$$\approx-\kappa_{G}^{\overline{\overline{wns}}}\chi_{ns}^{ss}\nabla\mathbf{\cdot}(\epsilon^{ws}\mathbf{G}^{ws})\mathbf{\cdot v}^{\overline{ws,\overline{s}}}-\kappa_{G}^{\overline{\overline{wns}}}\chi_{ns}^{ss}\epsilon^{ws}\mathbf{G}^{ws}\mathbf{:d}^{\overline{\overline{ws}}}$$

$$+\kappa_{G}^{\overline{\overline{wns}}}\chi_{ws}^{ss}\nabla\mathbf{\cdot}(\epsilon^{ns}\mathbf{G}^{ns})\mathbf{\cdot v}^{\overline{ns,\overline{s}}}+\kappa_{G}^{\overline{\overline{wns}}}\chi_{ws}^{ss}\epsilon^{ns}\mathbf{G}^{ns}\mathbf{:d}^{\overline{\overline{ns}}}$$

$$-\nabla\mathbf{\cdot}(\epsilon^{wns}\mathbf{G}^{wns})\mathbf{\cdot v}^{\overline{wns,\overline{s}}}-\epsilon^{wns}\mathbf{G}^{wns}\mathbf{:d}^{\overline{\overline{wns}}}.$$

TCAT9: Transition Region Details and Calculations

B.1. Phase Equations

Consider the overall conservation of total energy equation for a phase at the microscale, which may be written as

$$
\text{(B.1)} \quad \frac{\partial}{\partial t}\left[E_{i\iota} + \rho_{\iota}\omega_{i\iota}\left(\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2} + \psi_{i\iota}\right)\right] + \nabla\cdot\left\{\left[E_{i\iota} + \rho_{\iota}\omega_{i\iota}\left(\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2} + \psi_{i\iota}\right)\right]\mathbf{v}_{i\iota}\right\}
$$

$$
- \nabla\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}) - \psi_{i\iota}r_{i\iota} - h_{i\iota} - e_{i\iota} - \mathbf{p}_{i\iota}\cdot\mathbf{v}_{i\iota} - \frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2}r_{i\iota}
$$

$$
- \rho_{\iota}\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t} = 0 \qquad \text{for } \iota \in \mathcal{I}_{\mathrm{P}},
$$

where ι is a phase qualifier that is subscripted for microscale quantities, i is a species qualifier that is subscripted for microscale quantities, $\mathcal{I}_{\mathrm{P}}$ is the index set of phases, $E_{i\iota}$ is the internal energy density, ρ_{ι} is the mass density, $\omega_{i\iota}$ is the mass fraction of species i in the ι entity, $\mathbf{v}_{i\iota}$ is the velocity vector for species i in entity ι, $\psi_{i\iota}$ is the body source potential, $\mathbf{t}_{i\iota}$ is the stress tensor, $\mathbf{q}_{i\iota}$ is the non-advective heat flux density vector, $r_{i\iota}$ is inter-species reaction rate, $h_{i\iota}$ is the heat source density, $e_{i\iota}$ is the inter-species rate of transfer of internal energy, and $\mathbf{p}_{i\iota}$ is the inter-species rate of transfer of momentum. The interspecies transfer and reaction terms include the effects of all other species on species i.

Applying an instance of the averaging operator given by Eq. (3.1) to Eq. (B.1) yields

$$
\text{(B.2)} \quad \left\langle\frac{\partial}{\partial t}\left[E_{i\iota} + \rho_{\iota}\omega_{i\iota}\left(\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2} + \psi_{i\iota}\right)\right]\right\rangle_{\Omega_{\iota},\Omega}
$$

$$
+ \left\langle\nabla\cdot\left\{\left[E_{i\iota} + \rho_{\iota}\omega_{i\iota}\left(\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2} + \psi_{i\iota}\right)\right]\mathbf{v}_{i\iota}\right\}\right\rangle_{\Omega_{\iota},\Omega}
$$

$$
- \langle\nabla\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota} + \mathbf{q}_{i\iota})\rangle_{\Omega_{\iota},\Omega} - \langle\psi_{i\iota}r_{i\iota}\rangle_{\Omega_{\iota},\Omega} - \langle h_{i\iota}\rangle_{\Omega_{\iota},\Omega} - \langle e_{i\iota}\rangle_{\Omega_{\iota},\Omega}
$$

$$
- \langle\mathbf{p}_{i\iota}\cdot\mathbf{v}_{i\iota}\rangle_{\Omega_{\iota},\Omega} - \left\langle\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2}r_{i\iota}\right\rangle_{\Omega_{\iota},\Omega} - \left\langle\rho_{\iota}\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_{\iota},\Omega} = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{P}}.
$$

Eq. (B.2) contains averages of terms involving differential operators, and we wish to transform these to differential operators applied to averages. We also wish to accomplish this transformation, while evaluating the dimension corresponding to the transition region change at the megascale and the other two dimensions at the macroscale. Applying Theorems D[3,(2,0),1] and T[3,(2,0),1] given by Eqs. (3.2) and (3.4) to Eq. (B.2) and rearranging terms yields

(B.3)
$$
\frac{\partial'}{\partial t} \left\langle E_{\iota\iota} + \rho_\iota \omega_{\iota\iota} \left(\frac{\mathbf{v}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota}}{2} + \psi_{\iota\iota} \right) \right\rangle_{\Omega_\iota, \Omega}
$$
$$
+ \nabla' \cdot \left\langle \left[E_{\iota\iota} + \rho_\iota \omega_{\iota\iota} \left(\frac{\mathbf{v}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota}}{2} + \psi_{\iota\iota} \right) \right] \mathbf{v}_{\iota\iota} \right\rangle_{\Omega_\iota, \Omega}
$$
$$
- \nabla' \cdot \langle \mathbf{t}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota} + \mathbf{q}_{\iota\iota} \rangle_{\Omega_\iota, \Omega} - \langle \psi_{\iota\iota} r_{\iota\iota} \rangle_{\Omega_\iota, \Omega} - \langle h_{\iota\iota} \rangle_{\Omega_\iota, \Omega} - \langle e_{\iota\iota} \rangle_{\Omega_\iota, \Omega}
$$
$$
- \langle \mathbf{p}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota} \rangle_{\Omega_\iota, \Omega} - \left\langle \frac{\mathbf{v}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota}}{2} r_{\iota\iota} \right\rangle_{\Omega_\iota, \Omega} - \left\langle \rho_\iota \omega_{\iota\iota} \frac{\partial \psi_{\iota\iota}}{\partial t} \right\rangle_{\Omega_\iota, \Omega}
$$
$$
+ \sum_{\kappa \in \mathcal{I}_{C\iota}} \left\langle \left[E_{\iota\iota} + \rho_\iota \omega_{\iota\iota} \left(\frac{\mathbf{v}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota}}{2} + \psi_{\iota\iota} \right) \right] \mathbf{n}_\iota \cdot (\mathbf{v}_{\iota\iota} - \mathbf{v}_\kappa) \right\rangle_{\Omega_\kappa, \Omega}
$$
$$
+ \left\langle \left[E_{\iota\iota} + \rho_\iota \omega_{\iota\iota} \left(\frac{\mathbf{v}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota}}{2} + \psi_{\iota\iota} \right) \right] \mathbf{e} \cdot (\mathbf{v}_{\iota\iota} - \mathbf{v}_{\text{ext}}) \right\rangle_{\Gamma_{\iota M}, \Omega}
$$
$$
- \sum_{\kappa \in \mathcal{I}_{C\iota}} \langle \mathbf{n}_\iota \cdot (\mathbf{t}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota} + \mathbf{q}_{\iota\iota}) \rangle_{\Omega_\kappa, \Omega}
$$
$$
- \langle \mathbf{e} \cdot (\mathbf{t}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota} + \mathbf{q}_{\iota\iota}) \rangle_{\Gamma_{\iota M}, \Omega} = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{P}}.
$$

Considering Eq. (B.3) term by term to evaluate the averaging operators gives for the time derivative term

(B.4)
$$
\frac{\partial'}{\partial t} \left\langle E_{\iota\iota} + \rho_\iota \omega_{\iota\iota} \left(\frac{\mathbf{v}_{\iota\iota} \cdot \mathbf{v}_{\iota\iota}}{2} + \psi_{\iota\iota} \right) \right\rangle_{\Omega_\iota, \Omega}
$$
$$
= \frac{\partial'}{\partial t} \left[E^{\overline{\overline{\iota\iota}}} + \epsilon^\iota \rho^\iota \omega^{\overline{\iota\iota}} \left(\frac{\mathbf{v}^{\overline{\iota\iota}} \cdot \mathbf{v}^{\overline{\iota\iota}}}{2} + K_E^{\overline{\overline{\iota\iota}}} + \psi^{\overline{\iota\iota}} \right) \right],
$$

or

(B.5)
$$
\frac{\partial'}{\partial t} \langle E_{T\iota\iota} \rangle_{\Omega_\iota, \Omega} = \frac{\partial'}{\partial t} E_T^{\overline{\overline{\iota\iota}}},
$$

where

$$E_{T\iota\iota} \;=\; E_{\iota\iota} + \rho_\iota\omega_{\iota\iota}\left(\frac{\mathbf{v}_{\iota\iota}\boldsymbol{\cdot}\mathbf{v}_{\iota\iota}}{2} + \psi_{\iota\iota}\right), \tag{B.6}$$

$$E_T^{\overline{\overline{i\iota}}} \;=\; E^{\overline{\overline{i\iota}}} + \epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\left(\frac{\mathbf{v}^{\overline{i\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{i\iota}}}{2} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}}\right), \tag{B.7}$$

$$E_T^{\overline{\overline{i\iota}}} \;=\; \langle E_{T\iota\iota}\rangle_{\Omega_\iota,\Omega}, \tag{B.8}$$

$$E^{\overline{\overline{i\iota}}} \;=\; \langle E_{\iota\iota}\rangle_{\Omega_\iota,\Omega}, \tag{B.9}$$

$$\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}K_E^{\overline{\overline{i\iota}}} \;=\; \left\langle \rho_\iota\omega_{\iota\iota}\frac{\left(\mathbf{v}_{\iota\iota}-\mathbf{v}^{\overline{i\iota}}\right)\boldsymbol{\cdot}\left(\mathbf{v}_{\iota\iota}-\mathbf{v}^{\overline{i\iota}}\right)}{2}\right\rangle_{\Omega_\iota,\Omega}, \tag{B.10}$$

$$\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\psi^{\overline{i\iota}} \;=\; \langle \rho_\iota\omega_{\iota\iota}\psi_{\iota\iota}\rangle_{\Omega_\iota,\Omega}. \tag{B.11}$$

Introducing dispersion velocity $\mathbf{u}^{\overline{\overline{i\iota}}} = \mathbf{v}^{\overline{i\iota}} - \mathbf{v}^{\overline{\iota}}$, we can write Eq. (B.7) in the following form

$$E_T^{\overline{\overline{i\iota}}} = E^{\overline{\overline{i\iota}}} + \epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\left(\frac{\mathbf{v}^{\overline{\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}}}{2} + \frac{\mathbf{u}^{\overline{\overline{i\iota}}}\boldsymbol{\cdot}\mathbf{u}^{\overline{\overline{i\iota}}}}{2} + \mathbf{u}^{\overline{\overline{i\iota}}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}}\right). \tag{B.12}$$

For the first divergence term in Eq. (B.3) things are a bit more complicated by the existence of the product of the internal and kinetic energy terms with the velocity. This term can be written as

$$\nabla^\backprime\boldsymbol{\cdot}\langle E_{T\iota\iota}\mathbf{v}_{\iota\iota}\rangle_{\Omega_\iota,\Omega} = \tag{B.13}$$

$$\nabla^\backprime\boldsymbol{\cdot}\left\langle\left[\frac{E_T^{\overline{\overline{i\iota}}}}{\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}} + \left(\frac{E_{T\iota\iota}}{\rho_\iota\omega_{\iota\iota}} - \frac{E_T^{\overline{\overline{i\iota}}}}{\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\right]\rho_\iota\omega_{\iota\iota}\left[\mathbf{v}^{\overline{i\iota}} + \left(\mathbf{v}_{\iota\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\rangle_{\Omega_\iota,\Omega},$$

or

$$\nabla^\backprime\boldsymbol{\cdot}\langle E_{T\iota\iota}\mathbf{v}_{\iota\iota}\rangle_{\Omega_\iota,\Omega} = \nabla^\backprime\boldsymbol{\cdot}\left(E_T^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{i\iota}}\right) + \nabla^\backprime\boldsymbol{\cdot}\left\langle E_{T\iota\iota}\left(\mathbf{v}_{\iota\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}, \tag{B.14}$$

or

$$\nabla^\backprime\boldsymbol{\cdot}\langle E_{T\iota\iota}\mathbf{v}_{\iota\iota}\rangle_{\Omega_\iota,\Omega} = \nabla^\backprime\boldsymbol{\cdot}\left(E_T^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{\iota}}\right) + \nabla^\backprime\boldsymbol{\cdot}\left(E_T^{\overline{\overline{i\iota}}}\mathbf{u}^{\overline{\overline{i\iota}}}\right) + \nabla^\backprime\boldsymbol{\cdot}\left\langle E_{T\iota\iota}\left(\mathbf{v}_{\iota\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}. \tag{B.15}$$

Evaluating the last term in Eq. (B.15) gives

$$\text{(B.16)} \quad \nabla' \cdot \left\langle E_{T i \iota} \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \right\rangle_{\Omega_\iota, \Omega} = \nabla' \cdot \left\langle \left(E_{i \iota} + \rho_\iota \omega_{i \iota} \psi_{i \iota} \right) \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \nabla' \cdot \left\langle \left(\mathbf{v}^{\overline{i \iota}} \cdot \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) + \frac{\left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \cdot \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right)}{2} \right) \right.$$

$$\left. \rho_\iota \omega_{i \iota} \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \right\rangle_{\Omega_\iota, \Omega}.$$

The second divergence term in Eq. (B.3) may be written as

$$\text{(B.17)} \quad \nabla' \cdot \langle \mathbf{t}_{i \iota} \cdot \mathbf{v}_{i \iota} + \mathbf{q}_{i \iota} \rangle_{\Omega_\iota, \Omega} = \nabla' \cdot \left\langle \mathbf{t}_{i \iota} \cdot \mathbf{v}^{\overline{i \iota}} + \mathbf{t}_{i \iota} \cdot \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) + \mathbf{q}_{i \iota} \right\rangle_{\Omega_\iota, \Omega}.$$

Combining terms from Eqs. (B.16) and (B.17) and dropping the divergence operator, which is applied to all terms, gives

$$\text{(B.18)} \quad \epsilon^\iota \mathbf{t}^{\overline{\overline{i \iota}}} \cdot \mathbf{v}^{\overline{i \iota}} + \epsilon^\iota \mathbf{q}^{\overline{\overline{i \iota}}} = \left\langle \left[\mathbf{t}_{i \iota} - \rho_\iota \omega_{i \iota} \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \right] \cdot \mathbf{v}^{\overline{i \iota}} \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \left\langle \mathbf{q}_{i \iota} - \left[E_{i \iota} + \rho_\iota \omega_{i \iota} \left(\frac{\left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \cdot \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right)}{2} + \psi_{i \iota} \right) \right] \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \left\langle \mathbf{t}_{i \iota} \cdot \left(\mathbf{v}_{i \iota} - \mathbf{v}^{\overline{i \iota}} \right) \right\rangle_{\Omega_\iota, \Omega},$$

where the first term on the right hand side (RHS) is the dot product of the macroscale stress tensor and velocity for a species in a phase and the second two terms on the RHS sum to the macroscale heat source vector for a species in a phase.

The product of the potential and reaction term and the heat source term can be evaluated to give

$$\text{(B.19)} \quad \epsilon^\iota \psi^{\overline{i \iota}} r^{i \iota} + \epsilon^\iota h^{\overline{\overline{i \iota}}} = \langle \psi_{i \iota} r_{i \iota} + h_{i \iota} \rangle_{\Omega_\iota, \Omega},$$

where

$$\text{(B.20)} \quad \epsilon^\iota \psi^{\overline{i \iota}} r^{i \iota} = \left\langle \psi^{\overline{i \iota}} r_{i \iota} \right\rangle_{\Omega_\iota, \Omega},$$

and

(B.21)
$$\epsilon^\iota h^{\overline{\overline{i\iota}}} = \left\langle h_{i\iota} + \left(\psi_{i\iota} - \psi^{\overline{\overline{i\iota}}} \right) r_{i\iota} \right\rangle_{\Omega_\iota,\Omega}.$$

The inter-species energy transfer terms can be evaluated to give

(B.22)
$$\epsilon^\iota e_T^{i\iota} = \left\langle e_{i\iota} + \mathbf{p}_{i\iota}\boldsymbol{\cdot}\mathbf{v}_{i\iota} + \frac{\mathbf{v}_{i\iota}\boldsymbol{\cdot}\mathbf{v}_{i\iota}}{2} r_{i\iota} \right\rangle_{\Omega_\iota,\Omega},$$

where $e_T^{i\iota}$ is the total macroscale interspecies transfer of energy due to internal energy, momentum, and reaction transfer mechanisms from all other species in the ι entity to the i species in the ι entity.

Remaining terms to be evaluated in Eq. (B.3) involve transfer of energy at internal boundaries to interfaces and the transfer of energy at the external boundary of the transition region. The inter-entity transfer of energy can be written as

(B.23)
$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \langle E_{Ti\iota}\mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) + \mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{t}_{i\iota}\boldsymbol{\cdot}\mathbf{v}_{i\iota} + \mathbf{q}_{i\iota})\rangle_{\Omega_\kappa,\Omega} =$$

$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \left\langle \left[\frac{E_{Ti\iota}^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa \omega_{i\iota}^{\overline{\kappa}}} + \left(\frac{E_{Ti\iota}}{\rho_\iota \omega_{i\iota}} - \frac{E_{Ti\iota}^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa \omega_{i\iota}^{\overline{\kappa}}} \right) \right] \rho_\iota \omega_{i\iota} \mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) \right\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \left\langle \mathbf{n}_\iota \boldsymbol{\cdot} \left\{ \mathbf{t}_{i\iota}\boldsymbol{\cdot} \left[\mathbf{v}_{i\iota}^{\overline{\kappa}} + \left(\mathbf{v}_{i\iota} - \mathbf{v}_{i\iota}^{\overline{\kappa}} \right) \right] + \mathbf{q}_{i\iota} \right\} \right\rangle_{\Omega_\kappa,\Omega},$$

or as

(B.24)
$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \langle E_{Ti\iota}\mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) + \mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{t}_{i\iota}\boldsymbol{\cdot}\mathbf{v}_{i\iota} + \mathbf{q}_{i\iota})\rangle_{\Omega_\kappa,\Omega} =$$

$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \frac{E_{Ti\iota}^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa \omega_{i\iota}^{\overline{\kappa}}} \langle \rho_\iota \omega_{i\iota} \mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{v}_\kappa - \mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \left\langle \mathbf{n}_\iota \boldsymbol{\cdot} \left\{ \mathbf{t}_{i\iota}\boldsymbol{\cdot} \left[\mathbf{v}_{i\iota}^{\overline{\kappa}} + \left(\mathbf{v}_{i\iota} - \mathbf{v}_{i\iota}^{\overline{\kappa}} \right) \right] + \mathbf{q}_{i\iota} \right\} \right\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{C\iota}} \left\langle \left(\frac{E_{i\iota}}{\rho_\iota \omega_{i\iota}} - \frac{E_{i\iota}^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa \omega_{i\iota}^{\overline{\kappa}}} - K_{Ei\iota}^{\overline{\overline{\kappa}}} + \psi_{i\iota} - \psi_{i\iota}^{\overline{\kappa}} \right) \rho_\iota \omega_{i\iota} \mathbf{n}_\iota \boldsymbol{\cdot} (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) \right\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{c\iota}} \left\langle \left(\mathbf{v}_{i\iota}^{\overline{\kappa}}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}_{i\iota}^{\overline{\kappa}}\right)+\frac{\left(\mathbf{v}_{i\iota}-\mathbf{v}_{i\iota}^{\overline{\kappa}}\right)\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}_{i\iota}^{\overline{\kappa}}\right)}{2}\right)\right.$$
$$\left.\rho_{\iota}\omega_{i\iota}\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}_{i\iota}\right)\right\rangle_{\Omega_{\kappa},\Omega},$$

where

$$(\text{B.25}) \qquad E_{Ti\iota}^{\overline{\overline{\kappa}}} = \epsilon^{\iota}\langle E_{Ti\iota}\rangle_{\Omega_{\kappa},\Omega_{\kappa}},$$

$$(\text{B.26}) \qquad E_{i\iota}^{\overline{\overline{\kappa}}} = \epsilon^{\iota}\langle E_{i\iota}\rangle_{\Omega_{\kappa},\Omega_{\kappa}},$$

$$(\text{B.27}) \qquad \mathbf{v}_{i\iota}^{\overline{\kappa}} = \langle\mathbf{v}_{i\iota}\rangle_{\Omega_{\kappa},\Omega_{\kappa},\rho_{\iota}\omega_{i\iota}},$$

$$(\text{B.28}) \qquad \rho_{\iota}^{\kappa} = \langle\rho_{\iota}\rangle_{\Omega_{\kappa},\Omega_{\kappa}},$$

$$(\text{B.29}) \qquad \omega_{i\iota}^{\overline{\kappa}} = \langle\omega_{i\iota}\rangle_{\Omega_{\kappa},\Omega_{\kappa},\rho_{\iota}},$$

$$(\text{B.30}) \qquad \rho_{\iota}^{\kappa}\omega_{i\iota}^{\overline{\kappa}}K_{Ei\iota}^{\overline{\overline{\kappa}}} = \left\langle\rho_{\iota}\omega_{i\iota}\frac{\left(\mathbf{v}_{i\iota}-\mathbf{v}_{i\iota}^{\overline{\kappa}}\right)\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}_{i\iota}^{\overline{\kappa}}\right)}{2}\right\rangle_{\Omega_{\kappa},\Omega_{\kappa}},$$

and

$$(\text{B.31}) \qquad \psi_{i\iota}^{\overline{\kappa}} = \langle\psi_{i\iota}\rangle_{\Omega_{\kappa},\Omega_{\kappa},\rho_{\iota}\omega_{i\iota}}.$$

In the case where both subscript and superscript qualifiers are present in the variable, the superscript indicates the domain over which the subscripted microscale quantity has been averaged.

Eq. (B.24) can be written as

$$(\text{B.32}) \quad -\sum_{\kappa\in\mathcal{I}_{c\iota}} \langle E_{Ti\iota}\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}_{i\iota}\right)+\mathbf{n}_{\iota}\cdot\left(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}\right)\rangle_{\Omega_{\kappa},\Omega} =$$
$$-\sum_{\kappa\in\mathcal{I}_{c\iota}} \left[\overset{i\kappa\to i\iota}{M_{E_i}}+\sum_{j\in\mathcal{I}_s}\left(\overset{j\kappa\to i\iota}{T_{v_i}}+\overset{j\kappa\to i\iota}{Q}\right)\right],$$

where the transfer terms are

$$
(B.33) \qquad \overset{i\kappa\to i\iota}{M_{E_i}} = \begin{cases} \left(\dfrac{E^{\overline{\overline{\kappa}}}_{Ti\iota}}{\epsilon^\iota \rho^\kappa_\iota \omega^{\overline{\overline{\kappa}}}_{i\iota}}\right) \overset{i\kappa\to i\iota}{M} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] \left(\dfrac{E^{\overline{\overline{\iota}}}_{Ti\kappa}}{\epsilon^\kappa \rho^\iota_\kappa \omega^{\overline{\overline{\iota}}}_{i\kappa}}\right) \overset{i\kappa\to i\iota}{M} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(B.34) \qquad \overset{j\kappa\to i\iota}{T_{v_i}} = \begin{cases} \mathbf{v}^{\overline{\kappa}}_{i\iota} \cdot \overset{j\kappa\to i\iota}{\mathbf{T}} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] \mathbf{v}^{\overline{\iota}}_{j\kappa} \cdot \overset{j\kappa\to i\iota}{\mathbf{T}} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(B.35) \qquad \overset{i\kappa\to i\iota}{M} = \begin{cases} \langle \rho_\iota \omega_{i\iota} \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) \rangle_{\Omega_\kappa,\Omega} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2ex] -\langle \rho_\kappa \omega_{i\kappa} \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_{i\kappa}) \rangle_{\Omega_\iota,\Omega} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$(B.36)$

$$
\overset{j\kappa\to i\iota}{\mathbf{T}} = \begin{cases} \left\langle \underset{j\kappa\to i\iota}{z_T} \, \mathbf{n}_\iota \cdot \mathbf{t}_{i\iota} \right\rangle_{\Omega_\kappa,\Omega} + \delta_{ij}\langle \mathbf{n}_\iota \cdot [\rho_\iota \omega_{i\iota}(\mathbf{v}_\kappa - \mathbf{v}_{i\iota})(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\kappa}}_{i\iota})]\rangle_{\Omega_\kappa,\Omega} \\[1ex] \qquad\qquad \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[3ex] -\left\langle \underset{j\kappa\to i\iota}{z_T} \, \mathbf{n}_\kappa \cdot \mathbf{t}_{j\kappa} \right\rangle_{\Omega_\iota,\Omega} - \delta_{ij}\langle \mathbf{n}_\kappa \cdot [\rho_\kappa \omega_{i\kappa}(\mathbf{v}_\iota - \mathbf{v}_{i\kappa})(\mathbf{v}_{i\kappa} - \mathbf{v}^{\overline{\iota}}_{i\kappa})]\rangle_{\Omega_\iota,\Omega} \\[1ex] \qquad\qquad \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

$$
(B.37) \quad \overset{j\kappa\to i\iota}{Q} = \left\langle \underset{j\kappa\to i\iota}{z_Q} \, \mathbf{n}_\iota \cdot \mathbf{q}_{i\iota} \right\rangle_{\Omega_\kappa,\Omega} + \left\langle \underset{j\kappa\to i\iota}{z_T} \, \mathbf{n}_\iota \cdot \mathbf{t}_{i\iota} \cdot \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\kappa}}_{i\iota}\right) \right\rangle_{\Omega_\kappa,\Omega}
$$

$$
+\delta_{ij}\left\langle \rho_\iota \omega_{i\iota} \left(\frac{E_{i\iota}}{\rho_\iota \omega_{i\iota}} - \frac{E^{\overline{\overline{\kappa}}}_{i\iota}}{\epsilon^\iota \rho^\kappa_\iota \omega^{\overline{\overline{\kappa}}}_{i\iota}} + \psi_{i\iota} - \psi^{\overline{\kappa}}_{i\iota}\right) \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) \right\rangle_{\Omega_\kappa,\Omega}
$$

$$
+\delta_{ij}\left\langle \rho_\iota \omega_{i\iota} \left(\frac{(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\kappa}}_{i\iota}) \cdot (\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\kappa}}_{i\iota})}{2} - K^{\overline{\overline{\kappa}}}_{Ei\iota}\right) \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) \right\rangle_{\Omega_\kappa,\Omega}
$$

for $\dim\Omega_\iota > \dim\Omega_\kappa$,

$$
(B.38) \quad \overset{j\kappa\to i\iota}{Q} = -\left\langle \underset{j\kappa\to i\iota}{z_Q} \, \mathbf{n}_\kappa \cdot \mathbf{q}_{j\kappa} \right\rangle_{\Omega_\iota,\Omega} - \left\langle \underset{j\kappa\to i\iota}{z_T} \, \mathbf{n}_\kappa \cdot \mathbf{t}_{j\kappa} \cdot \left(\mathbf{v}_{j\kappa} - \mathbf{v}^{\overline{\iota}}_{j\kappa}\right) \right\rangle_{\Omega_\iota,\Omega}
$$

$$-\delta_{ij}\left\langle\left(\frac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}-\frac{E_{i\kappa}^{\bar{\bar{\iota}}}}{\epsilon^\kappa\rho_\kappa^\iota\omega_{i\kappa}^{\bar{\iota}}}+\psi_{i\kappa}-\psi_{i\kappa}^{\bar{\iota}}\right)\rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot(\mathbf{v}_\iota-\mathbf{v}_{i\kappa})\right\rangle_{\Omega_\iota,\Omega}$$

$$-\delta_{ij}\left\langle\left(\frac{(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\bar{\iota}})\cdot(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\bar{\iota}})}{2}-K_{Ei\kappa}^{\bar{\bar{\iota}}}\right)\rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot(\mathbf{v}_\iota-\mathbf{v}_{i\kappa})\right\rangle_{\Omega_\iota,\Omega}$$

for $\dim\Omega_\kappa>\dim\Omega_\iota$.

Here $\overset{i\kappa\to i\iota}{M}$ represents transfer of mass of species i in the κ entity to the i species in the ι entity per unit volume per unit time, $\overset{j\kappa\to i\iota}{\mathbf{T}}$ represents momentum transfer from species in the κ entity to the i species in the ι entity due to stress and deviation from mean processes per unit volume per unit time, $\overset{j\kappa\to i\iota}{Q}$ represents transfer of energy from species in the κ entity to the i species in the ι entity resulting from heat transfer and deviation from mean processes per unit volume per unit time, and δ_{ij} is the Kronecker delta function.

The terms $\underset{j\kappa\to i\iota}{z_T}$ and $\underset{j\kappa\to i\iota}{z_Q}$ are introduced to account for the fractional contributions of stress and heat energy, respectively, transferred from all of the species in a connected entity to a given species in the reference entity.

(B.39) $$\underset{j\kappa\to i\iota}{z_T}=\underset{j\kappa\to i\iota}{z_Q}=\delta_{ij}\qquad\text{for }\dim\Omega_\iota>\dim\Omega_\kappa.$$

These definitions change when the reference entity is a lower dimension than the connected entity. Because stress energy and heat energy transfer are not confined to the same species in each entity and overall conservation must be preserved, it follows that

(B.40) $$\sum_{i\in\mathcal{I}_s}\underset{j\kappa\to i\iota}{z_T}=\sum_{i\in\mathcal{I}_s}\underset{j\kappa\to i\iota}{z_Q}=1.$$

The definitions are constrained such that energy and momentum exchange when summed over all species and entities must vanish. This formulation is introduced so that the final conservation and balance equations are identical for each entity. While the details are somewhat complicated, the notions being represented are straightforward.

Combining Eqns.(B.3), (B.4), (B.15), (B.18), (B.19), (B.22), and (B.32) gives the conservation of energy equation for a species in a phase

$$
\text{(B.41)} \quad \mathcal{E}^{i\iota} = \frac{\mathrm{D}^{\overline{i\iota}} E_T^{\overline{\overline{i\iota}}}}{\mathrm{D}t} + E_T^{\overline{\overline{i\iota}}}\mathbf{I}\mathbf{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \nabla\mathbf{\cdot}\left(\epsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}}\mathbf{\cdot}\mathbf{v}^{\overline{i\iota}} + \epsilon^\iota \mathbf{q}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota \psi^{\overline{i\iota}} r^{i\iota} - \epsilon^\iota h^{\overline{i\iota}} - \epsilon^\iota e_T^{i\iota}
$$

$$
- \left\langle \rho_\iota \omega_{i\iota}\frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}}\left[\overset{i\kappa\to i\iota}{M_{E_i}} + \sum_{j \in \mathcal{I}_s}\left(\overset{j\kappa\to i\iota}{T_{v_i}} + \overset{j\kappa\to i\iota}{Q} \right) \right]
$$

$$
+\langle E_{T i\iota}\mathbf{e}\mathbf{\cdot}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right) - \mathbf{e}\mathbf{\cdot}\left(\mathbf{t}_{i\iota}\mathbf{\cdot}\mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}\right)\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota \in \mathcal{I}_{\mathrm{P}},
$$

where the rate of strain tensor is defined as

$$
\mathbf{d}^{\overline{\overline{i\iota}}} = \frac{1}{2}\left[\nabla\mathbf{v}^{\overline{i\iota}} + \left(\nabla\mathbf{v}^{\overline{i\iota}} \right)^{\mathrm{T}} \right].
$$

The continuum mechanical principle of Galilean invariance can be applied to Eq. (B.41) to derive the conservation of momentum equation for a species in a phase

$$
\text{(B.42)} \quad \boldsymbol{\mathcal{P}}^{i\iota} = \frac{\mathrm{D}^{\overline{i\iota}}\left(\epsilon^\iota \rho^\iota \omega^{i\overline{\iota}}\mathbf{v}^{\overline{i\iota}} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}}\mathbf{v}^{\overline{i\iota}}\mathbf{I}\mathbf{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \nabla\mathbf{\cdot}\left(\epsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota r^{i\iota}\mathbf{v}^{\overline{i\iota}} - \epsilon^\iota \mathbf{p}^{\overline{i\iota}}
$$

$$
-\epsilon^\iota \rho^\iota \omega^{i\overline{\iota}}\mathbf{g}^{\overline{i\iota}} - \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}}\left(\overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}} + \sum_{j \in \mathcal{I}_s}\overset{j\kappa\to i\iota}{\mathbf{T}} \right)
$$

$$
+\langle \mathbf{e}\mathbf{\cdot}\rho_\iota \omega_{i\iota}\mathbf{v}_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right) - \mathbf{e}\mathbf{\cdot}\mathbf{t}_{i\iota}\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota \in \mathcal{I}_{\mathrm{P}},
$$

where

$$
\text{(B.43)} \qquad \overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}} = \begin{cases} \mathbf{v}_{i\iota}^{\overline{\kappa}}\overset{i\kappa\to i\iota}{M} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[2mm] \mathbf{v}_{i\kappa}^{\overline{\iota}}\overset{i\kappa\to i\iota}{M} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}
$$

and the general macroscale conservation of mass equation for species in a phase

$$
\text{(B.44)} \quad \mathcal{M}^{i\iota} = \frac{\mathrm{D}^{\overline{i\iota}}\left(\epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \right)}{\mathrm{D}t} + \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}}\mathbf{I}\mathbf{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \epsilon^\iota r^{i\iota} - \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}}\overset{i\kappa\to i\iota}{M}
$$

$$
+\langle \mathbf{e}\mathbf{\cdot}\rho_\iota \omega_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right)\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota \in \mathcal{I}_{\mathrm{P}}.
$$

The microscale balance of entropy equation for species i in phase ι is

$$(\text{B.45}) \qquad \mathcal{S}_{i\iota} = \frac{\mathrm{D}_{i\iota}\eta_{i\iota}}{\mathrm{D}t} + \eta_{i\iota}\mathbf{I}{:}\mathbf{d}_{i\iota} - \nabla{\cdot}\boldsymbol{\varphi}_{i\iota} - b_{i\iota} = \Lambda_{i\iota},$$

where $\eta_{i\iota}$ is the entropy density of species i in entity ι, $\boldsymbol{\varphi}_{i\iota}$ is the non-advective entropy density flux vector, $b_{i\iota}$ is the entropy source density, and $\Lambda_{i\iota}$ is the entropy production rate density. Applying the averaging operator in Eq. (3.1) and Theorems D[3,(2,0),1] and T[3,(2,0),1] to Eq. (B.45) gives

$$(\text{B.46}) \quad \mathcal{S}^{i\iota} = \frac{\mathrm{D}^{\overline{\overline{i\iota}}}\eta^{\overline{\overline{i\iota}}}}{\mathrm{D}t} + \eta^{\overline{\overline{i\iota}}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \nabla{\cdot}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{i\iota}}}\right) - \epsilon^{\iota}b^{i\iota} - \sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\left(\overset{i\kappa\to i\iota}{M_{\eta_i}} + \sum_{j\in\mathcal{I}_s}\overset{j\kappa\to i\iota}{\Phi}\right)$$

$$+ \langle\mathbf{e}{\cdot}\left[(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}})\,\eta_{i\iota} - \boldsymbol{\varphi}_{i\iota}\right]\rangle_{\Gamma_{\iota M},\Omega} = \Lambda^{\overline{\overline{i\iota}}} \qquad \text{for } \iota\in\mathcal{I}_{\mathrm{P}},$$

where

$$(\text{B.47}) \qquad \eta^{\overline{\overline{i\iota}}} = \langle\eta_{i\iota}\rangle_{\Omega_\iota,\Omega}, \qquad \epsilon^{\iota}b^{i\iota} = \langle b_{i\iota}\rangle_{\Omega_\iota,\Omega}, \qquad \Lambda^{\overline{\overline{i\iota}}} = \langle\Lambda_{i\iota}\rangle_{\Omega_\iota,\Omega},$$

$$(\text{B.48}) \qquad \eta_{i\iota}^{\overline{\overline{\overline{\kappa}}}} = \epsilon^{\iota}\langle\eta_{i\iota}\rangle_{\Omega_\kappa,\Omega_\kappa}, \qquad \epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{i\iota}}} = \left\langle\boldsymbol{\varphi}_{i\iota} - \eta_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega},$$

$$(\text{B.49}) \qquad \overset{i\kappa\to i\iota}{M_{\eta_i}} = \begin{cases} \left(\dfrac{\eta_{i\iota}^{\overline{\overline{\overline{\kappa}}}}}{\epsilon^{\iota}\rho_\iota^{\kappa}\omega_{i\iota}^{\overline{\overline{\kappa}}}}\right)\overset{i\kappa\to i\iota}{M} & \text{for } \dim\Omega_\iota > \dim\Omega_\kappa, \\[3ex] \left(\dfrac{\eta_{i\kappa}^{\overline{\overline{\iota}}}}{\epsilon^{\kappa}\rho_\kappa^{\iota}\omega_{i\kappa}^{\overline{\iota}}}\right)\overset{i\kappa\to i\iota}{M} & \text{for } \dim\Omega_\kappa > \dim\Omega_\iota, \end{cases}$$

$$(\text{B.50}) \qquad \overset{j\kappa\to i\iota}{\Phi} = \left\langle z_\Phi\,\mathbf{n}_\iota\cdot\boldsymbol{\varphi}_{i\iota}\atop{j\kappa\to i\iota}\right\rangle_{\Omega_\kappa,\Omega}$$

$$+ \delta_{ij}\left\langle\rho_\iota\omega_{i\iota}\left(\frac{\eta_{i\iota}}{\rho_\iota\omega_{i\iota}} - \frac{\eta_{i\iota}^{\overline{\overline{\overline{\kappa}}}}}{\epsilon^{\iota}\rho_\iota^{\kappa}\omega_{i\iota}^{\overline{\overline{\kappa}}}}\right)\mathbf{n}_\iota\cdot(\mathbf{v}_\kappa - \mathbf{v}_{i\iota})\right\rangle_{\Omega_\kappa,\Omega}$$

$$\text{for } \dim\Omega_\iota > \dim\Omega_\kappa,$$

and

(B.51) $\overset{jκ \to iι}{Φ} = - \left\langle \underset{jκ \to iι}{z_Φ} \, \mathbf{n}_κ \cdot \boldsymbol{\varphi}_{iκ} \right\rangle_{Ω_ι, Ω}$

$- δ_{ij} \left\langle ρ_κ ω_{iκ} \left(\dfrac{η_{iκ}}{ρ_κ ω_{iκ}} - \dfrac{η_{iκ}^{\bar{ι}}}{ε^κ ρ_κ^ι ω_{iκ}^{\bar{ι}}} \right) \mathbf{n}_κ \cdot (\mathbf{v}_ι - \mathbf{v}_{iκ}) \right\rangle_{Ω_ι, Ω}$

for $\dim Ω_κ > \dim Ω_ι$,

where $\underset{jκ \to iι}{z_Φ}$ accounts for the fractional contribution of entropy from species j in entity $κ$ to species i in entity $ι$. As was the case for similar contributions of stress and heat, $\underset{jκ \to iι}{z_Φ} = δ_{ij}$ for $\dim Ω_ι > \dim Ω_κ$. The quantity $\overset{jκ \to iι}{Φ}$ represents the transfer of entropy from the $κ$ entity to the i species in the $ι$ entity due to processes other than phase change per unit volume per unit time.

B.2. Interface Equations

Conservation and balance equations for interfaces and common curves can be derived in the same manner as phases starting from the microscale form of the energy equation averaging to the macroscale, simplifying with an appropriate set of transport and divergence theorems, and applying the principle of Galilean invariance to obtain the macroscale version of the momentum and mass equations.

The microscale conservation of energy equation for a species i in an interface $ι$ is

(B.52) $\dfrac{∂' E_{Tiι}}{∂t} + ∇' \cdot (E_{Tiι} \mathbf{v}_{iι}) - ∇' \cdot (\mathbf{t}'_{iι} \cdot \mathbf{v}_{iι} + \mathbf{q}'_{iι}) - ψ_{iι} r_{iι} - h_{iι}$

$- e_{Tiι} - ρ_ι ω_{iι} \dfrac{∂' ψ_{iι}}{∂t} + \displaystyle\sum_{κ \in (\mathfrak{I}_{cι} \cap \mathfrak{I}_P)} E_{Tiκ} (\mathbf{v}_ι - \mathbf{v}_{iκ}) \cdot \mathbf{n}_κ \bigg|_{Ω_ι}$

$+ \displaystyle\sum_{κ \in (\mathfrak{I}_{cι} \cap \mathfrak{I}_P)} \sum_{j \in \mathfrak{I}_s} \mathbf{n}_κ \cdot \left(\underset{jκ \to iι}{z_T} \mathbf{t}_{jκ} \cdot \mathbf{v}_{jκ} + \underset{jκ \to iι}{z_Q} \mathbf{q}_{jκ} \right) \bigg|_{Ω_ι} = 0 \quad \text{for } ι \in \mathfrak{I}_I.$

Integrating Eq. (B.52) over the interfacial area $Ω_ι$ we have

(B.53) $\left\langle \dfrac{\partial' E_{Ti\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} + \left\langle \nabla' \cdot (E_{Ti\iota} \mathbf{v}_{i\iota}) \right\rangle_{\Omega_\iota,\Omega} - \left\langle \nabla' \cdot \left(\mathbf{t}_{i\iota}' \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}' \right) \right\rangle_{\Omega_\iota,\Omega}$

$\quad - \langle \psi_{i\iota} r_{i\iota} \rangle_{\Omega_\iota,\Omega} - \langle h_{i\iota} \rangle_{\Omega_\iota,\Omega} - \langle e_{Ti\iota} \rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota \omega_{i\iota} \dfrac{\partial' \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$

$\quad + \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{P}})} \langle E_{Ti\kappa} \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_{i\kappa}) \rangle_{\Omega_\iota,\Omega}$

$\quad + \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{P}})} \sum_{j \in \mathfrak{I}_s} \left\langle \mathbf{n}_\kappa \cdot \left(\underset{j\kappa \to i\iota}{z_T} \, \mathbf{t}_{j\kappa} \cdot \mathbf{v}_{j\kappa} + \underset{j\kappa \to i\iota}{z_Q} \, \mathbf{q}_{j\kappa} \right) \right\rangle_{\Omega_\iota,\Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}.$

Applying T[2,(2,0),1] given by Eq. (3.8) to the first term in Eq. (B.53) yields

(B.54) $\left\langle \dfrac{\partial' E_{Ti\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \dfrac{\partial'}{\partial t} \langle E_{Ti\iota} \rangle_{\Omega_\iota,\Omega} + \nabla' \cdot \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{v}_{i\iota} E_{Ti\iota} \rangle_{\Omega_\iota,\Omega}$

$\quad - \left\langle (\nabla' \cdot \mathbf{n}_\alpha) \, \mathbf{n}_\alpha \cdot \mathbf{v}_{i\iota} E_{Ti\iota} \right\rangle_{\Omega_\iota,\Omega} - \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{C}})} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa E_{Ti\iota} \rangle_{\Omega_\kappa,\Omega}$

$\quad - \left\langle \dfrac{\mathbf{e} \cdot \mathbf{v}_{\mathrm{ext}} E_{Ti\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$

Applying D[2,(2,0),1] given by Eq. (3.6) to the first divergence term in Eq. (B.53) provides

(B.55) $\langle \nabla' \cdot (E_{Ti\iota} \mathbf{v}_{i\iota}) \rangle_{\Omega_\iota,\Omega} = \nabla' \cdot \langle E_{Ti\iota} (\mathbf{v}_{i\iota} - \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{v}_{i\iota}) \rangle_{\Omega_\iota,\Omega}$

$\quad + \left\langle (\nabla' \cdot \mathbf{n}_\alpha) \, \mathbf{n}_\alpha \cdot E_{Ti\iota} \mathbf{v}_{i\iota} \right\rangle_{\Omega_\iota,\Omega} + \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{C}})} \langle \mathbf{n}_\iota \cdot E_{Ti\iota} \mathbf{v}_{i\iota} \rangle_{\Omega_\kappa,\Omega}$

$\quad + \left\langle \dfrac{\mathbf{e} \cdot \mathbf{v}_{i\iota} E_{Ti\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega},$

and to the second divergence term

(B.56) $\left\langle \nabla' \cdot \left(\mathbf{t}_{i\iota}' \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}' \right) \right\rangle_{\Omega_\iota,\Omega} = \nabla' \cdot \langle \mathbf{t}_{i\iota}' \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}' \rangle_{\Omega_\iota,\Omega}$

$\quad + \displaystyle\sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{\mathrm{C}})} \langle \mathbf{n}_\iota \cdot \left(\mathbf{t}_{i\iota}' \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}' \right) \rangle_{\Omega_\kappa,\Omega} + \left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{t}_{i\iota}' \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}' \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$

Substituting these into Eq. (B.53) and canceling like terms we get

$$\text{(B.57)} \quad \frac{\partial'}{\partial t}\langle E_{Ti\iota}\rangle_{\Omega_\iota,\Omega} + \nabla'\cdot\langle E_{Ti\iota}\mathbf{v}_{i\iota}\rangle_{\Omega_\iota,\Omega} - \nabla'\cdot\langle \mathbf{t}'_{i\iota}\cdot\mathbf{v}_{i\iota} + \mathbf{q}'_{i\iota}\rangle_{\Omega_\iota,\Omega}$$

$$-\langle\psi_{i\iota}r_{i\iota}\rangle_{\Omega_\iota,\Omega} - \langle h_{i\iota}\rangle_{\Omega_\iota,\Omega} - \langle e_{Ti\iota}\rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota\omega_{i\iota}\frac{\partial'\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_P)} \langle \mathbf{n}_\kappa\cdot(\mathbf{v}_\iota - \mathbf{v}_{i\kappa})\,E_{Ti\kappa}\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_C)} \langle \mathbf{n}_\iota\cdot(\mathbf{v}_{i\iota} - \mathbf{v}_\kappa)\,E_{Ti\iota}\rangle_{\Omega_\kappa,\Omega}$$

$$+ \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_P)} \sum_{j\in\mathcal{I}_s} \left\langle \mathbf{n}_\kappa\cdot\left(\underset{j\kappa\to i\iota}{z_T}\,\mathbf{t}_{j\kappa}\cdot\mathbf{v}_{j\kappa} + \underset{j\kappa\to i\iota}{z_Q}\,\mathbf{q}_{j\kappa}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$- \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_C)} \langle \mathbf{n}_\iota\cdot\mathbf{t}'_{i\iota}\cdot\mathbf{v}_{i\iota}\rangle_{\Omega_\kappa,\Omega} - \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_C)} \langle \mathbf{n}_\iota\cdot\mathbf{q}'_{i\iota}\rangle_{\Omega_\kappa,\Omega}$$

$$+\left\langle \frac{\mathbf{e}\cdot\left[E_{Ti\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}}\right) - \mathbf{t}'_{i\iota}\cdot\mathbf{v}_{i\iota} - \mathbf{q}'_{i\iota}\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = 0 \quad \text{for } \iota\in\mathcal{I}_I.$$

Considering Eq. (B.57) term by term to evaluate the averaging operators gives for the time derivative term

$$\text{(B.58)} \quad \frac{\partial'}{\partial t}\left\langle E_{i\iota} + \rho_\iota\omega_{i\iota}\left(\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2} + \psi_{i\iota}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$= \frac{\partial'}{\partial t}\left[E^{\overline{\overline{i\iota}}} + \epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\left(\frac{\mathbf{v}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{\overline{i\iota}}}}{2} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)\right].$$

Evaluating divergence terms in the same way as for the phase provides

$$\text{(B.59)} \quad \nabla'\cdot\langle E_{Ti\iota}\mathbf{v}_{i\iota}\rangle_{\Omega_\iota,\Omega} = \nabla'\cdot\left(E_T^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{\iota}}\right) + \nabla'\cdot\left(E_T^{\overline{\overline{i\iota}}}\mathbf{u}^{\overline{\overline{i\iota}}}\right)$$

$$+\nabla'\cdot\left\langle \left(E_{i\iota} + \rho_\iota\omega_{i\iota}\psi_{i\iota}\right)\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla'\cdot\left\langle\left(\mathbf{v}^{\overline{\overline{i\iota}}}\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right) + \frac{\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)}{2}\right)\right.$$

$$\left.\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}.$$

The second divergence term in Eq. (B.57) may be written as

$$(B.60) \qquad \nabla'\cdot\left\langle \mathbf{t}'_{i\iota}\cdot\mathbf{v}_{i\iota} + \mathbf{q}'_{i\iota}\right\rangle_{\Omega_\iota,\Omega} = \nabla'\cdot\left\langle \mathbf{t}'_{i\iota}\cdot\mathbf{v}^{\overline{\overline{i\iota}}} + \mathbf{t}'_{i\iota}\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right) + \mathbf{q}'_{i\iota}\right\rangle_{\Omega_\iota,\Omega}.$$

Combining equations Eqs. (B.59) and (B.60) gives

$$(B.61) \quad \epsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{\overline{i\iota}}} + \epsilon^\iota \mathbf{q}^{\overline{\overline{i\iota}}} = \left\langle \left[\mathbf{t}'_{i\iota} - \rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\right]\cdot\mathbf{v}^{\overline{\overline{i\iota}}}\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \mathbf{q}'_{i\iota} - \left[E_{i\iota} + \rho_\iota\omega_{i\iota}\left(\frac{\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{\overline{i\iota}}}\right)}{2} + \psi_{i\iota}\right)\right]\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \mathbf{t}'_{i\iota}\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega},$$

where the first term on the RHS is the macroscale stress tensor for a species in an interface and the second two terms on the RHS sum to the macroscale heat source vector for a species in an interface.

The inter-entity transfer of energy from the phases that form the interface to the interface can be written as

$$(B.62) \quad -\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_P\right)} \left\langle \mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{i\kappa}\right) E_{Ti\kappa}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_P\right)} \sum_{j\in\mathcal{I}_s} \left\langle \mathbf{n}_\kappa\cdot\left(\underset{j\kappa\to i\iota}{z_T}\,\mathbf{t}_{j\kappa}\cdot\mathbf{v}_{j\kappa} + \underset{j\kappa\to i\iota}{z_Q}\,\mathbf{q}_{j\kappa}\right)\right\rangle_{\Omega_\iota,\Omega} =$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_P\right)} \frac{E^{\overline{\overline{\iota}}}_{Ti\kappa}}{\epsilon^\kappa\rho^\iota_\kappa\omega^{\overline{\iota}}_{i\kappa}}\left\langle \rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{i\kappa}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_P\right)} \left\langle \left(\frac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}} - \frac{E^{\overline{\overline{\iota}}}_{i\kappa}}{\epsilon^\kappa\rho^\iota_\kappa\omega^{\overline{\iota}}_{i\kappa}} - K^{\overline{\iota}}_{Ei\kappa}\right)\rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{i\kappa}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_P\right)} \left\langle \left[\psi_{i\kappa} - \psi^{\overline{\iota}}_{i\kappa} + \mathbf{v}^{\overline{\iota}}_{i\kappa}\cdot\left(\mathbf{v}_{i\kappa} - \mathbf{v}^{\overline{\iota}}_{i\kappa}\right)\right]\rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{i\kappa}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_P\right)} \left\langle \frac{\left(\mathbf{v}_{i\kappa} - \mathbf{v}^{\overline{\iota}}_{i\kappa}\right)\cdot\left(\mathbf{v}_{i\kappa} - \mathbf{v}^{\overline{\iota}}_{i\kappa}\right)}{2}\rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{i\kappa}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \sum_{j \in \mathcal{I}_s} \left\langle \mathbf{n}_\kappa \cdot \left\{ \underset{j\kappa \to i\iota}{z_T} \, \mathbf{t}_{j\kappa} \cdot \left[\mathbf{v}_{j\kappa}^{\bar{\iota}} + \left(\mathbf{v}_{j\kappa} - \mathbf{v}_{j\kappa}^{\bar{\iota}} \right) \right] + \underset{j\kappa \to i\iota}{z_Q} \, \mathbf{q}_{j\kappa} \right\} \right\rangle_{\Omega_\iota, \Omega}.$$

Using notation from Eqs. (B.35)–(B.39), Eq. (B.62) can be written as

(B.63)
$$\sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \langle \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_{i\kappa}) \, E_{Ti\kappa} \rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \sum_{j \in \mathcal{I}_s} \left\langle \mathbf{n}_\kappa \cdot \left(\underset{j\kappa \to i\iota}{z_T} \, \mathbf{t}_{j\kappa} \cdot \mathbf{v}_{j\kappa} + \underset{j\kappa \to i\iota}{z_Q} \, \mathbf{q}_{j\kappa} \right) \right\rangle_{\Omega_\iota, \Omega} =$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_P)} \left[\overset{i\kappa \to i\iota}{M_{E_i}} + \sum_{j \in \mathcal{I}_s} \left(\overset{j\kappa \to i\iota}{T_{v_i}} + \overset{j\kappa \to i\iota}{Q} \right) \right].$$

The transfer of energy from a common curve to an interface is simplified analogously to the case of the transfer of energy from a phase to an interface, where integration is performed over the lower dimensional entity and the transfer terms are written with respect to the higher dimensional entity, resulting in the short-hand expression

(B.64)
$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_C)} \langle E_{Ti\iota} \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) + \mathbf{n}_\iota \cdot (\mathbf{t}_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}) \rangle_{\Omega_\kappa, \Omega} =$$

$$- \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_C)} \left[\overset{i\kappa \to i\iota}{M_{E_i}} + \sum_{j \in \mathcal{I}_s} \left(\overset{j\kappa \to i\iota}{T_{v_i}} + \overset{j\kappa \to i\iota}{Q} \right) \right].$$

Collecting results, Eq. (B.57) can be written in final form for the conservation of energy for a species in an interface as

(B.65)
$$\mathcal{E}^{i\iota} = \frac{\mathrm{D}^{\overline{\overline{i\iota}}} E_T^{\overline{\overline{i\iota}}}}{\mathrm{D}t} + E_T^{\overline{\overline{i\iota}}} \mathbf{I} : \mathbf{d}^{\overline{\overline{i\iota}}} - \nabla' \cdot \left(\epsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}} \cdot \mathbf{v}^{\overline{i\iota}} + \epsilon^\iota \mathbf{q}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota \psi^{\overline{i\iota}} r^{i\iota} - \epsilon^\iota h^{\overline{\overline{i\iota}}} - \epsilon^\iota e_T^{i\iota}$$

$$- \left\langle \rho_\iota \omega_{i\iota} \frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left[\overset{i\kappa \to i\iota}{M_{E_i}} + \sum_{j \in \mathcal{I}_s} \left(\overset{j\kappa \to i\iota}{T_{v_i}} + \overset{j\kappa \to i\iota}{Q} \right) \right]$$

$$+ \left\langle \frac{E_{Ti\iota} \mathbf{e} \cdot (\mathbf{v}_{i\iota} - \mathbf{v}_{ext}) - \mathbf{e} \cdot (\mathbf{t}'_{i\iota} \cdot \mathbf{v}_{i\iota} - \mathbf{q}'_{i\iota})}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = 0 \qquad \text{for } \iota \in \mathcal{I}_I.$$

The continuum mechanical principle of Galilean invariance can be applied to the macroscale conservation of energy equations for species i in interface ι to derive the conservation of momentum and conservation of mass equations for species i in interface ι

$$\text{(B.66)} \quad \boldsymbol{\mathcal{P}}^{i\iota} = \frac{\mathrm{D}^{\overline{i\iota}}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\mathbf{v}^{\overline{i\iota}}\right)}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\mathbf{v}^{\overline{i\iota}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \nabla^{\backprime}{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\overline{\overline{i\iota}}}\right) - \epsilon^{\iota}r^{i\iota}\mathbf{v}^{\overline{i\iota}} - \epsilon^{\iota}\mathbf{p}^{\overline{\overline{i\iota}}}$$

$$- \epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\mathbf{g}^{\overline{i\iota}} - \sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}} \left(\overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}} + \sum_{j\in\mathcal{I}_{\mathcal{S}}} \overset{j\kappa\to i\iota}{\mathbf{T}} \right)$$

$$+ \left\langle \frac{\mathbf{e}{\cdot}\rho_{\iota}\omega_{i\iota}\mathbf{v}_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right) - \mathbf{e}{\cdot}\mathbf{t}'_{i\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota\in\mathcal{I}_{\mathrm{I}},$$

where $\overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}}$ is defined as in Eq. (B.43), $\overset{j\kappa\to i\iota}{\mathbf{T}}$ is defined in Eq. (B.36), and the general macroscale conservation of mass equation for species i in interface ι can be written

$$\text{(B.67)} \quad \mathcal{M}^{i\iota} = \frac{\mathrm{D}^{\overline{i\iota}}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\right)}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \epsilon^{\iota}r^{i\iota} - \sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}} \overset{i\kappa\to i\iota}{M}$$

$$+ \left\langle \frac{\mathbf{e}{\cdot}\rho_{\iota}\omega_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota\in\mathcal{I}_{\mathrm{I}},$$

where $\overset{i\kappa\to i\iota}{M}$ is defined in Eq. (B.35).

The microscale balance of entropy equation for a species in an interface is

$$\text{(B.68)} \quad \mathcal{S}_{i\iota} = \frac{\partial'\eta_{i\iota}}{\partial t} + \nabla'{\cdot}\left(\eta_{i\iota}\mathbf{v}_{i\iota}\right) - \nabla'{\cdot}\boldsymbol{\varphi}'_{i\iota} - b_{i\iota}$$

$$- \sum_{\kappa\in\left(\mathcal{I}_{\mathrm{C}\iota}\cap\mathcal{I}_{\mathrm{P}}\right)} \left(-\sum_{j\in\mathcal{I}_{\mathcal{S}}} \overset{z_{\Phi}}{\underset{j\kappa\to i\iota}{}}\boldsymbol{\varphi}_{j\kappa} + \eta_{i\kappa}\left(\mathbf{v}_{i\kappa} - \mathbf{v}_{\iota}\right) \right){\cdot}\mathbf{n}_{\kappa}\bigg|_{\Omega_{\iota}} = \Lambda_{i\iota} \quad \text{for } \iota\in\mathcal{I}_{\mathrm{I}}.$$

Integrating Eq. (B.68) over the interface surface Ω_{ι} and applying T[2,(2,0),1] and D[2,(2,0),1] yields

$$\text{(B.69)} \quad \frac{\partial'}{\partial t}\langle\eta_{i\iota}\rangle_{\Omega_{\iota},\Omega} + \nabla^{\backprime}{\cdot}\langle\eta_{i\iota}\mathbf{v}_{i\iota}\rangle_{\Omega_{\iota},\Omega} - \nabla^{\backprime}{\cdot}\langle\boldsymbol{\varphi}'_{i\iota}\rangle_{\Omega_{\iota},\Omega} - \langle b_{i\iota}\rangle_{\Omega_{\iota},\Omega}$$

$$- \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{P})} \left\langle \mathbf{n}_{\kappa} \cdot \left(- \sum_{j \in \mathcal{I}_{s}} \underset{j\kappa \to i\iota}{z_{\Phi}} \, \boldsymbol{\varphi}_{j\kappa} + \eta_{i\kappa} \left(\mathbf{v}_{i\kappa} - \mathbf{v}_{\iota} \right) \right) \right\rangle_{\Omega_{\iota}, \Omega}$$

$$+ \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{C})} \left\langle \mathbf{n}_{\iota} \cdot \left[-\boldsymbol{\varphi}_{i\iota} + \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\kappa} \right) \right] \right\rangle_{\Omega_{\kappa}, \Omega}$$

$$+ \left\langle \frac{\mathbf{e} \cdot \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}} \right)}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} - \left\langle \frac{\mathbf{e} \cdot \boldsymbol{\varphi}_{i\iota}'}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \left\langle \Lambda_{i\iota} \right\rangle_{\Omega_{\iota}, \Omega}.$$

Setting $\mathbf{v}_{i\iota} = \mathbf{v}^{\overline{i\iota}} + \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right)$ in the second term and averaging to the macroscale we get

$$(\text{B.70}) \quad \frac{\partial^{\backslash} \eta^{\overline{\overline{i\iota}}}}{\partial t} + \nabla^{\backslash} \cdot \left(\eta^{\overline{\overline{i\iota}}} \mathbf{v}^{\overline{i\iota}} \right) - \nabla^{\backslash} \cdot \left(\epsilon^{\iota} \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} \right) - \epsilon^{\iota} b^{i\iota}$$

$$- \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{P})} \left\langle \mathbf{n}_{\kappa} \cdot \left(- \sum_{j \in \mathcal{I}_{s}} \underset{j\kappa \to i\iota}{z_{\Phi}} \, \boldsymbol{\varphi}_{j\kappa} + \eta_{i\kappa} \left(\mathbf{v}_{i\kappa} - \mathbf{v}_{\iota} \right) \right) \right\rangle_{\Omega_{\iota}, \Omega}$$

$$+ \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{C})} \left\langle \mathbf{n}_{\iota} \cdot \left[-\boldsymbol{\varphi}_{i\iota} + \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\kappa} \right) \right] \right\rangle_{\Omega_{\kappa}, \Omega}$$

$$+ \left\langle \frac{\mathbf{e} \cdot \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}} \right)}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} - \left\langle \frac{\mathbf{e} \cdot \boldsymbol{\varphi}_{i\iota}'}{\mathbf{n}_{\iota} \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\overline{\overline{i\iota}}},$$

where

$$(\text{B.71}) \qquad\qquad \epsilon^{\iota} \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} = \left\langle \boldsymbol{\varphi}_{i\iota}' - \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right) \right\rangle_{\Omega_{\iota}, \Omega}.$$

For the connected entities we can write

$$(\text{B.72}) \quad - \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{P})} \left\langle \mathbf{n}_{\kappa} \cdot \left(- \sum_{j \in \mathcal{I}_{s}} \underset{j\kappa \to i\iota}{z_{\Phi}} \, \boldsymbol{\varphi}_{j\kappa} + \eta_{i\kappa} \left(\mathbf{v}_{i\kappa} - \mathbf{v}_{\iota} \right) \right) \right\rangle_{\Omega_{\iota}, \Omega}$$

$$+ \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{C})} \left\langle \mathbf{n}_{\iota} \cdot \left[-\boldsymbol{\varphi}_{i\iota} + \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}_{\kappa} \right) \right] \right\rangle_{\Omega_{\kappa}, \Omega}$$

$$= - \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\overset{i\kappa \to i\iota}{M_{\eta}} + \sum_{j \in \mathcal{I}_{s}} \overset{j\kappa \to i\iota}{\Phi} \right),$$

where use is made of Eqs. (B.49)–(B.51).

Thus the macroscopic entropy equation for species i in entity ι can be written

(B.73)

$$
\mathcal{S}^{i\iota} = \frac{\partial^\backprime \eta^{\overline{\overline{i\iota}}}}{\partial t} + \nabla^\backprime \cdot \left(\eta^{\overline{\overline{i\iota}}} \mathbf{v}^{\overline{i\iota}} \right) - \nabla^\backprime \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota b^{i\iota} - \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\overset{i\kappa \to i\iota}{M_{\eta_i}} + \sum_{j \in \mathcal{I}_S} \overset{j\kappa \to i\iota}{\Phi} \right)
$$

$$
+ \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}} \right) \eta_{i\iota} - \boldsymbol{\varphi}'_{i\iota} \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\overline{\overline{i\iota}}},
$$

which putting into material derivative form gives us

$$
\text{(B.74)} \quad \mathcal{S}^{i\iota} = \frac{\mathrm{D}^{\overline{\overline{i\iota}}} \eta^{\overline{\overline{i\iota}}}}{\mathrm{D} t} + \eta^{\overline{\overline{i\iota}}} \mathbf{I}{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \nabla^\backprime \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota b^{i\iota} - \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\overset{i\kappa \to i\iota}{M_{\eta_i}} + \sum_{j \in \mathcal{I}_S} \overset{j\kappa \to i\iota}{\Phi} \right)
$$

$$
+ \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}} \right) \eta_{i\iota} - \boldsymbol{\varphi}'_{i\iota} \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\overline{\overline{i\iota}}} \qquad \text{for } \iota \in \mathcal{I}_{\mathrm{I}},
$$

where $\overset{i\kappa \to i\iota}{M_{\eta_i}}$ and $\overset{i\kappa \to i\iota}{\Phi}$ are defined in Eqs. (B.49)–(B.51).

B.3. Common Curve Equations

The microscale conservation of total energy equation for a species i in a common curve ι is

$$
\text{(B.75)} \quad \frac{\partial'' E_{Ti\iota}}{\partial t} + \nabla'' \cdot \left(E_{Ti\iota} \mathbf{v}_{i\iota} \right) - \nabla'' \cdot \left(\mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}''_{i\iota} \right) - \psi_{i\iota} r_{i\iota} - h_{i\iota}
$$

$$
- e_{Ti\iota} - \rho_\iota \omega_{i\iota} \frac{\partial'' \psi_{i\iota}}{\partial t} + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota} \cap \mathcal{I}_{\mathrm{I}}} \mathbf{n}_\kappa \cdot E_{Ti\kappa} \left(\mathbf{v}_\iota - \mathbf{v}_{i\kappa} \right) \Big|_{\Omega_\iota}
$$

$$
+ \sum_{\kappa \in \left(\mathcal{I}_{\mathrm{C}\iota} \cap \mathcal{I}_{\mathrm{I}} \right)} \sum_{j \in \mathcal{I}_S} \mathbf{n}_\kappa \cdot \left(\underset{j\kappa \to i\iota}{z_T} \mathbf{t}_{j\kappa} \cdot \mathbf{v}_{j\kappa} + \underset{j\kappa \to i\iota}{z_Q} \mathbf{q}_{j\kappa} \right) \Big|_{\Omega_\iota} = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{C}}.
$$

Integrating Eq. (B.75) over the ι common curve yields

(B.76) $\left\langle \dfrac{\partial'' E_{Ti\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} + \left\langle \nabla'' \cdot (E_{Ti\iota} \mathbf{v}_{i\iota}) \right\rangle_{\Omega_\iota,\Omega} - \left\langle \nabla'' \cdot (\mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}''_{i\iota}) \right\rangle_{\Omega_\iota,\Omega}$

$\quad - \langle \psi_{i\iota} r_{i\iota} \rangle_{\Omega_\iota,\Omega} - \langle h_{i\iota} \rangle_{\Omega_\iota,\Omega} - \langle e_{Ti\iota} \rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota \omega_{i\iota} \dfrac{\partial'' \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$

$\quad + \displaystyle\sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{\mathrm{I}})} \langle \mathbf{n}_\kappa \cdot E_{Ti\kappa} (\mathbf{v}_\iota - \mathbf{v}_{i\kappa}) \rangle_{\Omega_\kappa,\Omega}$

$\quad + \displaystyle\sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{\mathrm{I}})} \left\langle \sum_{j \in \mathcal{I}_s} \mathbf{n}_\kappa \cdot \left(\underset{j\kappa \to i\iota}{z_T} \mathbf{t}_{j\kappa} \cdot \mathbf{v}_{j\kappa} + \underset{j\kappa \to i\iota}{z_Q} \mathbf{q}_{j\kappa} \right) \right\rangle_{\Omega_\kappa,\Omega} = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{C}}.$

Applying T[1,(2,0),1] to the first term in Eq. (B.76) we get

(B.77) $\left\langle \dfrac{\partial'' E_{Ti\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \dfrac{\partial'}{\partial t} \langle E_{Ti\iota} \rangle_{\Omega_\iota,\Omega} + \nabla' \cdot \langle (\mathbf{v}_\iota - \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_\iota) E_{Ti\iota} \rangle_{\Omega_\iota,\Omega}$

$\quad + \left\langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot \mathbf{v}_\iota E_{Ti\iota} \right\rangle_{\Omega_\iota,\Omega} - \displaystyle\sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{\mathrm{Pt}})} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa E_{Ti\iota} \rangle_{\Omega_\kappa,\Omega}$

$\quad - \left\langle \dfrac{\mathbf{e} \cdot \mathbf{v}_{\mathrm{ext}} E_{Ti\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$

Since the term involving $\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota$ involves only normal components and since

(B.78) $$ \mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota \cdot \mathbf{l}_\iota = 0 $$

showing that the curvature term does not have a normal component, then Eq. (B.77) can be written as

(B.79) $\left\langle \dfrac{\partial'' E_{Ti\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \dfrac{\partial'}{\partial t} \langle E_{Ti\iota} \rangle_{\Omega_\iota,\Omega} + \nabla' \cdot \langle (\mathbf{v}_{i\iota} - \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_{i\iota}) E_{Ti\iota} \rangle_{\Omega_\iota,\Omega}$

$\quad + \left\langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot \mathbf{v}_{i\iota} E_{Ti\iota} \right\rangle_{\Omega_\iota,\Omega} - \displaystyle\sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{\mathrm{Pt}})} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa E_{Ti\iota} \rangle_{\Omega_\kappa,\Omega}$

$\quad - \left\langle \dfrac{\mathbf{e} \cdot \mathbf{v}_{\mathrm{ext}} E_{Ti\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$

Applying D[1,(2,0),1] to the first divergence term in Eq. (B.76) provides

(B.80) $\langle \nabla'' \cdot (E_{Ti\iota} \mathbf{v}_{i\iota}) \rangle_{\Omega_\iota,\Omega} = \nabla' \cdot \langle \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_{i\iota} E_{Ti\iota} \rangle_{\Omega_\iota,\Omega} - \left\langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot \mathbf{v}_{i\iota} E_{Ti\iota} \right\rangle_{\Omega_\iota,\Omega}$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot \mathbf{v}_{i\iota} E_{T i\iota} \rangle_{\Omega_\kappa,\Omega} + \left\langle \frac{\mathbf{e} \cdot \mathbf{v}_{i\iota} E_{T i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}$$

and to the second divergence term gives

(B.81) $\langle \nabla'' \cdot (\mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}''_{i\iota}) \rangle_{\Omega_\iota,\Omega}$

$$= \nabla' \cdot \langle \mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot \mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} \rangle_{\Omega_\kappa,\Omega} + \left\langle \frac{\mathbf{e} \cdot \mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+ \nabla' \cdot \langle \mathbf{q}''_{i\iota} \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot \mathbf{q}''_{i\iota} \rangle_{\Omega_\kappa,\Omega} + \left\langle \frac{\mathbf{e} \cdot \mathbf{q}''_{i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$$

Combining Eqs. (B.76)–(B.81) and simplifying yields

(B.82) $\dfrac{\partial'}{\partial t} \langle E_{T i\iota} \rangle_{\Omega_\iota,\Omega} + \nabla' \cdot \langle E_{T i\iota} \mathbf{v}_{i\iota} \rangle_{\Omega_\iota,\Omega} - \nabla' \cdot \langle \mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}''_{i\iota} \rangle_{\Omega_\iota,\Omega}$

$$- \langle \psi_{i\iota} r_{i\iota} \rangle_{\Omega_\iota,\Omega} - \langle h_{i\iota} \rangle_{\Omega_\iota,\Omega} - \langle e_{T i\iota} \rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota \omega_{i\iota} \frac{\partial'' \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_I)} \langle \mathbf{n}_\kappa \cdot (\mathbf{v}_\iota - \mathbf{v}_{i\kappa}) E_{T i\kappa} \rangle_{\Omega_\iota,\Omega}$$

$$- \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) E_{T i\iota} \rangle_{\Omega_\kappa,\Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_I)} \sum_{j \in \mathfrak{I}_s} \left\langle \mathbf{n}_\kappa \cdot \left(\underset{j\kappa \to i\iota}{z_T} \mathbf{t}'_{j\kappa} \cdot \mathbf{v}_{j\kappa} + \underset{j\kappa \to i\iota}{z_Q} \mathbf{q}'_{j\kappa} \right) \right\rangle_{\Omega_\iota,\Omega}$$

$$- \sum_{\kappa \in (\mathfrak{I}_{c\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot (\mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}''_{i\iota}) \rangle_{\Omega_\kappa,\Omega}$$

$$+ \left\langle \frac{\mathbf{e} \cdot [E_{T i\iota} (\mathbf{v}_{i\iota} - \mathbf{v}_{ext}) - \mathbf{t}''_{i\iota} \cdot \mathbf{v}_{i\iota} - \mathbf{q}''_{i\iota}]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = 0 \quad \text{for } \iota \in \mathfrak{I}_C.$$

Using the exchange term definitions, Eqs. (B.33)–(B.38), and defining the macroscale stress tensor and heat flux vector according to

(B.83) $\epsilon^\iota \overline{\overline{\mathbf{t}}}^{\overline{i\iota}} \cdot \mathbf{v}^{\overline{i\iota}} + \epsilon^\iota \mathbf{q}^{\overline{\overline{i\iota}}} = \left\langle [\mathbf{t}''_{i\iota} - \rho_\iota \omega_{i\iota} (\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}) (\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}})] \cdot \mathbf{v}^{\overline{i\iota}} \right\rangle_{\Omega_\iota,\Omega}$

$$+\left\langle \mathbf{q}''_{i\iota} - \left[E_{i\iota} + \rho_\iota\omega_{i\iota}\left(\frac{\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}\right)\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}\right)}{2} + \psi_{i\iota}\right)\right]\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$+\left\langle \mathbf{t}''_{i\iota}\cdot\left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega},$$

we arrive at the conservation of total energy equation for the common curve

$$(B.84) \quad \mathcal{E}^{i\iota} = \frac{D^{\overline{i\iota}}E_T^{\overline{\overline{i\iota}}}}{Dt} + E_T^{\overline{\overline{i\iota}}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{\backslash i\iota}}} - \nabla^{\backslash}{\cdot}\left(\epsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}{\cdot}\mathbf{v}^{\overline{i\iota}} + \epsilon^\iota\mathbf{q}^{\overline{i\iota}}\right) - \epsilon^\iota\psi^{\overline{i\iota}}r^{i\iota} - \epsilon^\iota h^{\overline{i\iota}} - \epsilon^\iota e_T^{i\iota}$$

$$-\left\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa\in\mathcal{I}_{C\iota}}\left[\overset{i\kappa\to i\iota}{M_{E_i}} + \sum_{j\in\mathcal{I}_s}\left(\overset{j\kappa\to i\iota}{T_{v_i}} + \overset{j\kappa\to i\iota}{Q}\right)\right]$$

$$+\left\langle\frac{E_{Ti\iota}\mathbf{e}{\cdot}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right) - \mathbf{e}{\cdot}\left(\mathbf{t}''_{i\iota}{\cdot}\mathbf{v}_{i\iota} + \mathbf{q}''_{i\iota}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota\in\mathcal{I}_C.$$

Applying Galilean invariance to the macroscale conservation of energy equations for species i in common curve ι yields the conservation of momentum and conservation of mass equations for species i in common curve ι. For the momentum equation we write

$$(B.85) \quad \boldsymbol{\mathcal{P}}^{i\iota} = \frac{D^{\overline{i\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{v}^{\overline{i\iota}}\right)}{Dt} + \epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{v}^{\overline{i\iota}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{\backslash i\iota}}} - \nabla^{\backslash}{\cdot}\left(\epsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\right) - \epsilon^\iota r^{i\iota}\mathbf{v}^{\overline{i\iota}} - \epsilon^\iota\mathbf{p}^{\overline{i\iota}}$$

$$-\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{g}^{\overline{i\iota}} - \sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}} + \sum_{j\in\mathcal{I}_s}\overset{j\kappa\to i\iota}{\mathbf{T}}\right)$$

$$+\left\langle\frac{\mathbf{e}{\cdot}\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right) - \mathbf{e}{\cdot}\mathbf{t}''_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota\in\mathcal{I}_C,$$

where $\overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}}$ is defined as in Eq. (B.43), and $\overset{i\kappa\to i\iota}{\mathbf{T}}$ is defined in Eq. (B.36).

The general macroscale conservation of mass equation for species i in common curve ι can be written

$$(B.86) \quad \mathcal{M}^{i\iota} = \frac{D^{\overline{i\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\right)}{Dt} + \epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{\backslash i\iota}}} - \epsilon^\iota r^{i\iota} - \sum_{\kappa\in\mathcal{I}_{C\iota}}\overset{i\kappa\to i\iota}{M}$$

$$+\left\langle \frac{\mathbf{e}\cdot\rho_{\iota}\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}_{\text{ext}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=0 \qquad \text{for } \iota\in\mathfrak{I}_{\text{C}},$$

where $\overset{i\kappa\to i\iota}{M}$ is defined in Eq. (B.35).

The microscale balance of entropy equation for species i in a common curve ι can be written as

(B.87)
$$\mathcal{S}_{i\iota}=\frac{\partial''\eta_{i\iota}}{\partial t}+\nabla''\cdot(\eta_{i\iota}\mathbf{v}_{i\iota})-\nabla''\cdot\boldsymbol{\varphi}''_{i\iota}-b_{i\iota}-\sum_{\kappa\in\left(\mathfrak{I}_{\text{c}\iota}\cap\mathfrak{I}_{\text{I}}\right)}\mathbf{n}_{\kappa}\cdot\left[-\boldsymbol{\varphi}_{i\kappa}+\eta_{i\kappa}\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{\iota}\right)\right]$$

$$=\Lambda_{i\iota} \qquad \text{for } \iota\in\mathfrak{I}_{\text{C}}.$$

Integrating Eq. (B.87) over the ι common curve and applying Theorem 3.4.7 and Theorem 3.4.9 yields

(B.88) $\quad \dfrac{\partial'}{\partial t}\langle\eta_{i\iota}\rangle_{\Omega_{\iota},\Omega}+\nabla'\cdot\langle\eta_{i\iota}\mathbf{v}_{i\iota}\rangle_{\Omega_{\iota},\Omega}-\nabla'\cdot\langle\boldsymbol{\varphi}''_{i\iota}\rangle_{\Omega_{\iota},\Omega}-\langle b_{i\iota}\rangle_{\Omega_{\iota},\Omega}$

$$-\sum_{\kappa\in\left(\mathfrak{I}_{\text{c}\iota}\cap\mathfrak{I}_{\text{I}}\right)}\langle\mathbf{n}_{\kappa}\cdot\left[\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{\iota}\right)\eta_{i\kappa}-\boldsymbol{\varphi}_{i\kappa}\right]\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\kappa\in\left(\mathfrak{I}_{\text{c}\iota}\cap\mathfrak{I}_{\text{Pt}}\right)}\langle\mathbf{n}_{\iota}\cdot\left[\left(\mathbf{v}_{i\iota}-\mathbf{v}_{\kappa}\right)\eta_{i\iota}-\boldsymbol{\varphi}_{i\iota}\right]\rangle_{\Omega_{\kappa},\Omega}$$

$$+\left\langle \frac{\mathbf{e}\cdot\left[\left(\mathbf{v}_{i\iota}-\mathbf{v}_{\text{ext}}\right)\eta_{i\iota}-\boldsymbol{\varphi}''_{i\iota}\right]}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=\langle\Lambda_{i\iota}\rangle_{\Omega_{\iota},\Omega}.$$

Setting $\mathbf{v}_{i\iota}=\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)$ in the second term and averaging to the macroscale we get

(B.89) $\quad \dfrac{\partial'\eta^{\overline{\overline{i\iota}}}}{\partial t}+\nabla'\cdot\left(\eta^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{i\iota}}\right)-\nabla'\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{i\iota}}}\right)-\epsilon^{\iota}b^{i\iota}$

$$-\sum_{\kappa\in\left(\mathfrak{I}_{\text{c}\iota}\cap\mathfrak{I}_{\text{I}}\right)}\langle\mathbf{n}_{\kappa}\cdot\left[\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{\iota}\right)\eta_{i\kappa}-\boldsymbol{\varphi}_{i\kappa}\right]\rangle_{\Omega_{\iota},\Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot [(\mathbf{v}_{i\iota} - \mathbf{v}_\kappa) \eta_{i\iota} - \boldsymbol{\varphi}_{i\iota}] \rangle_{\Omega_\kappa, \Omega}$$

$$+ \left\langle \frac{\mathbf{e} \cdot [(\mathbf{v}_{i\iota} - \mathbf{v}_{ext}) \eta_{i\iota} - \boldsymbol{\varphi}''_{i\iota}]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\overline{\overline{i\iota}}},$$

where

(B.90)
$$\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} = \left\langle \boldsymbol{\varphi}''_{i\iota} - \eta_{i\iota} \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right) \right\rangle_{\Omega_\iota, \Omega}.$$

For the connected entities we can write

(B.91)
$$- \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_{I})} \langle \mathbf{n}_\kappa \cdot [(\mathbf{v}_{i\kappa} - \mathbf{v}_\iota) \eta_{i\kappa} - \boldsymbol{\varphi}_{i\kappa}] \rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\kappa \in (\mathfrak{I}_{C\iota} \cap \mathfrak{I}_{Pt})} \langle \mathbf{n}_\iota \cdot [(\mathbf{v}_{i\iota} - \mathbf{v}_\kappa) \eta_{i\iota} - \boldsymbol{\varphi}_{i\iota}] \rangle_{\Omega_\kappa, \Omega}$$

$$= - \sum_{\kappa \in \mathfrak{I}_{C\iota}} \left(\overset{i\kappa \to i\iota}{M_\eta} + \sum_{j \in \mathfrak{I}_s} \overset{j\kappa \to i\iota}{\overline{\overline{\Phi}}} \right).$$

Thus the macroscopic entropy equation for species i in entity ι can be written

(B.92)
$$\mathcal{S}^{i\iota} = \frac{\partial^\backslash \eta^{\overline{\overline{i\iota}}}}{\partial t} + \nabla \cdot \left(\eta^{\overline{\overline{i\iota}}} \mathbf{v}^{\overline{i\iota}} \right) - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota b^{i\iota} - \sum_{\kappa \in \mathfrak{I}_{C\iota}} \left(\overset{i\kappa \to i\iota}{M_{\eta_i}} + \sum_{j \in \mathfrak{I}_s} \overset{j\kappa \to i\iota}{\overline{\overline{\Phi}}} \right)$$

$$+ \left\langle \frac{\mathbf{e} \cdot [(\mathbf{v}_{i\iota} - \mathbf{v}_{ext}) \eta_{i\iota} - \boldsymbol{\varphi}''_{i\iota}]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\overline{\overline{i\iota}}} \qquad \text{for } \iota \in \mathfrak{I}_C,$$

which putting into material derivative form gives us

(B.93) $$\mathcal{S}^{i\iota} = \frac{D^{\overline{i\iota}} \eta^{\overline{\overline{i\iota}}}}{Dt} + \eta^{\overline{\overline{i\iota}}} \mathbf{l} \colon \mathbf{d}^{\overline{\overline{i\iota}}} - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\overline{i\iota}}} \right) - \epsilon^\iota b^{i\iota} - \sum_{\kappa \in \mathfrak{I}_{C\iota}} \left(\overset{i\kappa \to i\iota}{M_{\eta_i}} + \sum_{j \in \mathfrak{I}_s} \overset{j\kappa \to i\iota}{\overline{\overline{\Phi}}} \right)$$

$$+ \left\langle \frac{\mathbf{e} \cdot [(\mathbf{v}_{i\iota} - \mathbf{v}_{ext}) \eta_{i\iota} - \boldsymbol{\varphi}''_{i\iota}]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\overline{\overline{i\iota}}} \qquad \text{for } \iota \in \mathfrak{I}_C.$$

Noting that $\mathbf{n}_\iota \cdot \mathbf{e} = 1$ for $\iota \in \mathcal{I}_P$, we can write the conservation of energy, mass, and momentum as well as the entropy inequality each in a single form for phases, interfaces, and common curves allowing for a single equation to be written for $\iota \in \mathcal{I}$.

B.4. General Conservation Equations

The general conservation of energy equation for species i in entity ι is given by

$$(B.94) \quad \mathcal{E}^{i\iota} = \frac{D^{\overline{i\iota}} E_T^{\overline{\overline{i\iota}}}}{Dt} + E_T^{\overline{\overline{i\iota}}} \mathbf{I}{:}\mathbf{d}^{\overline{\overline{i\iota}}} - \nabla'{\cdot}\left(\epsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}}{\cdot}\mathbf{v}^{\overline{i\iota}} + \epsilon^\iota \mathbf{q}^{\overline{\overline{i\iota}}}\right) - \epsilon^\iota \psi^{\overline{i\iota}} r^{i\iota} - \epsilon^\iota h^{\overline{\overline{i\iota}}} - \epsilon^\iota e_T^{i\iota}$$

$$- \left\langle \rho_\iota \omega_{i\iota} \frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left[\overset{i\kappa \to i\iota}{M_{E_i}} + \sum_{j \in \mathcal{I}_s} \left(\overset{j\kappa \to i\iota}{T_{v_i}} + \overset{j\kappa \to i\iota}{Q} \right) \right]$$

$$+ \left\langle \frac{E_{Ti\iota}\mathbf{e}{\cdot}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}}\right) - \mathbf{e}{\cdot}\left(\mathbf{t}_{i\iota}{\cdot}\mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota \in \mathcal{I}.$$

Summing $E_T^{\overline{\overline{i\iota}}}$ over all species with velocities written in terms of dispersion velocities, $\mathbf{u}^{\overline{i\iota}} = \mathbf{v}^{\overline{i\iota}} - \mathbf{v}^{\overline{\iota}}$ and $\mathbf{u}_{i\iota} = \mathbf{v}_{i\iota} - \mathbf{v}_\iota$,

$$(B.95) \quad \sum_{i \in \mathcal{I}_s} E_T^{\overline{\overline{i\iota}}} = E^{\overline{\overline{\iota}}} + \epsilon^\iota \rho^\iota \left(\frac{\mathbf{v}^{\overline{\iota}}{\cdot}\mathbf{v}^{\overline{\iota}}}{2} + K_E^{\overline{\iota}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\iota} \psi^{\overline{i\iota}},$$

where

$$(B.96) \quad E^{\overline{\overline{\iota}}} = \sum_{i \in \mathcal{I}_s} E^{\overline{\overline{i\iota}}}, \quad \text{and}$$

$$(B.97) \quad K_E^{\overline{\iota}} = \sum_{i \in \mathcal{I}_s} \omega^{i\iota} \left(\frac{\mathbf{u}^{\overline{\overline{i\iota}}}{\cdot}\mathbf{u}^{\overline{\overline{i\iota}}}}{2} + K_E^{\overline{\overline{i\iota}}} \right).$$

Using the definition of the dispersion velocity to replace all species velocities, we can define the macroscale stress tensor for entity ι as

$$(B.98) \quad \mathbf{t}^{\overline{\iota}} = \sum_{i \in \mathcal{I}_s} \left(\mathbf{t}^{\overline{\overline{i\iota}}} - \rho^\iota \omega^{i\iota} \mathbf{u}^{\overline{\overline{i\iota}}} \mathbf{u}^{\overline{\overline{i\iota}}} \right),$$

and the macroscale heat flux vector for entity ι as

$$(\text{B.99}) \quad \epsilon^{\iota} \mathbf{q}^{\bar{\bar{\iota}}} = \sum_{i \in \mathcal{I}_s} \left(\epsilon^{\iota} \mathbf{q}^{\overline{\bar{i\iota}}} - \left\{ \left[E^{\overline{\bar{i\iota}}} + \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(K_E^{\overline{\bar{i\iota}}} + \frac{\mathbf{u}^{\overline{\bar{i\iota}}} \cdot \mathbf{u}^{\overline{\bar{i\iota}}}}{2} \right) + \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \psi^{\overline{\bar{i\iota}}} \right] \mathbf{I} \right.$$
$$\left. - \epsilon^{\iota} \mathbf{t}^{\overline{\bar{i\iota}}} \right\} \cdot \mathbf{u}^{\overline{\bar{i\iota}}} \right).$$

For the transition region, the non-advective fluxes can be decomposed into the portions over the surface and the portion in the megascale direction. So for vectors, this means for example that

$$(\text{B.100}) \qquad \mathbf{q}^{\bar{\bar{\iota}}} = \mathbf{I}^{\backprime} \cdot \mathbf{q}^{\bar{\bar{\iota}}} + \mathbf{N}\mathbf{N} \cdot \mathbf{q}^{\bar{\bar{\iota}}} = \mathbf{q}^{\backprime\bar{\bar{\iota}}} + \mathbf{N}\mathbf{N} \cdot \mathbf{q}^{\bar{\bar{\iota}}}.$$

The divergence of the heat flux vector can then be written as

$$(\text{B.101}) \qquad \nabla^{\backprime} \cdot \left(\epsilon^{\iota} \mathbf{q}^{\bar{\bar{\iota}}} \right) = \nabla^{\backprime} \cdot \left(\epsilon^{\iota} \mathbf{q}^{\backprime\bar{\bar{\iota}}} \right) + \left(\nabla^{\backprime} \cdot \mathbf{N} \right) \left(\epsilon^{\iota} \mathbf{N} \cdot \mathbf{q}^{\bar{\bar{\iota}}} \right).$$

For tensors, for example the stress tensor, the decomposition can be written as

$$(\text{B.102}) \qquad \mathbf{t}^{\bar{\bar{\iota}}} = \mathbf{I}^{\backprime} \cdot \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{I}^{\backprime} + \mathbf{I}^{\backprime} \cdot \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{N}\mathbf{N} + \mathbf{N}\mathbf{N} \cdot \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{I}^{\backprime} + \mathbf{N}\mathbf{N} \cdot \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{N}\mathbf{N}.$$

We define $\mathbf{t}^{\backprime\bar{\bar{\iota}}} = \mathbf{t}^{\bar{\bar{\iota}}} - \mathbf{N}\mathbf{N} \cdot \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{N}\mathbf{N}$, then

$$(\text{B.103}) \qquad \nabla^{\backprime} \cdot \left(\epsilon^{\iota} \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} \right) = \nabla^{\backprime} \cdot \left(\epsilon^{\iota} \mathbf{t}^{\backprime\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} \right) + \left(\nabla^{\backprime} \cdot \mathbf{N} \right) \left(\epsilon^{\iota} \mathbf{N} \cdot \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{N}\mathbf{N} \cdot \mathbf{v}^{\bar{\iota}} \right).$$

Taking the decompositions and Eq. (B.7) into account, and summing over all species i gives

$$(\text{B.104}) \quad \mathcal{E}^{\iota} = \frac{\mathrm{D}^{\bar{\iota}} \left(E^{\bar{\bar{\iota}}} + \epsilon^{\iota} \rho^{\iota} \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \psi^{\overline{\bar{i\iota}}} \right)}{\mathrm{D}t}$$
$$+ \left[E^{\bar{\bar{\iota}}} + \epsilon^{\iota} \rho^{\iota} \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \psi^{\overline{\bar{i\iota}}} \right] \mathbf{I} : \mathbf{d}^{\backprime\bar{\bar{\iota}}}$$
$$- \nabla^{\backprime} \cdot \left(\epsilon^{\iota} \mathbf{t}^{\backprime\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} \right) - \nabla^{\backprime} \cdot \left(\epsilon^{\iota} \mathbf{q}^{\backprime\bar{\bar{\iota}}} \right) - \epsilon^{\iota} h_T^{\bar{\bar{\iota}}}$$

$$-\sum_{i\in\mathfrak{I}_S}\epsilon^\iota\rho^\iota\omega^{i\bar\iota}\left(\mathbf{g}_T^{\overline{\overline{i\iota}}}-\mathbf{g}^{\overline{i\iota}}\right)\cdot\mathbf{v}^{\bar\iota}-\sum_{i\in\mathfrak{I}_S}\left(\epsilon^\iota\psi^{\overline{\overline{i\iota}}}r^{i\iota}+\left\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega}\right)$$

$$-\sum_{\kappa\in\mathfrak{I}_{C\iota}}\sum_{i\in\mathfrak{I}_S}\left[\overset{i\kappa\to i\iota}{M_{E_i}}+\sum_{j\in\mathfrak{I}_S}\left(\overset{j\kappa\to i\iota}{T_{v_i}}+\overset{j\kappa\to i\iota}{Q}\right)\right]$$

$$+\sum_{i\in\mathfrak{I}_S}\left\langle\frac{E_{Ti\iota}\mathbf{e}\cdot(\mathbf{v}_{i\iota}-\mathbf{v}_{\text{ext}})-\mathbf{e}\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota})}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=0\qquad\text{for }\iota\in\mathfrak{I},$$

where

$$(\text{B.105})\qquad h_T^{\bar\iota}=\sum_{i\in\mathfrak{I}_S}h^{\overline{\overline{i\iota}}}+\left(\nabla^{\backslash}\cdot\mathbf{N}\right)\left(\mathbf{N}\cdot\mathbf{q}^{\bar\iota}\right),$$

and

$$(\text{B.106})\qquad\sum_{i\in\mathfrak{I}_S}\epsilon^\iota\rho^\iota\omega^{i\bar\iota}\mathbf{g}_T^{\overline{\overline{i\iota}}}=\sum_{i\in\mathfrak{I}_S}\epsilon^\iota\rho^\iota\omega^{i\bar\iota}\mathbf{g}^{\overline{i\iota}}+\left(\nabla^{\backslash}\cdot\mathbf{N}\right)\left(\epsilon^\iota\mathbf{N}\cdot\mathbf{t}^{\bar\iota}\cdot\mathbf{N}\mathbf{N}\right),$$

and

$$(\text{B.107})\qquad\sum_{i\in\mathfrak{I}_S}\epsilon^\iota e_T^{i\iota}=0.$$

We note that for $\dim\Omega_\iota>\dim\Omega_\kappa$

$$(\text{B.108})\quad\sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M_{E_i}}=\frac{E_{T\iota}^{\overline{\overline\kappa}}}{\epsilon^\iota\rho_\iota^\kappa}\sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M}+\sum_{i\in\mathfrak{I}_S}\left(\frac{E_{T i\iota}^{\overline{\overline\kappa}}}{\epsilon^\iota\rho_\iota^\kappa\omega_{i\iota}^{\overline\kappa}}-\frac{E_{T\iota}^{\overline{\overline\kappa}}}{\epsilon^\iota\rho_\iota^\kappa}\right)\overset{i\kappa\to i\iota}{M}$$

$$=\sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M_E}+\sum_{i\in\mathfrak{I}_S}\left(\frac{E_{T i\iota}^{\overline{\overline\kappa}}}{\epsilon^\iota\rho_\iota^\kappa\omega_{i\iota}^{\overline\kappa}}-\frac{E_{T\iota}^{\overline{\overline\kappa}}}{\epsilon^\iota\rho_\iota^\kappa}\right)\overset{i\kappa\to i\iota}{M},$$

and

$$(\text{B.109})\quad\sum_{i\in\mathfrak{I}_S}\sum_{j\in\mathfrak{I}_S}\overset{j\kappa\to i\iota}{T_{v_i}}=\sum_{i\in\mathfrak{I}_S}\sum_{j\in\mathfrak{I}_S}\mathbf{v}_\iota^{\overline\kappa}\cdot\overset{j\kappa\to i\iota}{\mathbf{T}}+\sum_{i\in\mathfrak{I}_S}\sum_{j\in\mathfrak{I}_S}\left(\mathbf{v}_{i\iota}^{\overline\kappa}-\mathbf{v}_\iota^{\overline\kappa}\right)\cdot\overset{j\kappa\to i\iota}{\mathbf{T}}$$

$$=\overset{\kappa\to\iota}{T_v}-\sum_{i\in\mathfrak{I}_S}\left(\mathbf{v}_\iota^{\overline\kappa}\cdot\left(\mathbf{v}_{i\iota}^{\overline\kappa}-\mathbf{v}_\iota^{\overline\kappa}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in\mathfrak{I}_S}\left(\mathbf{v}_{i\iota}^{\overline\kappa}-\mathbf{v}_\iota^{\overline\kappa}\right)\cdot\overset{j\kappa\to i\iota}{\mathbf{T}}\right),$$

where we have defined the microscale stress tensor as

$$(B.110) \qquad \mathbf{t}_\iota = \sum_{i \in \mathcal{I}_S} \left(\mathbf{t}_{i\iota} - \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \mathbf{u}_{i\iota} \right).$$

Similarly if $\dim \Omega_\kappa > \dim \Omega_\iota$ then

$$(B.111) \quad \sum_{i \in \mathcal{I}_S} \overset{i\kappa \to i\iota}{M_{E_i}} = \frac{E_{T\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota} \sum_{i \in \mathcal{I}_S} \overset{i\kappa \to i\iota}{M} + \sum_{i \in \mathcal{I}_S} \left(\frac{E_{Ti\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota \omega_{i\kappa}^{\overline{\iota}}} - \frac{E_{T\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota} \right) \overset{i\kappa \to i\iota}{M}$$

$$= \sum_{i \in \mathcal{I}_S} \overset{i\kappa \to i\iota}{M_E} + \sum_{i \in \mathcal{I}_S} \left(\frac{E_{Ti\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota \omega_{i\kappa}^{\overline{\iota}}} - \frac{E_{T\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota} \right) \overset{i\kappa \to i\iota}{M},$$

and

$$(B.112)$$

$$\sum_{i \in \mathcal{I}_S} \sum_{j \in \mathcal{I}_S} \overset{j\kappa \to i\iota}{T_{v_i}} = \overset{\kappa \to \iota}{T_v} - \sum_{i \in \mathcal{I}_S} \left(\mathbf{v}_\kappa^{\overline{\iota}} \cdot \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}} \right) \overset{i\kappa \to i\iota}{M} + \sum_{j \in \mathcal{I}_S} \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}} \right) \cdot \overset{j\kappa \to i\iota}{\mathbf{T}} \right).$$

The heat transfer term for an entity may then be defined as

$$(B.113) \quad \overset{\kappa \to \iota}{Q} = \sum_{i \in \mathcal{I}_S} \left[\sum_{j \in \mathcal{I}_S} \overset{j\kappa \to i\iota}{Q} - \mathbf{v}_\iota^{\overline{\kappa}} \cdot \left(\mathbf{v}_{i\iota}^{\overline{\kappa}} - \mathbf{v}_\iota^{\overline{\kappa}} \right) \overset{i\kappa \to i\iota}{M} + \sum_{j \in \mathcal{I}_S} \left(\mathbf{v}_{i\iota}^{\overline{\kappa}} - \mathbf{v}_\iota^{\overline{\kappa}} \right) \cdot \overset{j\kappa \to i\iota}{\mathbf{T}} \right.$$

$$\left. + \left(\frac{E_{Ti\iota}^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa \omega_{i\iota}^{\overline{\kappa}}} - \frac{E_{T\iota}^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa} \right) \overset{i\kappa \to i\iota}{M} \right] \qquad \text{for } \dim \Omega_\iota > \dim \Omega_\kappa,$$

and

$$(B.114) \quad \overset{\kappa \to \iota}{Q} = \sum_{i \in \mathcal{I}_S} \left[\sum_{j \in \mathcal{I}_S} \overset{j\kappa \to i\iota}{Q} - \mathbf{v}_\kappa^{\overline{\iota}} \cdot \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}} \right) \overset{i\kappa \to i\iota}{M} + \sum_{j \in \mathcal{I}_S} \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}} \right) \cdot \overset{j\kappa \to i\iota}{\mathbf{T}} \right.$$

$$\left. + \left(\frac{E_{Ti\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota \omega_{i\kappa}^{\overline{\iota}}} - \frac{E_{T\kappa}^{\overline{\overline{\iota}}}}{\epsilon^\kappa \rho_\kappa^\iota} \right) \overset{i\kappa \to i\iota}{M} \right] \qquad \text{for } \dim \Omega_\kappa > \dim \Omega_\iota,$$

such that the inter-entity exchange of energy may be written as

$$(B.115)$$

$$\sum_{\kappa \in \mathcal{I}_{\mathcal{C}\iota}} \sum_{i \in \mathcal{I}_S} \left[\overset{i\kappa \to i\iota}{M_{E_i}} + \sum_{j \in \mathcal{I}_S} \left(\overset{j\kappa \to i\iota}{T_{v_i}} + \overset{j\kappa \to i\iota}{Q} \right) \right] = \sum_{\kappa \in \mathcal{I}_{\mathcal{C}\iota}} \left(\sum_{i \in \mathcal{I}_S} \overset{i\kappa \to i\iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right).$$

Summing the last term of Eqn (B.104) over all species i provides

$$\sum_{i \in \mathfrak{I}_S} \left\langle \frac{E_{Ti\iota} \mathbf{e} \cdot (\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}})}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} - \sum_{i \in \mathfrak{I}_S} \left\langle \frac{\mathbf{e} \cdot (\mathbf{t}_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota})}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}.$$

which using the definition of the total energy density and microscale dispersion velocity can be written as

(B.116)
$$\sum_{i \in \mathfrak{I}_S} \frac{E_{Ti\iota} \mathbf{e} \cdot (\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}})}{\mathbf{n}_\iota \cdot \mathbf{e}} - \sum_{i \in \mathfrak{I}_S} \frac{\mathbf{e} \cdot (\mathbf{t}_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota})}{\mathbf{n}_\iota \cdot \mathbf{e}}$$

$$= \sum_{i \in \mathfrak{I}_S} \frac{\left(E_{i\iota} + \rho_\iota \omega_{i\iota} \frac{(\mathbf{v}_\iota + \mathbf{u}_{i\iota}) \cdot (\mathbf{v}_\iota + \mathbf{u}_{i\iota})}{2} + \rho_\iota \omega_{i\iota} \psi_{i\iota} \right) \mathbf{e} \cdot (\mathbf{v}_\iota + \mathbf{u}_{i\iota} - \mathbf{v}_{\text{ext}})}{\mathbf{n}_\iota \cdot \mathbf{e}}$$

$$- \sum_{i \in \mathfrak{I}_S} \frac{\mathbf{e} \cdot [\mathbf{t}_{i\iota} \cdot (\mathbf{v}_\iota + \mathbf{u}_{i\iota}) + \mathbf{q}_{i\iota}]}{\mathbf{n}_\iota \cdot \mathbf{e}}.$$

Considering

(B.117)
$$E_\iota = \sum_{i \in \mathfrak{I}_S} E_{i\iota}, \quad \mathbf{v}_\iota = \sum_{i \in \mathfrak{I}_S} \omega_{i\iota} \mathbf{v}_{i\iota},$$

(B.118)
$$\mathbf{q}_\iota = \sum_{i \in \mathfrak{I}_S} \left\{ \mathbf{q}_{i\iota} - \left[\left(E_{i\iota} + \rho_\iota \omega_{i\iota} \frac{\mathbf{u}_{i\iota} \cdot \mathbf{u}_{i\iota}}{2} + \rho_\iota \omega_{i\iota} \psi_{i\iota} \right) \mathbf{I} - \mathbf{t}_{i\iota} \right] \cdot \mathbf{u}_{i\iota} \right\},$$

and noting that

$$\sum_{i \in \mathfrak{I}_S} \omega_{i\iota} \mathbf{u}_{i\iota} = 0,$$

we rewrite Eqn (B.116) as

(B.119)
$$\sum_{i \in \mathfrak{I}_S} \frac{E_{Ti\iota} \mathbf{e} \cdot (\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}})}{\mathbf{n}_\iota \cdot \mathbf{e}} - \sum_{i \in \mathfrak{I}_S} \frac{\mathbf{e} \cdot (\mathbf{t}_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota})}{\mathbf{n}_\iota \cdot \mathbf{e}}$$

$$= \frac{\left(E_\iota + \rho_\iota \frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \sum_{i \in \mathfrak{I}_S} \rho_\iota \omega_{i\iota} \psi_{i\iota} \right) \mathbf{e} \cdot (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}})}{\mathbf{n}_\iota \cdot \mathbf{e}}$$

$$+ \sum_{i \in \mathfrak{I}_S} \frac{\rho_\iota \omega_{i\iota} \frac{\mathbf{u}_{i\iota} \cdot \mathbf{u}_{i\iota}}{2} \mathbf{e} \cdot (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}})}{\mathbf{n}_\iota \cdot \mathbf{e}} - \frac{\mathbf{e} \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota)}{\mathbf{n}_\iota \cdot \mathbf{e}}.$$

Therefore the conservation of energy equation for an entity within a transition region can be written

$$
\begin{aligned}
\text{(B.120)} \quad \mathcal{E}^{\iota} =\ & \frac{\mathrm{D}^{\bar{\iota}}\left(E^{\bar{\bar{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}}\right) + \sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\psi^{\overline{i\iota}}\right)}{\mathrm{D}t} \\
& + \left[E^{\bar{\bar{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}}\right) + \sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\psi^{\overline{i\iota}}\right]\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}} \\
& - \sum_{i\in\mathcal{I}_S}\nabla'{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\backslash\bar{\bar{\iota}}}{\cdot}\mathbf{v}^{\bar{\iota}}\right) - \nabla'{\cdot}\left(\epsilon^{\iota}\mathbf{q}^{\backslash\bar{\bar{\iota}}}\right) - \epsilon^{\iota}h_T^{\bar{\bar{\iota}}} - \sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\left(\mathbf{g}_T^{\overline{\overline{i\iota}}} - \mathbf{g}^{\overline{i\iota}}\right){\cdot}\mathbf{v}^{\bar{\iota}} \\
& - \sum_{i\in\mathcal{I}_S}\left(\epsilon^{\iota}\psi^{\overline{i\iota}}r^{i\iota} + \left\langle\rho_{\iota}\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_{\iota},\Omega}\right) - \sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\sum_{i\in\mathcal{I}_S}\overset{i\kappa\to i\iota}{M_E} + \overset{\kappa\to\iota}{T_v} + \overset{\kappa\to\iota}{Q}\right) \\
& + \left\langle\frac{\left(E_{\iota} + \rho_{\iota}\frac{\mathbf{v}_{\iota}\cdot\mathbf{v}_{\iota}}{2} + \sum_{i\in\mathcal{I}_S}\rho_{\iota}\omega_{i\iota}\left(\psi_{i\iota} + \frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2}\right)\right)\mathbf{e}{\cdot}\left(\mathbf{v}_{\iota} - \mathbf{v}_{\text{ext}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} \\
& - \left\langle\frac{\mathbf{e}{\cdot}\left(\mathbf{t}_{\iota}{\cdot}\mathbf{v}_{\iota} + \mathbf{q}_{\iota}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = 0.
\end{aligned}
$$

Applying the product rule to the material derivative and rearranging

$$
\begin{aligned}
\text{(B.121)} \quad \mathcal{E}^{\iota} =\ & \frac{\mathrm{D}^{\bar{\iota}}E^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \mathbf{v}^{\bar{\iota}}{\cdot}\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\right)}{\mathrm{D}t} + \sum_{i\in\mathcal{I}_S}\left(K_E^{\bar{\bar{\iota}}} - \frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2} + \psi^{\overline{i\iota}}\right)\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\right)}{\mathrm{D}t} \\
& + \sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\frac{\mathrm{D}^{\bar{\iota}}\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}}\right)}{\mathrm{D}t} \\
& + \left[E^{\bar{\bar{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}}\right) + \sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\psi^{\overline{i\iota}}\right]\mathbf{I}{:}\mathbf{d}^{\bar{\bar{\iota}}} \\
& - \sum_{i\in\mathcal{I}_S}\nabla'{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\backslash\bar{\bar{\iota}}}{\cdot}\mathbf{v}^{\bar{\iota}}\right) - \nabla'{\cdot}\left(\epsilon^{\iota}\mathbf{q}^{\backslash\bar{\bar{\iota}}}\right) - \epsilon^{\iota}h_T^{\bar{\bar{\iota}}} - \sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\left(\mathbf{g}_T^{\overline{\overline{i\iota}}} - \mathbf{g}^{\overline{i\iota}}\right){\cdot}\mathbf{v}^{\bar{\iota}} \\
& - \sum_{i\in\mathcal{I}_S}\left(\epsilon^{\iota}\psi^{\overline{i\iota}}r^{i\iota} + \left\langle\rho_{\iota}\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_{\iota},\Omega}\right) - \sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\sum_{i\in\mathcal{I}_S}\overset{i\kappa\to i\iota}{M_E} + \overset{\kappa\to\iota}{T_v} + \overset{\kappa\to\iota}{Q}\right)
\end{aligned}
$$

222

$$+\left\langle \frac{\left(E_\iota + \rho_\iota \frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} + \sum_{i\in\mathfrak{I}_s} \rho_\iota\omega_{i\iota}\left(\psi_{i\iota} + \frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2}\right)\right)\mathbf{e}\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\left\langle \frac{\mathbf{e}\cdot\left(\mathbf{t}_\iota\cdot\mathbf{v}_\iota + \mathbf{q}_\iota\right)}{\mathbf{n}_\iota \cdot \mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = 0,$$

or in shorthand notation we have

$$\text{(B.122)} \quad \mathcal{E}^\iota = \frac{\mathrm{D}^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \mathbf{v}^{\bar{\iota}}\cdot\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\mathbf{v}^{\bar{\iota}}\right)}{\mathrm{D}t} + \sum_{i\in\mathfrak{I}_s}\left(K_E^{\bar{\bar{\iota}}} - \frac{\mathbf{v}^{\bar{\iota}}\cdot\mathbf{v}^{\bar{\iota}}}{2} + \psi^{\bar{\bar{\iota}}}\right)\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{\bar{\iota}\iota}\right)}{\mathrm{D}t}$$

$$+\mathcal{E}_r^\iota = 0 \qquad \text{for } \iota \in \mathfrak{I},$$

where $\mathcal{E}_r^\iota$ accounts for the residual terms in Eq. (B.121) that are not explicitly written in Eq. (B.122).

The species-entity conservation of momentum equation can be written as

$$\text{(B.123)} \quad \boldsymbol{\mathcal{P}}^{i\iota} = \frac{\mathrm{D}^{\bar{i}\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{v}^{\bar{i}\bar{\iota}}\right)}{\mathrm{D}t} + \epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{v}^{\bar{i}\bar{\iota}}\mathbf{I}:\mathbf{d}^{\bar{\bar{i}\bar{\iota}}} - \nabla^{\backprime}\cdot\left(\epsilon^\iota\mathbf{t}^{\bar{\bar{i}\bar{\iota}}}\right) - \epsilon^\iota r^{i\iota}\mathbf{v}^{\bar{i}\bar{\iota}} - \epsilon^\iota\mathbf{p}^{\bar{\bar{i}\bar{\iota}}}$$

$$-\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{g}^{\bar{i}\bar{\iota}} - \sum_{\kappa\in\mathfrak{I}_{c\iota}}\left(\overset{i\kappa\rightarrow i\iota}{\mathbf{M}_{v_i}} + \sum_{j\in\mathfrak{I}_s}\overset{j\kappa\rightarrow i\iota}{\mathbf{T}}\right)$$

$$+\left\langle \frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\mathrm{ext}}\right) - \mathbf{e}\cdot\mathbf{t}_{i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = 0 \qquad \text{for } \iota \in \mathfrak{I},$$

but since we are interested in the overall conservation of momentum equation for an entity, we sum over all species i noting that

$$\text{(B.124)} \qquad\qquad \sum_{i\in\mathfrak{I}_s} \omega^{i\iota}\mathbf{v}^{\bar{i}\bar{\iota}} = \mathbf{v}^{\bar{\iota}}, \quad \text{and}$$

$$\text{(B.125)} \qquad\qquad \sum_{i\in\mathfrak{I}_s}\left(\mathbf{p}^{\bar{\bar{i}\bar{\iota}}} + r^{i\iota}\mathbf{v}^{\bar{i}\bar{\iota}}\right) = 0.$$

Summing over all species and recalling the definition for the microscale stress tensor, Eq. (B.110), we can write

$$\text{(B.126)} \quad \sum_{i\in\mathcal{I}_S} \left(\frac{D^{\overline{\overline{i\iota}}}\left(\epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{v}^{\overline{\overline{i\iota}}}\right)}{Dt} + \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{v}^{\overline{\overline{i\iota}}} \mathbf{I}{:}\mathbf{d}^{\backslash\overline{\overline{i\iota}}} - \nabla^\backslash\cdot\left(\epsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}}\right) \right)$$

$$= \frac{D^{\overline{\iota}}\left(\epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}}\right)}{Dt} + \epsilon^\iota \rho^\iota \mathbf{v}^{\overline{\iota}} \mathbf{I}{:}\mathbf{d}^{\backslash\overline{\iota}} - \nabla^\backslash\cdot\left(\epsilon^\iota \mathbf{t}^{\overline{\iota}}\right).$$

The inter-entity exchange terms can be written for $\dim\Omega_\iota > \dim\Omega_\kappa$ as

$$\text{(B.127)} \quad \sum_{i\in\mathcal{I}_S} \overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}} = \sum_{i\in\mathcal{I}_S} \mathbf{v}_{i\iota}^{\overline{\kappa}} \overset{i\kappa\to i\iota}{M} = \sum_{i\in\mathcal{I}_S} \left[\mathbf{v}_\iota^{\overline{\kappa}} + \left(\mathbf{v}_{i\iota}^{\overline{\kappa}} - \mathbf{v}_\iota^{\overline{\kappa}}\right)\right] \overset{i\kappa\to i\iota}{M}$$

$$= \sum_{i\in\mathcal{I}_S} \overset{i\kappa\to i\iota}{\mathbf{M}_v} + \sum_{i\in\mathcal{I}_S} \left(\mathbf{v}_{i\iota}^{\overline{\kappa}} - \mathbf{v}_\iota^{\overline{\kappa}}\right) \overset{i\kappa\to i\iota}{M},$$

or similarly for $\dim\Omega_\kappa > \dim\Omega_\iota$

$$\text{(B.128)} \quad \sum_{i\in\mathcal{I}_S} \overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}} = \sum_{i\in\mathcal{I}_S} \mathbf{v}_{i\kappa}^{\overline{\iota}} \overset{i\kappa\to i\iota}{M} = \sum_{i\in\mathcal{I}_S} \left[\mathbf{v}_\kappa^{\overline{\iota}} + \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}}\right)\right] \overset{i\kappa\to i\iota}{M}$$

$$= \sum_{i\in\mathcal{I}_S} \overset{i\kappa\to i\iota}{\mathbf{M}_v} + \sum_{i\in\mathcal{I}_S} \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}}\right) \overset{i\kappa\to i\iota}{M},$$

and the transfer of momentum from the κ to the ι entity as

$$\text{(B.129)} \quad \overset{\kappa\to\iota}{\mathbf{T}} = \sum_{i\in\mathcal{I}_S}\sum_{j\in\mathcal{I}_S} \overset{j\kappa\to i\iota}{\mathbf{T}} + \sum_{i\in\mathcal{I}_S} \left(\mathbf{v}_{i\iota}^{\overline{\kappa}} - \mathbf{v}_\iota^{\overline{\kappa}}\right) \overset{i\kappa\to i\iota}{M},$$

for $\dim\Omega_\iota > \dim\Omega_\kappa$, and as

$$\text{(B.130)} \quad \overset{\kappa\to\iota}{\mathbf{T}} = \sum_{i\in\mathcal{I}_S}\sum_{j\in\mathcal{I}_S} \overset{j\kappa\to i\iota}{\mathbf{T}} + \sum_{i\in\mathcal{I}_S} \left(\mathbf{v}_{i\kappa}^{\overline{\iota}} - \mathbf{v}_\kappa^{\overline{\iota}}\right) \overset{i\kappa\to i\iota}{M},$$

for $\dim\Omega_\kappa > \dim\Omega_\iota$.

Again recalling the definitions for microscale and macroscale stress tensors given in Eq. (B.110) and Eq. (B.98) respectively, we sum the last term in Eq. (B.123) over all species i yielding

$$\text{(B.131)}$$
$$\sum_{i\in\mathcal{I}_S} \left\langle \frac{\mathbf{e}\cdot\left[\rho_\iota \omega_{i\iota} \mathbf{v}_{i\iota}\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}}\right) - \mathbf{t}_{i\iota}\right]}{\mathbf{n}_\iota\cdot\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = \left\langle \frac{\mathbf{e}\cdot\left[\rho_\iota \mathbf{v}_\iota\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) - \mathbf{t}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$$

Combining Eqns (B.123)–(B.131), decomposing the stress tensor into its normal and surface components, and applying Eq. (B.106) yields a general entity-based momentum equation of the form

$$(B.132) \quad \boldsymbol{\mathcal{P}}^{\iota} = \frac{D^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\right)}{Dt} + \epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\mathbf{I}:\mathbf{d}^{\bar{\bar{\iota}}} - \nabla \boldsymbol{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\bar{\bar{\iota}}}\right) - \sum_{i\in\mathcal{I}_S} \epsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{g}_T^{\bar{\bar{i\iota}}}$$

$$- \sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\sum_{i\in\mathcal{I}_S} \overset{i\kappa\to i\iota}{\mathbf{M}_v} + \overset{\kappa\to\iota}{\mathbf{T}}\right) + \left\langle \frac{\mathbf{e}\boldsymbol{\cdot}\left[\rho_{\iota}\mathbf{v}_{\iota}\left(\mathbf{v}_{\iota} - \mathbf{v}_{\text{ext}}\right) - \mathbf{t}_{\iota}\right]}{\mathbf{n}_{\iota}\boldsymbol{\cdot}\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}$$

$$= 0 \quad \text{for } \iota \in \mathcal{I},$$

which may be written in shorthand as

$$(B.133) \qquad \boldsymbol{\mathcal{P}}^{\iota} = \frac{D^{\bar{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\bar{\iota}}\right)}{Dt} + \boldsymbol{\mathcal{P}}_r^{\iota} = 0 \qquad \text{for } \iota \in \mathcal{I},$$

where $\boldsymbol{\mathcal{P}}_r^{\iota}$ accounts for the residual terms from Eq. (B.132) that are not explicitly expressed in Eqn (B.133).

The balance of entropy equation for species i in entity ι is given by

$$(B.134) \quad \mathcal{S}^{i\iota} = \frac{D^{\bar{i\iota}}\eta^{\bar{\bar{i\iota}}}}{Dt} + \eta^{\bar{\bar{i\iota}}}\mathbf{I}:\mathbf{d}^{\bar{\bar{i\iota}}} - \nabla\boldsymbol{\cdot}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\bar{\bar{i\iota}}}\right) - \epsilon^{\iota}b^{i\iota} - \sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\overset{i\kappa\to i\iota}{M_{\eta_i}} + \sum_{j\in\mathcal{I}_S}\overset{j\kappa\to i\iota}{\Phi}\right)$$

$$+ \left\langle \frac{\mathbf{e}\boldsymbol{\cdot}\left[\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}}\right)\eta_{i\iota} - \boldsymbol{\varphi}_{i\iota}\right]}{\mathbf{n}_{\iota}\boldsymbol{\cdot}\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} = \Lambda^{\bar{\bar{i\iota}}} \qquad \text{for } \iota \in \mathcal{I},$$

where $\boldsymbol{\varphi}_{i\iota} = \boldsymbol{\varphi}'_{i\iota}$ when $\iota \in \mathcal{I}_{\text{I}}$ and $\boldsymbol{\varphi}_{i\iota} = \boldsymbol{\varphi}''_{i\iota}$ when $\iota \in \mathcal{I}_{\text{C}}$.

Since we are interested in balance of entropy for the whole entity, we sum over species i noting that

$$(B.135) \qquad \eta^{\bar{\iota}} = \sum_{i\in\mathcal{I}_S} \eta^{\bar{\bar{i\iota}}}, \quad b^{\iota} = \sum_{i\in\mathcal{I}_S} b^{i\iota}, \quad \epsilon^{\iota}\boldsymbol{\varphi}^{\bar{\iota}} = \sum_{i\in\mathcal{I}_S}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\bar{\bar{i\iota}}} - \eta^{\bar{\bar{i\iota}}}\mathbf{u}^{\bar{\bar{i\iota}}}\right),$$

and

$$(B.136) \qquad\qquad\qquad \Lambda^{\bar{\iota}} = \sum_{i\in\mathcal{I}_S} \Lambda^{\bar{\bar{i\iota}}}.$$

Using the dispersion velocity, we can write

$$
\text{(B.137)} \quad \sum_{i\in\mathfrak{I}_S}\left(\frac{\mathrm{D}^{\overline{\overline{i\iota}}}\eta^{\overline{\overline{i\iota}}}}{\mathrm{D}t}+\eta^{\overline{\overline{i\iota}}}\mathbf{I}\mathbf{:}\mathbf{d}^{\backslash\overline{\overline{i\iota}}}-\nabla^{\backslash}\mathbf{\cdot}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{i\iota}}}\right)-\epsilon^{\iota}b^{i\iota}\right)
$$

$$
=\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t}+\eta^{\overline{\iota}}\mathbf{I}\mathbf{:}\mathbf{d}^{\backslash\overline{\iota}}-\sum_{i\in\mathfrak{I}_S}\nabla^{\backslash}\mathbf{\cdot}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{i\iota}}}-\sum_{i\in\mathfrak{I}_S}\eta^{\overline{\overline{i\iota}}}\mathbf{u}^{\overline{\overline{i\iota}}}\right)-\epsilon^{\iota}b^{\iota}
$$

$$
=\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t}+\eta^{\overline{\iota}}\mathbf{I}\mathbf{:}\mathbf{d}^{\backslash\overline{\iota}}-\nabla^{\backslash}\mathbf{\cdot}\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\iota}}\right)-\epsilon^{\iota}b^{\iota}.
$$

The inter-entity exchange terms can be written for $\dim\Omega_\iota>\dim\Omega_\kappa$ as

$$
\text{(B.138)} \quad \sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M}_{\eta_i}=\sum_{i\in\mathfrak{I}_S}\eta^{\overline{\overline{\kappa}}}_{i\iota}\overset{i\kappa\to i\iota}{M}=\sum_{i\in\mathfrak{I}_S}\left[\eta^{\overline{\overline{\kappa}}}_{\iota}+\left(\eta^{\overline{\overline{\kappa}}}_{i\iota}-\eta^{\overline{\overline{\kappa}}}_{\iota}\right)\right]\overset{i\kappa\to i\iota}{M}
$$

$$
=\sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M}_{\eta}+\sum_{i\in\mathfrak{I}_S}\left(\eta^{\overline{\overline{\kappa}}}_{i\iota}-\eta^{\overline{\overline{\kappa}}}_{\iota}\right)\overset{i\kappa\to i\iota}{M},
$$

or similarly for $\dim\Omega_\kappa>\dim\Omega_\iota$

$$
\text{(B.139)} \quad \sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M}_{\eta_i}=\sum_{i\in\mathfrak{I}_S}\eta^{\overline{\iota}}_{i\kappa}\overset{i\kappa\to i\iota}{M}=\sum_{i\in\mathfrak{I}_S}\left[\eta^{\overline{\overline{\iota}}}_{\kappa}+\left(\eta^{\overline{\overline{\iota}}}_{i\kappa}-\eta^{\overline{\overline{\iota}}}_{\kappa}\right)\right]\overset{i\kappa\to i\iota}{M}
$$

$$
=\sum_{i\in\mathfrak{I}_S}\overset{i\kappa\to i\iota}{M}_{\eta}+\sum_{i\in\mathfrak{I}_S}\left(\eta^{\overline{\overline{\iota}}}_{i\kappa}-\eta^{\overline{\overline{\iota}}}_{\kappa}\right)\overset{i\kappa\to i\iota}{M},
$$

and the transfer of entropy from the κ to the ι entity as

$$
\text{(B.140)} \quad \overset{\kappa\to\iota}{\Phi}=\sum_{i\in\mathfrak{I}_S}\sum_{j\in\mathfrak{I}_S}\overset{j\kappa\to i\iota}{\Phi}+\sum_{i\in\mathfrak{I}_S}\left(\eta^{\overline{\overline{\kappa}}}_{i\iota}-\eta^{\overline{\overline{\kappa}}}_{\iota}\right)\overset{i\kappa\to i\iota}{M},
$$

for $\dim\Omega_\iota>\dim\Omega_\kappa$, and as

$$
\text{(B.141)} \quad \overset{\kappa\to\iota}{\Phi}=\sum_{i\in\mathfrak{I}_S}\sum_{j\in\mathfrak{I}_S}\overset{j\kappa\to i\iota}{\Phi}+\sum_{i\in\mathfrak{I}_S}\left(\eta^{\overline{\overline{\iota}}}_{i\kappa}-\eta^{\overline{\overline{\iota}}}_{\kappa}\right)\overset{i\kappa\to i\iota}{M},
$$

for $\dim\Omega_\kappa>\dim\Omega_\iota$.

Summing the last term in Eqn (B.134) over all species i and taking into account that

$$\boldsymbol{\varphi}_\iota = \sum_{i \in \mathcal{I}_s} \left(\boldsymbol{\varphi}_{i\iota} - \eta_{i\iota} \mathbf{u}_{i\iota} \right) \text{ yields}$$

(B.142)

$$\sum_{i \in \mathcal{I}_s} \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_{i\iota} - \mathbf{v}_{\text{ext}} \right) \eta_{i\iota} - \boldsymbol{\varphi}_{i\iota} \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}} \right) \eta_\iota - \boldsymbol{\varphi}_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}.$$

Combining Eqns (B.134)–(B.142), decomposing $\boldsymbol{\varphi}^{\bar{\iota}}$ into its normal and surface components and defining a total entropy source term

(B.143)
$$b_T^{\bar{\bar{\iota}}} = b^\iota + \left(\nabla' \cdot \mathbf{N} \right) \left(\mathbf{N} \cdot \boldsymbol{\varphi}^{\bar{\bar{\iota}}} \right),$$

a general entity-based entropy balance equation can be written as

(B.144) $\quad \mathcal{S}^\iota = \dfrac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \eta^{\bar{\bar{\iota}}} \mathbf{l} : \mathbf{d}^{\backslash\bar{\bar{\iota}}} - \nabla' \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\backslash\bar{\bar{\iota}}} \right) - \epsilon^\iota b_T^{\bar{\bar{\iota}}} - \displaystyle\sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\sum_{i \in \mathcal{I}_s} {}^{i\kappa \to i\iota} M_\eta + {}^{\kappa \to \iota} \overset{\scriptscriptstyle\frown}{\Phi} \right)$

$$+ \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}} \right) \eta_\iota - \boldsymbol{\varphi}_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda^{\bar{\bar{\iota}}}.$$

Summing over all entities provides the equation for the entropy of the system

(B.145) $\displaystyle\sum_{\iota \in \mathcal{I}} \mathcal{S}^\iota = \sum_{\iota \in \mathcal{I}} \left(\dfrac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \eta^{\bar{\bar{\iota}}} \mathbf{l} : \mathbf{d}^{\backslash\bar{\bar{\iota}}} - \nabla' \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\backslash\bar{\bar{\iota}}} \right) - \epsilon^\iota b_T^{\bar{\bar{\iota}}} \right.$

$$\left. + \left\langle \frac{\mathbf{e} \cdot \left[\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}} \right) \eta_\iota - \boldsymbol{\varphi}_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \right) = \Lambda \geq 0.$$

We can write a shorthand expression for the entropy inequality as

(B.146)
$$\sum_{\iota \in \mathcal{I}} \mathcal{S}^\iota = \sum_{\iota \in \mathcal{I}} \left(\frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} + \mathcal{S}_r^\iota \right) = \Lambda \geq 0,$$

where $\mathcal{S}_r^\iota$ represents the residual terms in the entropy inequality, Eq. (B.145).

B.5. Fluid-Phase Thermodynamics

We will consider liquids and solids separately, because of the differences that exist in the underlying microscale CIT formulations for these different types of matter. The microscale CIT expression for the energy of a fluid phase per unit volume, denoted $\iota \in \mathcal{I}_f$, where $\mathcal{I}_f$ is the index set of fluid phases, is the Euler equation given by [18, 42]

$$(B.147) \qquad E_\iota - \eta_\iota \theta_\iota - \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \mu_{i\iota} + p_\iota = 0 \quad \text{for } \iota \in \mathcal{I}_f,$$

where θ_ι is the temperature, $\mu_{i\iota}$ is the chemical potential, and p_ι is the fluid pressure. The averaging operator can be applied to Eq. (B.147) to derive the macroscale Euler equation of the form

$$(B.148) \qquad E^{\bar{\iota}} - \eta^{\bar{\iota}} \theta^{\bar{\iota}} - \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mu^{\overline{i\iota}} + \epsilon^\iota p^\iota = 0 \quad \text{for } \iota \in \mathcal{I}_f,$$

where

$$(B.149) \qquad \theta^{\bar{\iota}} = \langle \theta_\iota \rangle_{\Omega_\iota, \Omega_\iota, \eta_\iota}.$$

Taking the partial derivative of Eq. (B.147) with respect to time, adding and subtracting products involving macroscale temperature and chemical potential, applying an instance of the microscale Gibbs-Duhem equation,

$$(B.150) \qquad \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \frac{\partial \mu_{i\iota}}{\partial t} + \eta_\iota \frac{\partial \theta_\iota}{\partial t} - \frac{\partial p_\iota}{\partial t} = 0,$$

and rearranging yields

$$(B.151) \quad \frac{\partial E_\iota}{\partial t} - \theta^{\bar{\iota}} \frac{\partial \eta_\iota}{\partial t} - \sum_{i \in \mathcal{I}_s} \mu^{\overline{i\iota}} \frac{\partial (\rho_\iota \omega_{i\iota})}{\partial t} - \left(\theta_\iota - \theta^{\bar{\iota}} \right) \frac{\partial \eta_\iota}{\partial t}$$

$$- \sum_{i \in \mathcal{I}_s} \left(\mu_{i\iota} - \mu^{\overline{i\iota}} \right) \frac{\partial (\rho_\iota \omega_{i\iota})}{\partial t} = 0 \quad \text{for } \iota \in \mathcal{I}_f.$$

Applying the averaging operator, the transport theorem given by Eq. (3.4), and the product rule to Eq. (B.151) results in

(B.152)
$$
\frac{\partial^{\backslash} E^{\overline{\overline{\iota}}}}{\partial t} - \theta^{\overline{\iota}}\frac{\partial^{\backslash} \eta^{\overline{\overline{\iota}}}}{\partial t} - \sum_{i \in \mathfrak{I}_s} \mu^{\overline{\overline{i\iota}}}\frac{\partial^{\backslash}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\right)}{\partial t}
$$

$$
- \sum_{\kappa \in \mathfrak{I}_{c\iota}} \left\langle \mathbf{n}_{\iota} \cdot \mathbf{v}_{\kappa} \left(E_{\iota} - \theta^{\overline{\iota}}\eta_{\iota} - \sum_{i \in \mathfrak{I}_s} \mu^{\overline{\overline{i\iota}}}\rho_{\iota}\omega_{i\iota} \right) \right\rangle_{\Omega_{\kappa},\Omega}
$$

$$
- \left\langle \mathbf{e} \cdot \mathbf{v}_{\text{ext}} \left(E_{\iota} - \theta^{\overline{\iota}}\eta_{\iota} - \sum_{i \in \mathfrak{I}_s} \mu^{\overline{\overline{i\iota}}}\rho_{\iota}\omega_{i\iota} \right) \right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
- \left\langle \frac{\partial\left[\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)\eta_{\iota}\right]}{\partial t} + \sum_{i \in \mathfrak{I}_s} \frac{\partial\left[\left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)\rho_{\iota}\omega_{i\iota}\right]}{\partial t} \right\rangle_{\Omega_{\iota},\Omega}
$$

$$
+ \left\langle \eta_{\iota}\frac{\partial\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)}{\partial t} + \sum_{i \in \mathfrak{I}_s} \rho_{\iota}\omega_{i\iota}\frac{\partial\left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)}{\partial t} \right\rangle_{\Omega_{\iota},\Omega} = 0.
$$

Substituting Eq. (B.147) in Eq. (B.152) and applying the transport theorem given by Eq. (3.4) to the fourth line of this equation results in

(B.153)
$$
\frac{\partial^{\backslash} E^{\overline{\overline{\iota}}}}{\partial t} - \theta^{\overline{\iota}}\frac{\partial^{\backslash} \eta^{\overline{\overline{\iota}}}}{\partial t} - \sum_{i \in \mathfrak{I}_s} \mu^{\overline{\overline{i\iota}}}\frac{\partial^{\backslash}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\right)}{\partial t}
$$

$$
- \sum_{\kappa \in \mathfrak{I}_{c\iota}} \left\langle \mathbf{n}_{\iota} \cdot \mathbf{v}_{\kappa} \left(\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)\eta_{\iota} + \sum_{i \in \mathfrak{I}_s} \left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)\rho_{\iota}\omega_{i\iota} - p_{\iota} \right) \right\rangle_{\Omega_{\kappa},\Omega}
$$

$$
- \left\langle \mathbf{e} \cdot \mathbf{v}_{\text{ext}} \left(\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)\eta_{\iota} - \sum_{i \in \mathfrak{I}_s} \left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)\rho_{\iota}\omega_{i\iota} - p_{\iota} \right) \right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
- \frac{\partial^{\backslash}}{\partial t} \left\langle \left(\theta_{\iota} - \theta^{\overline{\iota}}\right)\eta_{\iota} + \sum_{i \in \mathfrak{I}_s} \left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)\rho_{\iota}\omega_{i\iota} \right\rangle_{\Omega_{\iota},\Omega}
$$

$$
+ \sum_{\kappa \in \mathfrak{I}_{c\iota}} \left\langle \mathbf{n}_{\iota} \cdot \mathbf{v}_{\kappa} \left(\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)\eta_{\iota} + \sum_{i \in \mathfrak{I}_s} \left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)\rho_{\iota}\omega_{i\iota} \right) \right\rangle_{\Omega_{\kappa},\Omega}
$$

$$+\left\langle \mathbf{e}\cdot\mathbf{v}_{\text{ext}}\left(\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota + \sum_{i\in\mathfrak{I}_s}\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)\rho_\iota\omega_{i\iota}\right)\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle \eta_\iota\frac{\partial\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)}{\partial t} + \sum_{i\in\mathfrak{I}_s}\rho_\iota\omega_{i\iota}\frac{\partial\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = 0,$$

which may be written as

(B.154) $\quad\dfrac{\partial^\backprime E^{\overline{\overline{\iota}}}}{\partial t} - \theta^{\overline{\overline{\iota}}}\dfrac{\partial^\backprime\eta^{\overline{\overline{\iota}}}}{\partial t} - \displaystyle\sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\iota}}\dfrac{\partial^\backprime\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\right)}{\partial t}$

$$+\sum_{\kappa\in\mathfrak{I}_{c\iota}}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa p_\iota\rangle_{\Omega_\kappa,\Omega} + \langle\mathbf{e}\cdot\mathbf{v}_{\text{ext}}p_\iota\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\partial\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)}{\partial t} + \sum_{i\in\mathfrak{I}_s}\rho_\iota\omega_{i\iota}\frac{\partial\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = 0.$$

Applying the gradient operator to Eq. (B.147), adding and subtracting macroscale temperature and chemical potential terms, and applying the microscale Gibbs-Duhem equation,

(B.155) $$\sum_{i\in\mathfrak{I}_s}\rho_\iota\omega_{i\iota}\nabla\mu_{i\iota} + \eta_\iota\nabla\theta_\iota - \nabla p_\iota = 0,$$

yields

(B.156) $\quad\nabla E_\iota - \theta^{\overline{\overline{\iota}}}\nabla\eta_\iota - \displaystyle\sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\iota}}\nabla\left(\rho_\iota\omega_{i\iota}\right) - \left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\nabla\eta_\iota$

$$-\sum_{i\in\mathfrak{I}_s}\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)\nabla(\rho_\iota\omega_{i\iota}) = 0.$$

Applying the averaging operator, the gradient theorem given by Eq. (3.3), and the product rule to Eq. (B.156) gives

(B.157) $\quad\nabla^\backprime E^{\overline{\overline{\iota}}} - \theta^{\overline{\overline{\iota}}}\nabla^\backprime\eta^{\overline{\overline{\iota}}} - \displaystyle\sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\iota}}\nabla^\backprime\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\right)$

$$+ \sum_{\kappa \in \mathcal{I}_{C\iota}} \left\langle \mathbf{n}_\iota \left(E_\iota - \theta^{\bar{\bar{\iota}}} \eta_\iota - \sum_{i \in \mathcal{I}_S} \mu^{\bar{i\iota}} \rho_\iota \omega_{i\iota} \right) \right\rangle_{\Omega_\kappa, \Omega}$$

$$+ \left\langle \mathbf{e} \left(E_\iota - \theta^{\bar{\bar{\iota}}} \eta_\iota - \sum_{i \in \mathcal{I}_S} \mu^{\bar{i\iota}} \rho_\iota \omega_{i\iota} \right) \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \left\langle \nabla \left[\left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right) \eta_\iota \right] \right\rangle_{\Omega_\iota, \Omega} - \left\langle \sum_{i \in \mathcal{I}_S} \nabla \left[\left(\mu_{i\iota} - \mu^{\bar{i\iota}} \right) \rho_\iota \omega_{i\iota} \right] \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \left\langle \eta_\iota \nabla \left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right) \right\rangle_{\Omega_\iota, \Omega} + \left\langle \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \nabla \left(\mu_{i\iota} - \mu^{\bar{i\iota}} \right) \right\rangle_{\Omega_\iota, \Omega} = 0.$$

Applying the gradient theorem to the fourth line in Eq. (B.157), canceling the gradient of the average term that vanishes, using Eq. (B.147), and rearranging yields

$$(B.158) \quad \nabla^\backprime E^{\bar{\bar{\iota}}} - \theta^{\bar{\bar{\iota}}} \nabla^\backprime \eta^{\bar{\bar{\iota}}} - \sum_{i \in \mathcal{I}_S} \mu^{\bar{i\iota}} \nabla^\backprime \left(\epsilon^\iota \rho^\iota \omega^{\bar{i\iota}} \right) - \sum_{\kappa \in \mathcal{I}_{C\iota}} \left\langle \mathbf{n}_\iota p_\iota \right\rangle_{\Omega_\kappa, \Omega} - \left\langle \mathbf{e} p_\iota \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \left\langle \eta_\iota \nabla \left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right) \right\rangle_{\Omega_\iota, \Omega} + \left\langle \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \nabla \left(\mu_{i\iota} - \mu^{\bar{i\iota}} \right) \right\rangle_{\Omega_\iota, \Omega} = 0.$$

Taking the dot product of Eq. (B.158) with $\mathbf{v}^{\bar{\iota}}$ and addition to Eq. (B.154) yields

$$(B.159) \quad \mathcal{T}^\iota = \frac{D^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{Dt} - \theta^{\bar{\bar{\iota}}} \frac{D^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{Dt} - \sum_{i \in \mathcal{I}_S} \mu^{\bar{i\iota}} \frac{D^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{\bar{i\iota}} \right)}{Dt}$$

$$+ \sum_{\kappa \in \mathcal{I}_{C\iota}} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\bar{\iota}} \right) p_\iota \right\rangle_{\Omega_\kappa, \Omega} + \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{\iota}} \right) p_\iota \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \left\langle \eta_\iota \frac{D^{\bar{\iota}} \left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right)}{Dt} + \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \frac{D^{\bar{\iota}} \left(\mu_{i\iota} - \mu^{\bar{i\iota}} \right)}{Dt} \right\rangle_{\Omega_\iota, \Omega} = 0 \quad \text{for } \iota \in \mathcal{I}_\text{f}.$$

Eq. (B.159) can also be converted to a form where the material derivatives are referenced to the solid-phase velocity $\mathbf{v}^{\bar{s}}$ by noting

$$(B.160) \qquad\qquad \frac{D^{\bar{\iota}}}{Dt} = \frac{D^{\bar{s}}}{Dt} + \left(\mathbf{v}^{\bar{\iota}} - \mathbf{v}^{\bar{s}} \right) \cdot \nabla,$$

and defining

(B.161)
$$\mathbf{v}^{\overline{\iota},\overline{s}} = \mathbf{v}^{\overline{\iota}} - \mathbf{v}^{\overline{s}}.$$

Application of Eq. (B.160) to the material derivatives within averaging operators in Eq. (B.159) yields

(B.162) $\quad \mathcal{T}^{\iota} = \dfrac{\mathrm{D}^{\overline{\iota}} E^{\overline{\iota}}}{\mathrm{D}t} - \theta^{\overline{\iota}} \dfrac{\mathrm{D}^{\overline{\iota}} \eta^{\overline{\iota}}}{\mathrm{D}t} - \displaystyle\sum_{i\in\mathcal{I}_s} \mu^{\overline{i\iota}} \dfrac{\mathrm{D}^{\overline{\iota}} \left(\epsilon^{\iota}\rho^{\iota}\omega^{i\iota}\right)}{\mathrm{D}t}$

$\qquad + \displaystyle\sum_{\kappa\in\mathcal{I}_{c\iota}} \left\langle \mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa} - \mathbf{v}^{\overline{\iota}}\right) p_{\iota}\right\rangle_{\Omega_{\kappa},\Omega} + \left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{\iota}}\right) p_{\iota}\right\rangle_{\Gamma_{\iota M},\Omega}$

$\qquad + \left\langle \eta_{\iota} \dfrac{\mathrm{D}^{\overline{s}}\left(\theta_{\iota} - \theta^{\overline{\iota}}\right)}{\mathrm{D}t} + \displaystyle\sum_{i\in\mathcal{I}_s} \rho_{\iota}\omega_{i\iota} \dfrac{\mathrm{D}^{\overline{s}}\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}$

$\qquad + \mathbf{v}^{\overline{\iota},\overline{s}}\cdot\left\langle \eta_{\iota}\nabla\left(\theta_{\iota} - \theta^{\overline{\iota}}\right) + \displaystyle\sum_{i\in\mathcal{I}_s} \rho_{\iota}\omega_{i\iota}\nabla\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)\right\rangle_{\Omega_{\iota},\Omega} = 0 \quad \text{for } \iota\in\mathcal{I}_{\mathrm{f}}.$

Using the Gibbs-Duhem equation, Eq. (B.155), we can write the last term in Eq. (B.162) as

(B.163) $\quad \mathbf{v}^{\overline{\iota},\overline{s}}\cdot\left\langle \eta_{\iota}\nabla\left(\theta_{\iota} - \theta^{\overline{\iota}}\right) + \displaystyle\sum_{i\in\mathcal{I}_s} \rho_{\iota}\omega_{i\iota}\nabla\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)\right\rangle_{\Omega_{\iota},\Omega}$

$\qquad = \mathbf{v}^{\overline{\iota},\overline{s}}\cdot\left\langle -\eta_{\iota}\nabla\theta^{\overline{\iota}} - \displaystyle\sum_{i\in\mathcal{I}_s} \rho_{\iota}\omega_{i\iota}\nabla\mu^{\overline{i\iota}} + \nabla p_{\iota}\right\rangle_{\Omega_{\iota},\Omega}.$

Application of the product rule yields

(B.164) $\quad \mathbf{v}^{\overline{\iota},\overline{s}}\cdot\left\langle -\eta_{\iota}\nabla\theta^{\overline{\iota}} - \displaystyle\sum_{i\in\mathcal{I}_s} \rho_{\iota}\omega_{i\iota}\nabla\mu^{\overline{i\iota}} + \nabla p_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$

$\qquad = \mathbf{v}^{\overline{\iota},\overline{s}}\cdot\left\langle -\nabla\left(\eta_{\iota}\theta^{\overline{\iota}}\right) + \theta^{\overline{\iota}}\nabla\eta_{\iota} + \nabla p_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$

$\qquad - \mathbf{v}^{\overline{\iota},\overline{s}}\cdot\left\langle \displaystyle\sum_{i\in\mathcal{I}_s} \left[\nabla\left(\rho_{\iota}\omega_{i\iota}\mu^{\overline{i\iota}}\right) - \mu^{\overline{i\iota}}\nabla\left(\rho_{\iota}\omega_{i\iota}\right)\right]\right\rangle_{\Omega_{\iota},\Omega}.$

Applying the gradient averaging theorem given by Eq. (3.3) to Eq. (B.164) and canceling like terms, we get

$$
(B.165) \quad \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left\langle -\eta_\iota \nabla \theta^{\bar{\bar{\iota}}} - \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \nabla \mu^{\overline{i\iota}} + \nabla p_\iota \right\rangle_{\Omega_\iota,\Omega}
$$

$$
= \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left(-\nabla^{\backprime} \left(\eta^{\bar{\iota}} \theta^{\bar{\bar{\iota}}} \right) + \theta^{\bar{\bar{\iota}}} \nabla^{\backprime} \eta^{\bar{\iota}} - \sum_{i \in \mathcal{I}_S} \left[\nabla^{\backprime} \left(\epsilon^\iota \rho^\iota \omega^{i\iota} \mu^{\overline{i\iota}} \right) - \mu^{\overline{i\iota}} \nabla^{\backprime} \left(\epsilon^\iota \rho^\iota \omega^{i\iota} \right) \right] \right.
$$

$$
+ \nabla^{\backprime} \left(\epsilon^\iota p^\iota \right) + \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(-\left\langle \mathbf{n}_\iota \eta_\iota \theta^{\bar{\bar{\iota}}} \right\rangle_{\Omega_\kappa,\Omega} + \theta^{\bar{\bar{\iota}}} \langle \mathbf{n}_\iota \eta_\iota \rangle_{\Omega_\kappa,\Omega} + \langle \mathbf{n}_\iota p_\iota \rangle_{\Omega_\kappa,\Omega} \right)
$$

$$
+ \sum_{\kappa \in \mathcal{I}_{c\iota}} \sum_{i \in \mathcal{I}_S} \left(-\left\langle \mathbf{n}_\iota \rho_\iota \omega_{i\iota} \mu^{\overline{i\iota}} \right\rangle_{\Omega_\kappa,\Omega} + \mu^{\overline{i\iota}} \langle \mathbf{n}_\iota \rho_\iota \omega_{i\iota} \rangle_{\Omega_\kappa,\Omega} \right)
$$

$$
- \left\langle \mathbf{e} \eta_\iota \theta^{\bar{\bar{\iota}}} \right\rangle_{\Gamma_{\iota M},\Omega} + \theta^{\bar{\bar{\iota}}} \langle \mathbf{e} \eta_\iota \rangle_{\Gamma_{\iota M},\Omega} + \langle \mathbf{e} p_\iota \rangle_{\Gamma_{\iota M},\Omega}
$$

$$
\left. + \sum_{i \in \mathcal{I}_S} \left(-\left\langle \mathbf{e} \rho_\iota \omega_{i\iota} \mu^{\overline{i\iota}} \right\rangle_{\Gamma_{\iota M},\Omega} + \mu^{\overline{i\iota}} \langle \mathbf{e} \rho_\iota \omega_{i\iota} \rangle_{\Gamma_{\iota M},\Omega} \right) \right)
$$

$$
= \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left(-\eta^{\bar{\iota}} \nabla^{\backprime} \theta^{\bar{\bar{\iota}}} - \sum_{i \in \mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\iota} \nabla^{\backprime} \mu^{\overline{i\iota}} + \nabla^{\backprime} \left(\epsilon^\iota p^\iota \right) \right)
$$

$$
+ \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \left(\sum_{\kappa \in \mathcal{I}_{c\iota}} \langle \mathbf{n}_\iota p_\iota \rangle_{\Omega_\kappa,\Omega} + \langle \mathbf{e} p_\iota \rangle_{\Gamma_{\iota M},\Omega} \right) .
$$

Substituting Eq. (B.165) into Eq. (B.162), we can write the macroscale thermodynamic expression for a fluid phase as

$$
(B.166) \quad \mathcal{T}^\iota = \frac{\mathrm{D}^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \theta^{\bar{\bar{\iota}}} \frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\iota}}}{\mathrm{D}t} - \sum_{i \in \mathcal{I}_S} \mu^{\overline{i\iota}} \frac{\mathrm{D}^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{i\iota} \right)}{\mathrm{D}t}
$$

$$
+ \sum_{\kappa \in \mathcal{I}_{c\iota}} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}} \right) p_\iota \right\rangle_{\Omega_\kappa,\Omega} + \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\bar{s}} \right) p_\iota \right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
+ \left\langle \eta_\iota \frac{\mathrm{D}^{\bar{s}} \left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right)}{\mathrm{D}t} + \sum_{i \in \mathcal{I}_S} \rho_\iota \omega_{i\iota} \frac{\mathrm{D}^{\bar{s}} \left(\mu_{i\iota} - \mu^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}
$$

$$-\mathbf{v}^{\overline{\iota,\overline{s}}} \cdot \left(\eta^{\overline{\overline{\iota}}} \nabla^{\backprime} \theta^{\overline{\overline{\iota}}} + \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{\overline{\overline{i\iota}}} \nabla^{\backprime} \mu^{\overline{\overline{i\iota}}} - \nabla^{\backprime} \left(\epsilon^{\iota} p^{\iota} \right) \right) = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathsf{f}}.$$

B.6. Solid-Phase Thermodynamics

The microscale Euler equation for internal energy per unit volume of the solid phase can be written as

$$(\text{B.167}) \qquad E_s - \theta_s \eta_s - \sum_{i \in \mathcal{I}_s} \rho_s \omega_{is} \mu_{is} - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} = 0.$$

The macroscale Euler equation for internal energy per total volume is then

$$(\text{B.168}) \qquad E^{\overline{\overline{s}}} - \theta^{\overline{\overline{s}}} \eta^{\overline{\overline{s}}} - \sum_{i \in \mathcal{I}_s} \epsilon^s \rho^s \omega^{\overline{\overline{is}}} \mu^{\overline{\overline{is}}} - \epsilon^s \boldsymbol{\sigma}^{\overline{\overline{s}}} : \frac{\mathbf{C}^s}{j^s} = 0,$$

where

$$(\text{B.169}) \qquad \boldsymbol{\sigma}^{\overline{\overline{s}}} : \frac{\mathbf{C}^s}{j^s} = \left\langle \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \right\rangle_{\Omega_s, \Omega_s}.$$

Taking the partial derivative of Eq. (B.167) with respect to time and applying the Gibbs-Duhem equation gives us

$$(\text{B.170}) \qquad \frac{\partial E_s}{\partial t} - \theta_s \frac{\partial \eta_s}{\partial t} - \sum_{i \in \mathcal{I}_s} \mu_{is} \frac{\partial (\rho_s \omega_{is})}{\partial t} - \boldsymbol{\sigma}_s : \frac{\partial}{\partial t} \left(\frac{\mathbf{C}_s}{j_s} \right) = 0.$$

Introduction of macroscale variables $\theta^{\overline{\overline{s}}}$, $\mu^{\overline{\overline{s}}}$, and $\boldsymbol{\sigma}^{\overline{\overline{s}}}$, allows this equation to be rearranged to

$$(\text{B.171}) \quad \frac{\partial E_s}{\partial t} - \theta^{\overline{\overline{s}}} \frac{\partial \eta_s}{\partial t} - \sum_{i \in \mathcal{I}_s} \mu^{\overline{\overline{is}}} \frac{\partial (\rho_s \omega_{is})}{\partial t} - \boldsymbol{\sigma}^{\overline{\overline{s}}} : \frac{\partial}{\partial t} \left(\frac{\mathbf{C}_s}{j_s} \right) - \left(\theta_s - \theta^{\overline{\overline{s}}} \right) \frac{\partial \eta_s}{\partial t}$$

$$- \sum_{i \in \mathcal{I}_s} \left(\mu_{is} - \mu^{\overline{\overline{is}}} \right) \frac{\partial (\rho_s \omega_{is})}{\partial t} - \left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}} \right) : \frac{\partial}{\partial t} \left(\frac{\mathbf{C}_s}{j_s} \right) = 0.$$

Applying an averaging operator from the general form given by Eq. (3.1), transport Theorem 3.4.3, and the product rule to Eq. (B.171) results in

(B.172)
$$\frac{\partial^{\backprime} E^{\overline{\overline{s}}}}{\partial t} - \theta^{\overline{s}}\frac{\partial^{\backprime}\eta^{\overline{s}}}{\partial t} - \sum_{i\in\mathcal{I}_s}\mu^{\overline{is}}\frac{\partial^{\backprime}\left(\epsilon^s\rho^s\omega^{\overline{is}}\right)}{\partial t} - \boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\partial^{\backprime}}{\partial t}\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right)$$

$$-\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle \mathbf{n}_s\cdot\mathbf{v}_\kappa\left(E_s - \theta^{\overline{s}}\eta_s - \sum_{i\in\mathcal{I}_s}\mu^{\overline{is}}\rho_s\omega_{is} - \boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle \mathbf{e}\cdot\mathbf{v}_{\text{ext}}\left(E_s - \theta^{\overline{s}}\eta_s - \sum_{i\in\mathcal{I}_s}\mu^{\overline{is}}\rho_s\omega_{is} - \boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$-\left\langle \frac{\partial}{\partial t}\left[\left(\theta_s - \theta^{\overline{s}}\right)\eta_s\right] + \sum_{i\in\mathcal{I}_s}\frac{\partial}{\partial t}\left[\left(\mu_{is} - \mu^{\overline{is}}\right)\rho_s\omega_{is}\right]\right\rangle_{\Omega_s,\Omega}$$

$$-\left\langle \frac{\partial}{\partial t}\left(\left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\right):\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega}$$

$$+\left\langle \eta_s\frac{\partial\left(\theta_s - \theta^{\overline{s}}\right)}{\partial t} + \sum_{i\in\mathcal{I}_s}\rho_s\omega_{is}\frac{\partial\left(\mu_{is} - \mu^{\overline{is}}\right)}{\partial t} + \frac{\mathbf{C}_s}{j_s}:\frac{\partial\left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\right)}{\partial t}\right\rangle_{\Omega_s,\Omega} = 0.$$

Substituting Eq. (B.167) into Eq. (B.172), applying the transport theorem given by Eq. (3.4) to the fourth and fifth lines of this equation, and cancelling like terms results in

(B.173)
$$\frac{\partial^{\backprime} E^{\overline{\overline{s}}}}{\partial t} - \theta^{\overline{s}}\frac{\partial^{\backprime}\eta^{\overline{\overline{s}}}}{\partial t} - \sum_{i\in\mathcal{I}_s}\mu^{\overline{is}}\frac{\partial^{\backprime}\left(\epsilon^s\rho^s\omega^{\overline{is}}\right)}{\partial t} - \boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\partial^{\backprime}}{\partial t}\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right)$$

$$+\left\langle \eta_s\frac{\partial\left(\theta_s - \theta^{\overline{s}}\right)}{\partial t} + \sum_{i\in\mathcal{I}_s}\rho_s\omega_{is}\frac{\partial\left(\mu_{is} - \mu^{\overline{is}}\right)}{\partial t} + \frac{\mathbf{C}_s}{j_s}:\frac{\partial\left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\right)}{\partial t}\right\rangle_{\Omega_s,\Omega} = 0.$$

Applying the gradient operator to Eq. (B.167), adding and subtracting the macroscale temperature, the chemical potential, and the Lagrangian stress tensor yields

(B.174)
$$\nabla E_s - \theta^{\overline{s}}\nabla\eta_s - \sum_{i\in\mathcal{I}_s}\mu^{\overline{is}}\nabla\left(\rho_s\omega_{is}\right) - \boldsymbol{\sigma}^{\overline{\overline{s}}}:\nabla\left(\frac{\mathbf{C}_s}{j_s}\right) - \left(\theta_s - \theta^{\overline{s}}\right)\nabla\eta_s$$

$$-\sum_{i\in\mathcal{I}_S}\left(\mu_{is}-\mu^{\overline{is}}\right)\nabla(\rho_s\omega_{is})-\left(\boldsymbol{\sigma}_s-\boldsymbol{\sigma}^{\overline{\overline{s}}}\right):\nabla\left(\frac{\mathbf{C}_s}{j_s}\right)=0.$$

Applying the averaging operator, the dot product rule to the last three terms, and the gradient theorem given by Eq. (3.3) to Eq. (B.174) gives us

$$(B.175)\quad \nabla'E^{\overline{\overline{s}}}-\theta^{\overline{\overline{s}}}\nabla'\eta^{\overline{s}}-\sum_{i\in\mathcal{I}_S}\mu^{\overline{is}}\nabla'\left(\epsilon^s\rho^s\omega^{\overline{is}}\right)-\boldsymbol{\sigma}^{\overline{\overline{s}}}:\nabla'\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right)$$

$$+\left\langle\eta_s\nabla\left(\theta_s-\theta^{\overline{\overline{s}}}\right)\right\rangle_{\Omega_s,\Omega}+\sum_{i\in\mathcal{I}_S}\left\langle\rho_s\omega_{is}\nabla\left(\mu_{is}-\mu^{\overline{is}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$+\left\langle\frac{\mathbf{C}_s}{j_s}:\nabla\left(\boldsymbol{\sigma}_s-\boldsymbol{\sigma}^{\overline{\overline{s}}}\right)\right\rangle_{\Omega_s,\Omega}=0.$$

Taking the dot product of Eq. (B.175) with $\mathbf{v}^{\overline{s}}$ and adding to Eq. (B.173) produces

$$(B.176)\quad \mathcal{T}^s=\frac{D^{\overline{s}}E^{\overline{\overline{s}}}}{Dt}-\theta^{\overline{s}}\frac{D^{\overline{s}}\eta^{\overline{s}}}{Dt}-\sum_{i\in\mathcal{I}_S}\mu^{\overline{is}}\frac{D^{\overline{s}}\left(\epsilon^s\rho^s\omega^{\overline{is}}\right)}{Dt}-\boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{D^{\overline{s}}}{Dt}\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right)$$

$$+\left\langle\eta_s\frac{D^{\overline{s}}\left(\theta_s-\theta^{\overline{\overline{s}}}\right)}{Dt}+\sum_{i\in\mathcal{I}_S}\rho_s\omega_{is}\frac{D^{\overline{s}}\left(\mu_{is}-\mu^{\overline{is}}\right)}{Dt}\right\rangle_{\Omega_s,\Omega}$$

$$+\left\langle\frac{\mathbf{C}_s}{j_s}:\frac{D^{\overline{s}}\left(\boldsymbol{\sigma}_s-\boldsymbol{\sigma}^{\overline{\overline{s}}}\right)}{Dt}\right\rangle_{\Omega_s,\Omega}.$$

Consider the terms that appear in Eq. (B.176)

$$(B.177)\qquad T=\left\langle\frac{\mathbf{C}_s}{j_s}:\frac{D^{\overline{s}}\left(\boldsymbol{\sigma}_s-\boldsymbol{\sigma}^{\overline{\overline{s}}}\right)}{Dt}\right\rangle_{\Omega_s,\Omega}-\boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{D^{\overline{s}}}{Dt}\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right).$$

Application of the product rule yields

$$(B.178)\qquad T=-\frac{D^{\overline{s}}}{Dt}\left(\epsilon^s\boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\mathbf{C}^s}{j^s}\right)+\left\langle\frac{\mathbf{C}_s}{j_s}:\frac{D^{\overline{s}}\boldsymbol{\sigma}_s}{Dt}\right\rangle_{\Omega_s,\Omega}.$$

Application of the averaging theorems given by Eq. (3.3) and Eq. (3.4) provides

$$(B.179)\quad T=-\left\langle\frac{D^{\overline{s}}}{Dt}\left(\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega}-\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}+\left\langle \frac{\mathbf{C}_s}{j_s}:\frac{\mathrm{D}^{\overline{s}}\boldsymbol{\sigma}_s}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}.$$

Applying the product rule and regrouping terms

$$(B.180)\quad T=-\left\langle\boldsymbol{\sigma}_s:\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega}-\sum_{\kappa\in\mathfrak{I}_{cs}}\left\langle\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

The reference velocity for the material derivative can be converted to the microscale using

$$(B.181)\qquad\qquad\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}=\frac{\mathrm{D}_s}{\mathrm{D}t}-\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\cdot\nabla,$$

which may be applied to Eq. (B.180) giving

$$(B.182)\quad T=-\left\langle\boldsymbol{\sigma}_s:\frac{\mathrm{D}_s}{\mathrm{D}t}\left(\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega}+\left\langle\boldsymbol{\sigma}_s:\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\cdot\nabla\left(\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathfrak{I}_{cs}}\left\langle\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

Making use of the identities

$$(B.183)\qquad\qquad\frac{\mathrm{D}_s}{\mathrm{D}t}\left(\frac{1}{j_s}\right)\;=\;-\frac{1}{j_s}\mathbf{I}{:}\mathbf{d}_s$$

$$\text{and}$$

$$(B.184)\qquad\qquad\frac{\mathrm{D}_s\mathbf{C}_s}{\mathrm{D}t}\;=\;2\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right){:}\mathbf{d}_s,$$

where $\nabla_X\mathbf{x}$ is the derivative of a microscale location on the solid phase with respect to its initial location [67], yields

$$(B.185)\qquad\qquad\frac{\mathrm{D}_s}{\mathrm{D}t}\left(\frac{\mathbf{C}_s}{j_s}\right)=\left(\frac{2}{j_s}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right)-\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right){:}\mathbf{d}_s,$$

and using Eq. (B.181) allows Eq. (B.185) to be written as

$$(B.186)\qquad\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\frac{\mathbf{C}_s}{j_s}\right)=\left(\frac{2}{j_s}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right)-\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right){:}\mathbf{d}_s-\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\cdot\nabla\left(\frac{\mathbf{C}_s}{j_s}\right).$$

Substituting Eq. (B.185) for the first term in Eq. (B.182) we have

$$
\text{(B.187)} \quad T = -\left\langle \frac{2}{j_s} \boldsymbol{\sigma}_s \colon (\nabla_X \mathbf{x} \nabla_X \mathbf{x}) \colon \mathbf{d}_s \right\rangle_{\Omega_s,\Omega} + \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \mathbf{I} \colon \mathbf{d}_s \right\rangle_{\Omega_s,\Omega}
$$

$$
+ \left\langle \boldsymbol{\sigma}_s \colon \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \cdot \nabla \left(\frac{\mathbf{C}_s}{j_s} \right) \right\rangle_{\Omega_s,\Omega} - \sum_{\kappa \in \mathcal{I}_{cs}} \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa,\Omega}
$$

$$
- \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \right\rangle_{\Gamma_{sM},\Omega}.
$$

Applying the product rule to the third term on the RHS of Eq. (B.187) and combining terms gives

$$
\text{(B.188)} \quad T = -\left\langle \frac{2}{j_s} \boldsymbol{\sigma}_s \colon (\nabla_X \mathbf{x} \nabla_X \mathbf{x}) \colon \mathbf{d}_s \right\rangle_{\Omega_s,\Omega} + \left\langle \nabla \cdot \left(\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \frac{\mathbf{C}_s}{j_s} \right) \colon \boldsymbol{\sigma}_s \right\rangle_{\Omega_s,\Omega}
$$

$$
+ \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \mathbf{I} \colon \mathbf{d}^{\overline{\overline{s}}} \right\rangle_{\Omega_s,\Omega} - \sum_{\kappa \in \mathcal{I}_{cs}} \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa,\Omega}
$$

$$
- \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \right\rangle_{\Gamma_{sM},\Omega}.
$$

Adding and subtracting $\mathbf{d}^{\backslash \overline{s}}$ to the first term on the RHS of Eq. (B.188), and evaluating the third term on the RHS of this equation yields

(B.189)

$$
T = -\left\langle \frac{2}{j_s} \boldsymbol{\sigma}_s \colon (\nabla_X \mathbf{x} \nabla_X \mathbf{x}) \colon \left(\mathbf{d}_s - \mathbf{d}^{\backslash \overline{s}} \right) \right\rangle_{\Omega_s,\Omega} - \left\langle \frac{2}{j_s} \boldsymbol{\sigma}_s \colon (\nabla_X \mathbf{x} \nabla_X \mathbf{x}) \colon \mathbf{d}^{\backslash \overline{s}} \right\rangle_{\Omega_s,\Omega}
$$

$$
+ \left\langle \nabla \cdot \left(\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \frac{\mathbf{C}_s}{j_s} \right) \colon \boldsymbol{\sigma}_s \right\rangle_{\Omega_s,\Omega} + \epsilon^s \boldsymbol{\sigma}^{\overline{\overline{s}}} \colon \frac{\mathbf{C}^s}{j^s} \mathbf{I} \colon \mathbf{d}^{\backslash \overline{s}}
$$

$$
- \sum_{\kappa \in \mathcal{I}_{cs}} \left\langle \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa,\Omega} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}_s \colon \frac{\mathbf{C}_s}{j_s} \right\rangle_{\Gamma_{sM},\Omega}.
$$

Finally, the product rule and the averaging theorem given by Eq. (3.2) are applied to the first and third terms on the RHS of Eq. (B.189), which is a derived expression for Eq. (B.177), resulting in

$$\text{(B.190)} \quad -\boldsymbol{\sigma}^{\overline{\overline{s}}}\!:\!\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right) + \left\langle\frac{\mathbf{C}_s}{j_s}\!:\!\frac{\mathrm{D}^{\overline{s}}\left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega} =$$

$$-\left\langle\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x})\right\rangle_{\Omega_s,\Omega}\!:\!\mathbf{d}^{\backslash\overline{\overline{s}}} + \epsilon^s\boldsymbol{\sigma}^{\overline{\overline{s}}}\!:\!\frac{\mathbf{C}^s}{j^s}\mathbf{I}\!:\!\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-\nabla^{\backslash}\!\cdot\!\left\langle\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x}) - \boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\mathbf{n}_s\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x}) - \boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle\mathbf{e}\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x}) - \boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$+\left\langle\left[\nabla\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x})\right) - \frac{\mathbf{C}_s}{j_s}\!:\!\nabla\boldsymbol{\sigma}_s\right]\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

Eq. (B.190) can be simplified to

$$\text{(B.191)} \quad -\boldsymbol{\sigma}^{\overline{\overline{s}}}\!:\!\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\epsilon^s\frac{\mathbf{C}^s}{j^s}\right) + \left\langle\frac{\mathbf{C}_s}{j_s}\!:\!\frac{\mathrm{D}^{\overline{s}}\left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}^{\overline{\overline{s}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega} =$$

$$-\left\langle\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x})\right\rangle_{\Omega_s,\Omega}\!:\!\mathbf{d}^{\backslash\overline{\overline{s}}} + \epsilon^s\boldsymbol{\sigma}^{\overline{\overline{s}}}\!:\!\frac{\mathbf{C}^s}{j^s}\mathbf{I}\!:\!\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-\nabla^{\backslash}\!\cdot\!\left\langle\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x}) - \boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\mathbf{n}_s\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x})\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle\mathbf{e}\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x})\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$+\left\langle\left[\nabla\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s\!:\!(\nabla_X\mathbf{x}\nabla_X\mathbf{x})\right) - \frac{\mathbf{C}_s}{j_s}\!:\!\nabla\boldsymbol{\sigma}_s\right]\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa - \mathbf{v}_s\right)\right\rangle_{\Omega_\kappa,\Omega} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}_s\right)\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

Substitution of Eq. (B.191) into Eq. (B.176) provides the macroscale thermodynamic expression for the solid phase in the transition region

$$(\text{B.192}) \quad \mathcal{T}^s = \frac{\mathrm{D}^{\bar{s}} E^{\bar{s}}}{\mathrm{D}t} - \theta^{\bar{s}}\frac{\mathrm{D}^{\bar{s}}\eta^{\bar{s}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{is}}\frac{\mathrm{D}^{\bar{s}}\left(\epsilon^s\rho^s\omega^{\overline{is}}\right)}{\mathrm{D}t}$$

$$+\left\langle \eta_s\frac{\mathrm{D}^{\bar{s}}\left(\theta_s-\theta^{\bar{s}}\right)}{\mathrm{D}t} + \sum_{i\in\mathfrak{I}_s}\rho_s\omega_{is}\frac{\mathrm{D}^{\bar{s}}\left(\mu_{is}-\mu^{\overline{is}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}$$

$$-\left\langle\frac{2}{j_s}\boldsymbol{\sigma}_s{:}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right)\right\rangle_{\Omega_s,\Omega}{:}\mathbf{d}^{\backslash\bar{s}} + \epsilon^s\boldsymbol{\sigma}^{\bar{s}}{:}\frac{\mathbf{C}^s}{j^s}\mathbf{I}{:}\mathbf{d}^{\backslash\bar{s}}$$

$$-\nabla^{\backslash}{\cdot}\left\langle\left(\frac{2}{j_s}\boldsymbol{\sigma}_s{:}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right) - \boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathfrak{I}_{cs}}\left\langle\mathbf{n}_s\cdot\left(\frac{2}{j_s}\boldsymbol{\sigma}_s{:}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right)\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle\mathbf{e}{\cdot}\left(\frac{2}{j_s}\boldsymbol{\sigma}_s{:}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right)\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$+\left\langle\left[\nabla{\cdot}\left(\frac{2}{j_s}\boldsymbol{\sigma}_s{:}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right)\right) - \frac{\mathbf{C}_s}{j_s}{:}\nabla\boldsymbol{\sigma}_s\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathfrak{I}_{cs}}\left\langle\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa-\mathbf{v}_s\right)\right\rangle_{\Omega_\kappa,\Omega} - \left\langle\mathbf{e}{\cdot}\left(\mathbf{v}_{\text{ext}}-\mathbf{v}_s\right)\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

Defining the solid phase stress tensor such that,

$$(\text{B.193}) \qquad\qquad \mathbf{t}_s = \frac{2}{j_s}\boldsymbol{\sigma}_s{:}\left(\nabla_X\mathbf{x}\nabla_X\mathbf{x}\right),$$

noting that

$$(\text{B.194}) \qquad \langle\mathbf{t}_s\rangle_{\Omega_s,\Omega_s}{:}\mathbf{d}^{\backslash\bar{s}} = \mathbf{t}^s{:}\mathbf{d}^{\backslash\bar{s}} = \left(\mathbf{t}^{\backslash s} + \mathbf{N}\mathbf{N}{\cdot}\mathbf{t}^s{\cdot}\mathbf{N}\mathbf{N}\right){:}\mathbf{d}^{\backslash\bar{s}} = \mathbf{t}^{\backslash s}{:}\mathbf{d}^{\backslash\bar{s}},$$

and that integration over the solid surface, Ω_{ss}, is equivalent to the summation of integration over the interfaces in $\mathfrak{I}_{cs}$, allows the macroscale thermodynamic expression for the solid phase in the transition region to be written as

$$\text{(B.195)} \quad \mathcal{T}^s = \frac{D^{\bar{s}}E^{\bar{\bar{s}}}}{Dt} - \theta^{\bar{\bar{s}}}\frac{D^{\bar{s}}\eta^{\bar{\bar{s}}}}{Dt} - \sum_{i\in\mathcal{I}_S} \mu^{\overline{is}}\frac{D^{\bar{s}}\left(\epsilon^s\rho^s\omega^{\overline{is}}\right)}{Dt}$$

$$+\left\langle \eta_s\frac{D^{\bar{s}}\left(\theta_s - \theta^{\bar{\bar{s}}}\right)}{Dt} + \sum_{i\in\mathcal{I}_S} \rho_s\omega_{is}\frac{D^{\bar{s}}\left(\mu_{is} - \mu^{\overline{is}}\right)}{Dt}\right\rangle_{\Omega_s,\Omega}$$

$$-\epsilon^s\mathbf{t}^{\backslash s}\!:\!\mathbf{d}^{\backslash\bar{\bar{s}}} + \epsilon^s\boldsymbol{\sigma}^{\bar{\bar{s}}}\!:\!\frac{\mathbf{C}^s}{j^s}\mathbf{I}\!:\!\mathbf{d}^{\backslash\bar{\bar{s}}} - \nabla'\!\cdot\!\left\langle \left(\mathbf{t}_s - \boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{ss},\Omega} - \left\langle \mathbf{e}\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$+\left\langle \left(\nabla\cdot\mathbf{t}_s - \frac{\mathbf{C}_s}{j_s}\!:\!\nabla\boldsymbol{\sigma}_s\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\sum_{\kappa\in\mathcal{I}_{cs}} \left\langle \boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa - \mathbf{v}_s\right)\right\rangle_{\Omega_\kappa,\Omega} - \left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}_s\right)\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}.$$

B.7. Interface Thermodynamics

An interface is a two-dimensional entity and the stress in a surface is due to interfacial tension effects. The microscale thermodynamic expression obtained from CIT for an interface ι is

$$\text{(B.196)} \qquad\qquad E_\iota - \theta_\iota\eta_\iota - \sum_{i\in\mathcal{I}_S} \rho_\iota\omega_{i\iota}\mu_{i\iota} - \gamma_\iota = 0,$$

where γ_ι is the interfacial tension. Application of an averaging operator yields

$$\text{(B.197)} \qquad\qquad E^{\bar{\bar{\iota}}} - \theta^{\bar{\iota}}\eta^{\bar{\iota}} - \sum_{i\in\mathcal{I}_S} \epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mu^{\overline{i\iota}} - \epsilon^\iota\gamma^\iota = 0.$$

The partial time derivative of Eq. (B.196) is taken while holding the surface coordinates constant and the Gibbs-Duhem equation is applied such that

$$\text{(B.198)} \qquad\qquad \frac{\partial' E_\iota}{\partial t} - \theta_\iota\frac{\partial'\eta_\iota}{\partial t} - \sum_{i\in\mathcal{I}_S} \mu_{i\iota}\frac{\partial'(\rho_\iota\omega_{i\iota})}{\partial t} = 0,$$

or after introduction of macroscale variables

(B.199) $\quad \dfrac{\partial' E_\iota}{\partial t} - \theta^{\bar{\bar{\iota}}}\dfrac{\partial'\eta_\iota}{\partial t} - \displaystyle\sum_{i\in\mathcal{I}_s} \mu^{\overline{\overline{i\iota}}}\dfrac{\partial'(\rho_\iota\omega_{i\iota})}{\partial t} - \left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right)\dfrac{\partial'\eta_\iota}{\partial t}$

$\quad - \displaystyle\sum_{i\in\mathcal{I}_s}\left(\mu_{i\iota} - \mu^{\overline{\overline{i\iota}}}\right)\dfrac{\partial'(\rho_\iota\omega_{i\iota})}{\partial t} = 0.$

Applying an averaging operator and the transport theorem given by Eq. (3.8) to the first three terms in Eq. (B.199) we see that

(B.200) $\quad \left\langle \dfrac{\partial' E_\iota}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = \dfrac{\partial^{\backslash}}{\partial t}\langle E_\iota\rangle_{\Omega_\iota,\Omega} + \nabla^{\backslash}\!\cdot\!\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\!\cdot\!\mathbf{v}_\iota E_\iota\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\nabla'\!\cdot\!\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\!\cdot\!\mathbf{v}_\iota E_\iota\right\rangle_{\Omega_\iota,\Omega}$

$\quad - \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_C)}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa E_\iota\rangle_{\Omega_\kappa,\Omega} - \left\langle\dfrac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}E_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega},$

(B.201) $\quad -\theta^{\bar{\bar{\iota}}}\left\langle\dfrac{\partial'\eta_\iota}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = -\theta^{\bar{\bar{\iota}}}\dfrac{\partial^{\backslash}}{\partial t}\langle\eta_\iota\rangle_{\Omega_\iota,\Omega} - \theta^{\bar{\bar{\iota}}}\nabla^{\backslash}\!\cdot\!\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\!\cdot\!\mathbf{v}_\iota\eta_\iota\rangle_{\Omega_\iota,\Omega}$

$\quad +\theta^{\bar{\bar{\iota}}}\left\langle\left(\nabla'\!\cdot\!\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\!\cdot\!\mathbf{v}_\iota\eta_\iota\right\rangle_{\Omega_\iota,\Omega} + \displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_C)}\theta^{\bar{\bar{\iota}}}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa\eta_\iota\rangle_{\Omega_\kappa,\Omega}$

$\quad +\theta^{\bar{\bar{\iota}}}\left\langle\dfrac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega},$

and

(B.202) $\quad -\displaystyle\sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\left\langle\dfrac{\partial'(\rho_\iota\omega_{i\iota})}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = -\sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\dfrac{\partial^{\backslash}}{\partial t}\langle\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}$

$\quad -\displaystyle\sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\nabla^{\backslash}\!\cdot\!\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\!\cdot\!\mathbf{v}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\left\langle\left(\nabla'\!\cdot\!\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\!\cdot\!\mathbf{v}_\iota\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$

$\quad +\displaystyle\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_C)}\sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa\rho_\iota\omega_{i\iota}\rangle_{\Omega_\kappa,\Omega} + \sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\left\langle\dfrac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}\rho_\iota\omega_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}.$

Applying the product rule to the last two terms in Eq. (B.199) and using the transport theorem given by Eq. (3.8) we arrive at

(B.203) $\quad -\left\langle\left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right)\dfrac{\partial'\eta_\iota}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = -\dfrac{\partial^{\backslash}}{\partial t}\left\langle\left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$

$$-\nabla'\cdot\left\langle \mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega} + \left\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\kappa\in\left(\mathfrak{I}_{c\iota}\cap\mathfrak{I}_C\right)}\left\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\kappa,\Omega} + \left\langle\frac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\partial'}{\partial t}\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

and

$$(B.204)\quad -\sum_{i\in\mathfrak{I}_S}\left\langle\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\frac{\partial'(\rho_\iota\omega_{i\iota})}{\partial t}\right\rangle_{\Omega_\iota,\Omega} = -\sum_{i\in\mathfrak{I}_S}\frac{\partial'}{\partial t}\left\langle\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{i\in\mathfrak{I}_S}\nabla'\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{i\in\mathfrak{I}_S}\left\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\kappa\in\left(\mathfrak{I}_{c\iota}\cap\mathfrak{I}_C\right)}\sum_{i\in\mathfrak{I}_S}\left\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\kappa,\Omega}$$

$$+\sum_{i\in\mathfrak{I}_S}\left\langle\frac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\rho_\iota\omega_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{i\in\mathfrak{I}_S}\left\langle\rho_\iota\omega_{i\iota}\frac{\partial'}{\partial t}\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}.$$

Combining Eqs. (B.196)–(B.204) results in

$$(B.205)\quad \frac{\partial'E^{\bar{\bar{\iota}}}}{\partial t}-\theta^{\bar{\bar{\iota}}}\frac{\partial'\eta^{\bar{\bar{\iota}}}}{\partial t}-\sum_{i\in\mathfrak{I}_S}\mu^{\bar{\bar{i\iota}}}\frac{\partial'\left(\epsilon^\iota\rho^\iota\omega^{\bar{\bar{i\iota}}}\right)}{\partial t}+\nabla'\cdot\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\gamma_\iota\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla'\theta^{\bar{\bar{\iota}}}\cdot\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\eta_\iota\rangle_{\Omega_\iota,\Omega}+\sum_{i\in\mathfrak{I}_S}\nabla'\mu^{\bar{\bar{i\iota}}}\cdot\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}$$

$$-\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\mathbf{v}_\iota\gamma_\iota\rangle_{\Omega_\iota,\Omega}-\sum_{\kappa\in\left(\mathfrak{I}_{c\iota}\cap\mathfrak{I}_C\right)}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa\gamma_\iota\rangle_{\Omega_\kappa,\Omega}-\left\langle\frac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\partial'}{\partial t}\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}+\sum_{i\in\mathfrak{I}_S}\left\langle\rho_\iota\omega_{i\iota}\frac{\partial'}{\partial t}\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}=0.$$

The surface gradient of Eq. (B.196) can be evaluated to obtain a form similar to Eq. (B.199)

$$(\text{B.206}) \quad \nabla' E_\iota - \theta^{\bar{\bar{\iota}}} \nabla' \eta_\iota - \sum_{i \in \mathcal{I}_S} \mu^{\overline{i\iota}} \nabla'(\rho_\iota \omega_{i\iota}) - \left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right) \nabla' \eta_\iota$$

$$- \sum_{i \in \mathcal{I}_S} \left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right) \nabla'(\rho_\iota \omega_{i\iota}) = 0.$$

Applying an averaging operator and the product rule to Eq. (B.206) yields

$$(\text{B.207}) \quad \langle \nabla' E_\iota \rangle_{\Omega_\iota,\Omega} - \theta^{\bar{\bar{\iota}}} \langle \nabla' \eta_\iota \rangle_{\Omega_\iota,\Omega} - \sum_{i \in \mathcal{I}_S} \mu^{\overline{i\iota}} \langle \nabla'(\rho_\iota \omega_{i\iota}) \rangle_{\Omega_\iota,\Omega}$$

$$- \left\langle \nabla' \left[\left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right) \eta_\iota \right] \right\rangle_{\Omega_\iota,\Omega} - \sum_{i \in \mathcal{I}_S} \left\langle \nabla' \left[\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right) \rho_\iota \omega_{i\iota} \right] \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \eta_\iota \nabla' \left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right) \right\rangle_{\Omega_\iota,\Omega} + \sum_{i \in \mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \nabla' \left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right) \right\rangle_{\Omega_\iota,\Omega} = 0.$$

Gradient Theorem 3.4.4 can be applied to line one and line two of Eq. (B.207). Some terms in line two vanish as a result of the definitions of the macroscale variables. Then Eq. (B.196) can be applied so that

$$(\text{B.208}) \quad \nabla' E^{\bar{\bar{\iota}}} - \theta^{\bar{\bar{\iota}}} \nabla' \eta^{\bar{\bar{\iota}}} - \sum_{i \in \mathcal{I}_S} \mu^{\overline{i\iota}} \nabla' \left(\epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \right) - \nabla' \cdot \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \gamma_\iota \rangle_{\Omega_\iota,\Omega}$$

$$+ \langle (\nabla' \cdot \mathbf{n}_\alpha) \mathbf{n}_\alpha \gamma_\iota \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in (\mathcal{I}_{C\iota} \cap \mathcal{I}_C)} \langle \mathbf{n}_\iota \gamma_\iota \rangle_{\Omega_\kappa,\Omega} + \left\langle \frac{\mathbf{e} \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}$$

$$- \nabla' \theta^{\bar{\bar{\iota}}} \cdot \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \eta_\iota \rangle_{\Omega_\iota,\Omega} - \sum_{i \in \mathcal{I}_S} \nabla' \mu^{\overline{i\iota}} \cdot \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \rho_\iota \omega_{i\iota} \rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \eta_\iota \nabla' \left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right) \right\rangle_{\Omega_\iota,\Omega} + \sum_{i \in \mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \nabla' \left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right) \right\rangle_{\Omega_\iota,\Omega} = 0.$$

Taking the dot product of Eq. (B.208) with $\mathbf{v}^{\bar{\iota}}$ and addition to Eq. (B.205) yields the transition region thermodynamic expression for interface ι as

$$(\text{B.209}) \quad \mathcal{T}^\iota = \frac{D^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{Dt} - \theta^{\bar{\bar{\iota}}} \frac{D^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{Dt} - \sum_{i \in \mathcal{I}_S} \mu^{\overline{i\iota}} \frac{D^{\bar{\iota}} \left(\epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \right)}{Dt} + \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \gamma_\iota \rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\bar{\bar{\iota}}}$$

$$+\nabla'\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}-\left\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla'\theta^{\bar{\bar{\iota}}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}-\sum_{\kappa\in(\mathcal{I}_{C\iota}\cap\mathcal{I}_C)}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$+\sum_{i\in\mathcal{I}_s}\nabla'\mu^{\bar{\bar{i\iota}}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\mathrm{D}'^\iota\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}'^\iota\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}=0.$$

The material derivative expressions within averaging operators can be converted to material derivatives referenced to the macroscale solid-phase velocity taking into account Eq. (B.160) and Eq. (B.161)

$$(\text{B.210})\quad\mathcal{T}^\iota=\frac{\mathrm{D}^{\bar{\iota}}E^{\bar{\bar{\iota}}}}{\mathrm{D}t}-\theta^{\bar{\bar{\iota}}}\frac{\mathrm{D}^{\bar{\iota}}\eta^{\bar{\bar{\iota}}}}{\mathrm{D}t}-\sum_{i\in\mathcal{I}_s}\mu^{\bar{\bar{i\iota}}}\frac{\mathrm{D}^{\bar{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{\bar{\bar{i\iota}}}\right)}{\mathrm{D}t}+\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\bar{\bar{\iota}}}$$

$$+\nabla'\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}-\left\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla'\theta^{\bar{\bar{\iota}}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}-\sum_{\kappa\in(\mathcal{I}_{C\iota}\cap\mathcal{I}_C)}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$+\sum_{i\in\mathcal{I}_s}\nabla'\mu^{\bar{\bar{i\iota}}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar{\iota}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\bar{\iota}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\mathrm{D}'^{\bar{s}}\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}'^{\bar{s}}\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle\eta_\iota\nabla'\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\nabla'\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}=0\qquad\text{for }\iota\in\mathcal{I}_\mathrm{I}.$$

The last term in Eq. (B.210) can be transformed in the same way as for the fluid phases, i.e., taking into account the microscale Gibbs-Duhem equation, applying the product rule, and using the averaging gradient theorem given by Eq. (3.7).

$$(\text{B.211})\quad\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle\eta_\iota\nabla'\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\nabla'\left(\mu_{i\iota}-\mu^{\bar{\bar{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$= \mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle \eta_\iota\nabla'\theta_\iota - \eta_\iota\nabla'\theta^{\bar{\bar{\iota}}} + \sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\nabla'\mu_{i\iota} - \sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\nabla'\mu^{\overline{i\iota}}\right\rangle_{\Omega_\iota,\Omega}$$

$$= \mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle -\eta_\iota\nabla'\theta^{\bar{\bar{\iota}}} - \sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\nabla'\mu^{\overline{i\iota}} - \nabla'\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$= \mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle -\nabla'\left(\eta_\iota\theta^{\bar{\iota}}\right) + \theta^{\bar{\iota}}\nabla'\eta_\iota - \nabla'\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$\quad - \mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle \sum_{i\in\mathcal{I}_s}\left[\nabla'\left(\rho_\iota\omega_{i\iota}\mu^{\overline{i\iota}}\right) - \mu^{\overline{i\iota}}\nabla'\left(\rho_\iota\omega_{i\iota}\right)\right]\right\rangle_{\Omega_\iota,\Omega}$$

$$= \mathbf{v}^{\bar{\iota},\bar{s}}\cdot\bigg(-\nabla^{\backprime}\left(\eta^{\bar{\bar{\iota}}}\theta^{\bar{\iota}}\right) - \nabla^{\backprime}\left(\epsilon^\iota\gamma^\iota\right) + \theta^{\bar{\iota}}\nabla^{\backprime}\eta^{\bar{\iota}}$$

$$\quad - \sum_{i\in\mathcal{I}_s}\left[\nabla^{\backprime}\left(\epsilon^\iota\rho^\iota\omega^{i\bar{\iota}}\mu^{\overline{i\iota}}\right) - \mu^{\overline{i\iota}}\nabla^{\backprime}\left(\epsilon^\iota\rho^\iota\omega^{i\bar{\iota}}\right)\right] + \nabla^{\backprime}\cdot\left\langle \mathbf{n}_\alpha\mathbf{n}_\alpha\eta_\iota\theta^{\bar{\iota}}\right\rangle_{\Omega_\iota,\Omega}$$

$$\quad - \theta^{\bar{\iota}}\nabla^{\backprime}\cdot\langle \mathbf{n}_\alpha\mathbf{n}_\alpha\eta_\iota\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_s}\nabla^{\backprime}\cdot\left\langle \mathbf{n}_\alpha\mathbf{n}_\alpha\rho_\iota\omega_{i\iota}\mu^{\overline{i\iota}}\right\rangle_{\Omega_\iota,\Omega}$$

$$\quad - \sum_{i\in\mathcal{I}_s}\mu^{\overline{i\iota}}\nabla^{\backprime}\cdot\langle \mathbf{n}_\alpha\mathbf{n}_\alpha\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega} + \nabla^{\backprime}\cdot\langle \mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\rangle_{\Omega_\iota,\Omega} - \left\langle \left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\eta_\iota\theta^{\bar{\iota}}\right\rangle_{\Omega_\iota,\Omega}$$

$$\quad + \theta^{\bar{\iota}}\left\langle \left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\eta_\iota\right\rangle_{\Omega_\iota,\Omega} - \sum_{i\in\mathcal{I}_s}\left\langle \left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\rho_\iota\omega_{i\iota}\mu^{\overline{i\iota}}\right\rangle_{\Omega_\iota,\Omega}$$

$$\quad + \sum_{i\in\mathcal{I}_s}\mu^{\overline{i\iota}}\left\langle \left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega} - \left\langle \left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$\quad + \sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_C\right)}\left(-\left\langle \mathbf{n}_\iota\eta_\iota\theta^{\bar{\iota}}\right\rangle_{\Omega_\kappa,\Omega} + \theta^{\bar{\iota}}\langle \mathbf{n}_\iota\eta_\iota\rangle_{\Omega_\kappa,\Omega} - \langle \mathbf{n}_\iota\gamma_\iota\rangle_{\Omega_\kappa,\Omega}\right)$$

$$\quad + \sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_C\right)}\sum_{i\in\mathcal{I}_s}\left(-\left\langle \mathbf{n}_\iota\rho_\iota\omega_{i\iota}\mu^{\overline{i\iota}}\right\rangle_{\Omega_\kappa,\Omega} + \mu^{\overline{i\iota}}\langle \mathbf{n}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\kappa,\Omega}\right)$$

$$\quad - \left\langle \frac{\mathbf{e}\eta_\iota\theta^{\bar{\iota}}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} + \theta^{\bar{\iota}}\left\langle \frac{\mathbf{e}\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} - \left\langle \frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$\quad + \sum_{i\in\mathcal{I}_s}\left(-\left\langle \frac{\mathbf{e}\rho_\iota\omega_{i\iota}\mu^{\overline{i\iota}}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} + \mu^{\overline{i\iota}}\left\langle \frac{\mathbf{e}\rho_\iota\omega_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}\right)\bigg)$$

$$= \mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left(-\eta^{\bar{\iota}}\nabla^{\backprime}\theta^{\bar{\iota}} - \sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\bar{\iota}}\nabla^{\backprime}\mu^{\overline{i\iota}} - \nabla^{\backprime}\left(\epsilon^\iota\gamma^\iota\right)\right)$$

$$+\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\left(\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}{\cdot}\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\eta_\iota\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathfrak{I}_s}\nabla^{\backprime}\mu^{\overline{\overline{i\iota}}}{\cdot}\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}\right)$$

$$+\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\left[\nabla^{\backprime}{\cdot}\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\nabla'{\cdot}\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}\right]$$

$$-\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\left(\sum_{\kappa\in\left(\mathfrak{I}_{c\iota}\cap\mathfrak{I}_C\right)}\langle\mathbf{n}_\iota\gamma_\iota\rangle_{\Omega_\kappa,\Omega} + \left\langle\frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}\right).$$

Substituting Eq. (B.211) into Eq. (B.210) yields

$$(B.212)\quad \mathcal{T}^\iota = \frac{\mathrm{D}^{\overline{\iota}}E^{\overline{\overline{\iota}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\iota}}}\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{\overline{i\iota}}}\frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t} + \langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\rangle_{\Omega_\iota,\Omega}{:}\mathbf{d}^{\backprime\overline{\overline{s}}}$$

$$+\nabla^{\backprime}{\cdot}\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\nabla'{\cdot}\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}{\cdot}\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha{\cdot}\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa\in\left(\mathfrak{I}_{c\iota}\cap\mathfrak{I}_C\right)}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$+\sum_{i\in\mathfrak{I}_s}\nabla^{\backprime}\mu^{\overline{\overline{i\iota}}}{\cdot}\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha{\cdot}\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega} - \left\langle\frac{\mathbf{e}{\cdot}\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\mathrm{D}'^{\overline{s}}\left(\theta_\iota-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t} + \sum_{i\in\mathfrak{I}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}'^{\overline{s}}\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\mathbf{v}^{\overline{\iota},\overline{s}}{\cdot}\left(\eta^{\overline{\overline{\iota}}}\nabla^{\backprime}\theta^{\overline{\overline{\iota}}} + \sum_{i\in\mathfrak{I}_s}\epsilon^\iota\rho^\iota\omega^{\overline{\overline{i\iota}}}\nabla^{\backprime}\mu^{\overline{\overline{i\iota}}} + \nabla^{\backprime}\left(\epsilon^\iota\gamma^\iota\right)\right) = 0 \qquad \text{for } \iota\in\mathfrak{I}_\mathrm{I}.$$

B.8. Common Curve Thermodynamics

The microscale thermodynamic expression obtained from CIT for a common curve ι is

$$(B.213)\qquad\qquad E_\iota - \theta_\iota\eta_\iota - \sum_{i\in\mathfrak{I}_s}\rho_\iota\omega_{i\iota}\mu_{i\iota} + \gamma_\iota = 0,$$

where γ_ι is the lineal tension. The corresponding macroscale Euler equation derived by applying an averaging operator is

$$(B.214) \qquad E^{\bar{\bar{\iota}}} - \theta^{\bar{\bar{\iota}}} \eta^{\bar{\iota}} - \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mu^{\overline{i\iota}} + \epsilon^\iota \gamma^\iota = 0.$$

The partial time derivative of Eq. (B.213) is taken while holding the curvilinear coordinates constant such that

$$(B.215) \qquad \frac{\partial'' E_\iota}{\partial t} - \theta_\iota \frac{\partial'' \eta_\iota}{\partial t} - \sum_{i \in \mathcal{I}_s} \mu_{i\iota} \frac{\partial'' (\rho_\iota \omega_{i\iota})}{\partial t} = 0,$$

and it follows from the Gibbs-Duhem equation that

$$(B.216) \qquad \eta_\iota \frac{\partial'' \theta_\iota}{\partial t} + \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \frac{\partial'' \mu_{i\iota}}{\partial t} - \frac{\partial'' \gamma_\iota}{\partial t} = 0.$$

Eq. (B.215) can be written adding and subtracting macroscale variables as

$$(B.217) \qquad \frac{\partial'' E_\iota}{\partial t} - \theta^{\bar{\bar{\iota}}} \frac{\partial'' \eta_\iota}{\partial t} - \sum_{i \in \mathcal{I}_s} \mu^{\overline{i\iota}} \frac{\partial'' (\rho_\iota \omega_{i\iota})}{\partial t} - \left(\theta_\iota - \theta^{\bar{\bar{\iota}}} \right) \frac{\partial'' \eta_\iota}{\partial t}$$

$$- \sum_{i \in \mathcal{I}_s} \left(\mu_{i\iota} - \mu^{\overline{i\iota}} \right) \frac{\partial'' (\rho_\iota \omega_{i\iota})}{\partial t} = 0.$$

Applying an averaging operator and Theorem 3.4.9 to Eq. (B.217) results in

$$(B.218) \qquad \left\langle \frac{\partial'' E_\iota}{\partial t} \right\rangle_{\Omega_\iota, \Omega} = \frac{\partial'}{\partial t} \langle E_\iota \rangle_{\Omega_\iota, \Omega} + \nabla' \cdot \langle (\mathbf{v}_\iota - \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_\iota) E_\iota \rangle_{\Omega_\iota, \Omega}$$

$$+ \langle (\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota) \cdot \mathbf{v}_\iota E_\iota \rangle_{\Omega_\iota, \Omega} - \sum_{\kappa \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{Pt})} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa E_\iota \rangle_{\Omega_\kappa, \Omega} - \left\langle \frac{\mathbf{e} \cdot \mathbf{v}_{ext} E_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}.$$

Averaging the second and third terms of Eq. (B.217) in the same way, applying the product rule to the last two terms, averaging these terms, and simplifying the resultant expression using Eq. (B.213) yields

$$(B.219) \qquad \frac{\partial' E^{\bar{\bar{\iota}}}}{\partial t} - \theta^{\bar{\bar{\iota}}} \frac{\partial' \eta^{\bar{\iota}}}{\partial t} - \sum_{i \in \mathcal{I}_s} \mu^{\overline{i\iota}} \frac{\partial' \left(\epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \right)}{\partial t} - \nabla' \cdot \langle (\mathbf{v}_\iota - \mathbf{l}_\iota \mathbf{l}_\iota \cdot \mathbf{v}_\iota) \gamma_\iota \rangle_{\Omega_\iota, \Omega}$$

$$-\langle(\mathbf{l}_\iota \cdot \nabla''\mathbf{l}_\iota)\cdot\mathbf{v}_\iota\gamma_\iota\rangle_{\Omega_\iota,\Omega} + \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{Pt})}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa\gamma_\iota\rangle_{\Omega_\kappa,\Omega} + \left\langle\frac{\mathbf{e}\cdot\mathbf{v}_{\text{ext}}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\nabla^\backprime\theta^{\bar{\bar\iota}}\cdot\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\mathbf{v}_\iota\eta_\iota\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_s}\nabla^\backprime\mu^{\overline{\overline{i\iota}}}\cdot\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\mathbf{v}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}$$

$$+\left\langle\eta_\iota\frac{\partial''}{\partial t}\left(\theta_\iota-\theta^{\bar{\bar\iota}}\right)\right\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_s}\left\langle\rho_\iota\omega_{i\iota}\frac{\partial''}{\partial t}\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega} = 0.$$

The curvilinear gradient of Eq. (B.213) can be evaluated to obtain a form similar to Eq. (B.217),

$$(\text{B.220})\quad \nabla''E_\iota - \theta^{\bar{\bar\iota}}\nabla''\eta_\iota - \sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\nabla''(\rho_\iota\omega_{i\iota}) - \left(\theta_\iota-\theta^{\bar{\bar\iota}}\right)\nabla''\eta_\iota$$

$$-\sum_{i\in\mathcal{I}_s}\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)\nabla''(\rho_\iota\omega_{i\iota}) = 0.$$

Application of an averaging operator and Theorem 3.4.8 to the first term in Eq. (B.220) yields

$$(\text{B.221})\quad \langle\nabla''E_\iota\rangle_{\Omega_\iota,\Omega} = \nabla^\backprime\cdot\langle\mathbf{l}_\iota\mathbf{l}_\iota E_\iota\rangle_{\Omega_\iota,\Omega} - \langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)E_\iota\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{Pt})}\langle\mathbf{n}_\iota E_\iota\rangle_{\Omega_\kappa,\Omega} + \left\langle\frac{\mathbf{e}E_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}.$$

Adding and subtracting $\nabla^\backprime\langle E_\iota\rangle_{\Omega_\iota,\Omega}$, we obtain

$$(\text{B.222})\quad \langle\nabla''E_\iota\rangle_{\Omega_\iota,\Omega} = \nabla^\backprime E^{\bar{\bar\iota}} + \nabla^\backprime\cdot\langle(\mathbf{l}_\iota\mathbf{l}_\iota-\mathbf{I})E_\iota\rangle_{\Omega_\iota,\Omega} - \langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)E_\iota\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{Pt})}\langle\mathbf{n}_\iota E_\iota\rangle_{\Omega_\kappa,\Omega} + \left\langle\frac{\mathbf{e}E_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}.$$

Using a similar procedure for the second two terms in Eq. (B.220) we get

$$(\text{B.223})\quad -\theta^{\bar{\bar\iota}}\langle\nabla''\eta_\iota\rangle_{\Omega_\iota,\Omega} = -\theta^{\bar{\bar\iota}}\nabla^\backprime\eta^{\bar{\bar\iota}} - \theta^{\bar{\bar\iota}}\nabla^\backprime\cdot\langle(\mathbf{l}_\iota\mathbf{l}_\iota-\mathbf{I})\eta_\iota\rangle_{\Omega_\iota,\Omega} + \theta^{\bar{\bar\iota}}\langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\eta_\iota\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{Pt})}\theta^{\bar{\bar\iota}}\langle\mathbf{n}_\iota\eta_\iota\rangle_{\Omega_\kappa,\Omega} - \theta^{\bar{\bar\iota}}\left\langle\frac{\mathbf{e}\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

and

$$\text{(B.224)} \quad -\sum_{i\in\mathcal{I}_S} \mu^{\overline{\overline{\imath\iota}}} \langle \nabla''(\rho_\iota\omega_{i\iota})\rangle_{\Omega_\iota,\Omega} = -\sum_{i\in\mathcal{I}_S} \mu^{\overline{\overline{\imath\iota}}} \nabla^{\backprime}\left(\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\right)$$

$$-\sum_{i\in\mathcal{I}_S} \mu^{\overline{\overline{\imath\iota}}}\nabla^{\backprime}\cdot\langle(\mathbf{l}_\iota\mathbf{l}_\iota - \mathbf{I})\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_S} \mu^{\overline{\overline{\imath\iota}}}\langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\,\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{i\in\mathcal{I}_S}\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{Pt}})} \mu^{\overline{\overline{\imath\iota}}}\langle\mathbf{n}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\kappa,\Omega} - \sum_{i\in\mathcal{I}_S} \mu^{\overline{\overline{\imath\iota}}}\left\langle\frac{\mathbf{e}\rho_\iota\omega_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}.$$

Applying the product rule to the last two terms in Eq. (B.220) and using the gradient theorem given by Eq. (3.12) yields

$$\text{(B.225)} \quad -\left\langle\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\nabla''\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$= -\left\langle\nabla''\left[\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota\right]\right\rangle_{\Omega_\iota,\Omega} + \left\langle\eta_\iota\nabla''\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$= -\nabla^{\backprime}\left[\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota\right] - \nabla^{\backprime}\cdot\left\langle(\mathbf{l}_\iota\mathbf{l}_\iota - \mathbf{I})\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\left\langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega} - \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\left\langle\mathbf{n}_\iota\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\left\langle\frac{\mathbf{e}\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} + \left\langle\eta_\iota\nabla''\left(\theta_\iota - \theta^{\overline{\overline{\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

and

$$\text{(B.226)} \quad -\sum_{i\in\mathcal{I}_S}\left\langle\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\nabla''(\rho_\iota\omega_{i\iota})\right\rangle_{\Omega_\iota,\Omega}$$

$$= -\sum_{i\in\mathcal{I}_S}\left\langle\nabla''\left[\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\rho_\iota\omega_{i\iota}\right]\right\rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_S}\left\langle\rho_\iota\omega_{i\iota}\nabla''\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$= -\sum_{i\in\mathcal{I}_S}\nabla^{\backprime}\left[\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\rho_\iota\omega_{i\iota}\right] - \sum_{i\in\mathcal{I}_S}\nabla^{\backprime}\cdot\left\langle(\mathbf{l}_\iota\mathbf{l}_\iota - \mathbf{I})\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{i\in\mathcal{I}_S}\left\langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\mathrm{Pt}})}\sum_{i\in\mathcal{I}_S}\left\langle\mathbf{n}_\iota\left(\mu_{i\iota} - \mu^{\overline{\overline{\imath\iota}}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{i\in\mathcal{I}_s}\left\langle\frac{\mathbf{e}\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{i\in\mathcal{I}_s}\left\langle\rho_\iota\omega_{i\iota}\nabla''\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}.$$

Combining Eqs. (B.221)–(B.226) and substituting Eq. (B.213),

$$(\text{B.227})\quad \nabla^{\backslash}E^{\overline{\overline{\iota}}}-\theta^{\overline{\overline{\iota}}}\nabla^{\backslash}\eta^{\overline{\overline{\iota}}}-\sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\nabla^{\backslash}\left(\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\right)-\nabla^{\backslash}\cdot\langle(\mathbf{l}_\iota\mathbf{l}_\iota-\mathbf{I})\gamma_\iota\rangle_{\Omega_\iota,\Omega}$$

$$-\nabla^{\backslash}\theta^{\overline{\overline{\iota}}}\cdot\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\,\eta_\iota\rangle_{\Omega_\iota,\Omega}-\sum_{i\in\mathcal{I}_s}\nabla^{\backslash}\mu^{\overline{\overline{i\iota}}}\cdot\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\,\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}$$

$$+\left\langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\,\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}-\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\text{Pt}})}\langle\mathbf{n}_\iota\gamma_\iota\rangle_{\Omega_\kappa,\Omega}-\left\langle\frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\nabla''\left(\theta_\iota-\theta^{\overline{\overline{\iota}}}\right)+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\nabla''\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)\right\rangle_{\Omega_\iota,\Omega}=0.$$

Taking the dot product of Eq. (B.227) with $\mathbf{v}^{\overline{\iota}}$ and addition to Eq. (B.219) yields the transition region thermodynamic expression for common curve ι

$$(\text{B.228})\quad \mathcal{T}^\iota=\frac{\mathrm{D}^{\overline{\iota}}E^{\overline{\overline{\iota}}}}{\mathrm{D}t}-\theta^{\overline{\overline{\iota}}}\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t}-\sum_{i\in\mathcal{I}_s}\mu^{\overline{\overline{i\iota}}}\frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\right)}{\mathrm{D}t}$$

$$-\nabla^{\backslash}\cdot\left\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}-\left\langle(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\nabla^{\backslash}\theta^{\overline{\overline{\iota}}}\cdot\left\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{\iota}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{i\in\mathcal{I}_s}\nabla^{\backslash}\mu^{\overline{\overline{i\iota}}}\cdot\left\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{\iota}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}-\langle(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\gamma_\iota\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\overline{\overline{\iota}}}$$

$$+\sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{\text{Pt}})}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{\iota}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}+\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{\iota}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\eta_\iota\frac{\mathrm{D}''^\iota\left(\theta_\iota-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}''^\iota\left(\mu_{i\iota}-\mu^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}=0.$$

The material derivative expressions found within an averaging operator can be converted to material derivatives referenced to the solid-phase velocity,

(B.229) $\quad \mathcal{T}^\iota = \dfrac{\mathrm{D}^{\bar\iota} E^{\bar{\bar\iota}}}{\mathrm{D}t} - \theta^{\bar\iota}\dfrac{\mathrm{D}^{\bar\iota}\eta^{\bar{\bar\iota}}}{\mathrm{D}t} - \sum_{i\in\mathcal{I}_S}\mu^{\overline{i\iota}}\dfrac{\mathrm{D}^{\bar\iota}\left(\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\right)}{\mathrm{D}t}$

$\qquad -\nabla'\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar\iota}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar\iota}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$

$\qquad +\nabla'\theta^{\bar\iota}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar\iota}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$

$\qquad +\sum_{i\in\mathcal{I}_S}\nabla'\mu^{\overline{i\iota}}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar\iota}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega} - \left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}{:}\mathbf{d}^{\bar{\bar\iota}}$

$\qquad +\sum_{\kappa\in\left(\mathcal{I}_{c\iota}\cap\mathcal{I}_{Pt}\right)}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\bar\iota}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega} + \left\langle\dfrac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\bar\iota}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$

$\qquad +\left\langle\eta_\iota\dfrac{\mathrm{D}''^{\bar s}\left(\theta_\iota-\theta^{\bar\iota}\right)}{\mathrm{D}t} + \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\dfrac{\mathrm{D}''^{\bar s}\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$

$\qquad +\mathbf{v}^{\bar\iota,\bar s}\cdot\left\langle\eta_\iota\nabla''\left(\theta_\iota-\theta^{\bar\iota}\right) + \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\nabla''\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega} = 0.$

The last term in Eq. (B.229) can be modified in the same way as for the fluid phases and interfaces. First we use the microscale Gibbs-Duhem equation such that

(B.230) $\quad \mathbf{v}^{\bar\iota,\bar s}\cdot\left\langle\eta_\iota\nabla''\left(\theta_\iota-\theta^{\bar\iota}\right) + \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\nabla''\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}$

$\qquad = \mathbf{v}^{\bar\iota,\bar s}\cdot\left\langle\eta_\iota\nabla''\theta_\iota - \eta_\iota\nabla''\theta^{\bar\iota} + \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\nabla''\mu_{i\iota} - \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\nabla''\mu^{\overline{i\iota}}\right\rangle_{\Omega_\iota,\Omega}$

$\qquad = \mathbf{v}^{\bar\iota,\bar s}\cdot\left\langle-\eta_\iota\nabla''\theta^{\bar\iota} - \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\nabla''\mu^{\overline{i\iota}} + \nabla''\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}.$

Next, we apply the product rule as well as the averaging gradient theorem given by Eq. (3.12) to obtain

(B.231) $\quad \mathbf{v}^{\bar\iota,\bar s}\cdot\left\langle-\eta_\iota\nabla''\theta^{\bar\iota} - \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\nabla''\mu^{\overline{i\iota}} + \nabla''\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$

$\qquad = \mathbf{v}^{\bar\iota,\bar s}\cdot\left\langle-\nabla''\left(\eta_\iota\theta^{\bar\iota}\right) + \theta^{\bar\iota}\nabla''\eta_\iota + \nabla''\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$

$$-\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left\langle \sum_{i\in\mathcal{I}_S}\left[\nabla''\left(\rho_\iota\omega_{i\iota}\mu^{\overline{\overline{i\iota}}}\right)-\mu^{\overline{\overline{i\iota}}}\nabla''\left(\rho_\iota\omega_{i\iota}\right)\right]\right\rangle_{\Omega_\iota,\Omega}$$

$$=\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left(\nabla`\cdot\left\langle-\mathbf{l}_\iota\mathbf{l}_\iota\eta_\iota\theta^{\overline{\overline{\iota}}}\right\rangle_{\Omega_\iota,\Omega}+\theta^{\overline{\overline{\iota}}}\nabla`\cdot\langle\mathbf{l}_\iota\mathbf{l}_\iota\eta_\iota\rangle_{\Omega_\iota,\Omega}\right.$$

$$-\sum_{i\in\mathcal{I}_S}\left(\nabla`\cdot\left\langle\mathbf{l}_\iota\mathbf{l}_\iota\rho_\iota\omega_{i\iota}\mu^{\overline{\overline{i\iota}}}\right\rangle_{\Omega_\iota,\Omega}-\mu^{\overline{\overline{i\iota}}}\nabla`\cdot\langle\mathbf{l}_\iota\mathbf{l}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}\right)$$

$$+\nabla`\cdot\langle\mathbf{l}_\iota\mathbf{l}_\iota\gamma_\iota\rangle_{\Omega_\iota,\Omega}+\left\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\eta_\iota\theta^{\overline{\overline{\iota}}}\right\rangle_{\Omega_\iota,\Omega}-\theta^{\overline{\overline{\iota}}}\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\eta_\iota\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{i\in\mathcal{I}_S}\left[\left\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\rho_\iota\omega_{i\iota}\mu^{\overline{\overline{i\iota}}}\right\rangle_{\Omega_\iota,\Omega}-\mu^{\overline{\overline{i\iota}}}\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}\right]$$

$$-\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\gamma_\iota\rangle_{\Omega_\iota,\Omega}-\left\langle\frac{\mathbf{e}\eta_\iota\theta^{\overline{\overline{\iota}}}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\theta^{\overline{\overline{\iota}}}\left\langle\frac{\mathbf{e}\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\left\langle\frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{Pt}\right)}\left\langle\mathbf{n}_\iota\eta_\iota\theta^{\overline{\overline{\iota}}}\right\rangle_{\Omega_\kappa,\Omega}+\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{Pt}\right)}\theta^{\overline{\overline{\iota}}}\langle\mathbf{n}_\iota\eta_\iota\rangle_{\Omega_\kappa,\Omega}+\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{Pt}\right)}\langle\mathbf{n}_\iota\gamma_\iota\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{Pt}\right)}\sum_{i\in\mathcal{I}_S}\left\langle\mathbf{n}_\iota\rho_\iota\omega_{i\iota}\mu^{\overline{\overline{i\iota}}}\right\rangle_{\Omega_\kappa,\Omega}+\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{Pt}\right)}\sum_{i\in\mathcal{I}_S}\mu^{\overline{\overline{i\iota}}}\langle\mathbf{n}_\iota\rho_\iota\omega_{i\iota}\rangle_{\Omega_\kappa,\Omega}$$

$$\left.+\sum_{i\in\mathcal{I}_S}\left(-\left\langle\frac{\mathbf{e}\rho_\iota\omega_{i\iota}\mu^{\overline{\overline{i\iota}}}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\mu^{\overline{\overline{i\iota}}}\left\langle\frac{\mathbf{e}\rho_\iota\omega_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}\right)\right)$$

$$=\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left(-\eta^{\overline{\overline{\iota}}}\nabla`\theta^{\overline{\overline{\iota}}}-\sum_{i\in\mathcal{I}_S}\epsilon^\iota\rho^\iota\omega^{\overline{\overline{i\iota}}}\nabla`\mu^{\overline{\overline{i\iota}}}+\nabla`\left(\epsilon^\iota\gamma^\iota\right)\right)$$

$$+\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\left(\nabla`\theta^{\overline{\overline{\iota}}}\cdot\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\eta_\iota\rangle_{\Omega_\iota,\Omega}+\sum_{i\in\mathcal{I}_S}\nabla`\mu^{\overline{\overline{i\iota}}}\cdot\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}\right.$$

$$-\nabla`\cdot\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\gamma_\iota\rangle_{\Omega_\iota,\Omega}-\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\gamma_\iota\rangle_{\Omega_\iota,\Omega}+\left\langle\frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$\left.+\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_{Pt}\right)}\langle\mathbf{n}_\iota\gamma_\iota\rangle_{\Omega_\kappa,\Omega}\right).$$

Substituting Eq. (B.231) into Eq. (B.229) we get the expression for the thermodynamics of a common curve,

253

(B.232)
$$\mathcal{T}^\iota = \frac{D^{\bar\iota} E^{\bar\iota}}{Dt} - \theta^{\bar\iota}\frac{D^{\bar\iota}\eta^{\bar\iota}}{Dt} - \sum_{i\in\mathcal{I}_S} \mu^{\overline{i\iota}}\frac{D^{\bar\iota}\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\right)}{Dt}$$

$$- \nabla^\backprime\cdot\left\langle (\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar s}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega} - \left\langle (\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar s}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \nabla^\backprime\theta^{\bar\iota}\cdot\left\langle (\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar s}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{i\in\mathcal{I}_S} \nabla^\backprime\mu^{\overline{i\iota}}\cdot\left\langle (\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\bar s}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega} - \left\langle (\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\bar{\bar s}}$$

$$+ \sum_{\kappa\in(\mathcal{I}_{c\iota}\cap\mathcal{I}_{Pt})} \left\langle \mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\bar s}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega} + \left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{ext}-\mathbf{v}^{\bar s}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+ \left\langle \eta_\iota\frac{D''^{\bar s}\left(\theta_\iota-\theta^{\bar\iota}\right)}{Dt} + \sum_{i\in\mathcal{I}_S} \rho_\iota\omega_{i\iota}\frac{D''^{\bar s}\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)}{Dt}\right\rangle_{\Omega_\iota,\Omega}$$

$$- \mathbf{v}^{\overline{\iota,s}}\cdot\left(\eta^{\bar\iota}\nabla^\backprime\theta^{\bar\iota} + \sum_{i\in\mathcal{I}_S} \epsilon^\iota\rho^\iota\omega^{i\iota}\nabla^\backprime\mu^{\overline{i\iota}} - \nabla^\backprime\left(\epsilon^\iota\gamma^\iota\right)\right) = 0 \qquad \text{for } \iota\in\mathcal{I}_C.$$

B.9. End Term Manipulations

The end terms arising from the energy, momentum, mass, and entropy equations respectively are:

(B.233)

$$+ \left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{ext}\right)\left(E_\iota + \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2} + \rho_\iota\frac{\mathbf{v}_\iota\cdot\mathbf{v}_\iota}{2} + \sum_{i\in\mathcal{I}_S}\rho_\iota\omega_{i\iota}\psi_{i\iota}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$- \left\langle \frac{\mathbf{e}\cdot\left(\mathbf{t}_\iota\cdot\mathbf{v}_\iota+\mathbf{q}_\iota\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega},$$

(B.234)
$$\left\langle \frac{\mathbf{e}\cdot\left[\rho_\iota\mathbf{v}_\iota\left(\mathbf{v}_\iota-\mathbf{v}_{ext}\right)-\mathbf{t}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega},$$

$$\text{(B.235)} \qquad \left\langle \frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} + \left\langle \frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\mathbf{u}_{i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega},$$

and

$$\text{(B.236)} \qquad \left\langle \frac{\mathbf{e}\cdot\left[\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right)\eta_\iota - \boldsymbol{\varphi}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$$

The end terms arising from the thermodynamics depend on the entity being considered, for fluid phases we have

$$\text{(B.237)} \qquad \left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)p_\iota \right\rangle_{\Gamma_{\iota M},\Omega} \quad \text{or equivalently} \quad \left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)p_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega},$$

because $\mathbf{n}_\iota \cdot \mathbf{e} = 1$ when ι is a phase. Therefore, for the solid phase we can write the end terms as

$$\text{(B.238)} \qquad -\left\langle \frac{\mathbf{e}\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega} - \left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}_s\right)\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega}.$$

The interface end term is

$$\text{(B.239)} \qquad -\left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega},$$

and the end term arising from the thermodynamics of common curves is

$$\text{(B.240)} \qquad \left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}.$$

In the CEI, the terms from Eqs. (B.233)–(B.240) will appear multiplied by their respective Lagrange multipliers (see Eq. (3.30)) and summed over all entities. If we write out just the end term contributions as they will appear in the CEI we have

$$\text{(B.241)} \qquad -\sum_{\iota\in\mathcal{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right)\left(E_\iota + \sum\limits_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\left(\frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2} + \psi_{i\iota}\right) + \rho_\iota\frac{\mathbf{v}_\iota\cdot\mathbf{v}_\iota}{2}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{t}_\iota\cdot\mathbf{v}_\iota+\mathbf{q}_\iota\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{J}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\left[\rho_\iota\mathbf{v}_\iota\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)-\mathbf{t}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}}\sum_{i\in\mathcal{J}_s}\frac{1}{\theta^{\overline{\iota}}}\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}}{2}\right)\left\langle\frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}}\sum_{i\in\mathcal{J}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\left\langle\frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\mathbf{u}_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}}\left\langle\frac{\mathbf{e}\cdot\left[\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)\eta_\iota-\boldsymbol{\varphi}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\text{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)p_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\frac{\mathbf{e}\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_s\cdot\mathbf{e}}\right\rangle_{\Gamma_{sM},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}_s\right)\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{js}}{\mathbf{n}_s\cdot\mathbf{e}}\right\rangle_{\Gamma_{sM},\Omega}-\sum_{\iota\in\mathcal{J}_{\text{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\text{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}.$$

Looking at just the terms multiplied by energy and entropy and applying Eq. (B.147) when ι is a fluid phase, we have

$$\text{(B.242)}\quad-\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)E_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$=-\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)\left(E_\iota-\theta_\iota\eta_\iota\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\left(\frac{1}{\theta_\iota}-\frac{1}{\theta^{\overline{\overline{\iota}}}}\right)\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)\theta_\iota\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$=-\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{i\in\mathcal{J}_s}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)\rho_\iota\omega_{i\iota}\mu_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)p_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\left\langle\left(\frac{1}{\theta_\iota}-\frac{1}{\theta^{\overline{\overline{\iota}}}}\right)\frac{\mathbf{e}\cdot\left(\mathbf{v}_\iota-\mathbf{v}_{\text{ext}}\right)\theta_\iota\eta_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}\quad\text{for }\iota\in\mathcal{J}_{\text{f}}.$$

When $\iota = s$, we apply Eq. (B.167) such that

$$
\begin{aligned}
\text{(B.243)} \quad & -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}}\right) E_s}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega} + \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}}\right) \eta_s}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega} \\
= & -\frac{1}{\theta^{\overline{\overline{s}}}} \sum_{i \in \mathcal{I}_s} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}}\right) \rho_s \omega_{is} \mu_{is}}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega} \\
& -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}}\right) \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s}}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega} \\
& +\left\langle \left(\frac{1}{\theta_s} - \frac{1}{\theta^{\overline{\overline{s}}}}\right) \frac{\mathbf{e} \cdot \left(\mathbf{v}_s - \mathbf{v}_{\text{ext}}\right) \theta_s \eta_s}{\mathbf{n}_s \cdot \mathbf{e}} \right\rangle_{\Gamma_{sM},\Omega} .
\end{aligned}
$$

We apply Eq. (B.196) when ι is an interface

$$
\begin{aligned}
\text{(B.244)} \quad & -\frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) E_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} + \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \eta_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \\
= & -\frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i \in \mathcal{I}_s} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \rho_\iota \omega_{i\iota} \mu_{i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} - \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \\
& +\left\langle \left(\frac{1}{\theta_\iota} - \frac{1}{\theta^{\overline{\overline{\iota}}}}\right) \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \theta_\iota \eta_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathcal{I}_{\text{I}}.
\end{aligned}
$$

Finally, Eq. (B.213) is applied when ι is a common curve

$$
\begin{aligned}
\text{(B.245)} \quad & -\frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) E_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} + \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \eta_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \\
= & -\frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i \in \mathcal{I}_s} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \rho_\iota \omega_{i\iota} \mu_{i\iota}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} + \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \\
& +\left\langle \left(\frac{1}{\theta_\iota} - \frac{1}{\theta^{\overline{\overline{\iota}}}}\right) \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}\right) \theta_\iota \eta_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathcal{I}_{\text{C}}.
\end{aligned}
$$

Substituting Eqns (B.242)–(B.245) into Eq. (B.241) and regrouping we have

(B.246)

$$\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \mathbf{t}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} + \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right) p_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \mathbf{t}'_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right) \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \mathbf{t}''_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} + \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right) \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \left\langle \left(\frac{1}{\theta_\iota} - \frac{1}{\theta^{\bar{\iota}}}\right) \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}}\right) \theta_\iota \eta_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}}\right) \rho_\iota \omega_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} - K_E^{\bar{\iota}} - \mu^{\overline{i\iota}} - \psi^{\overline{i\iota}}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\bar{\iota}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}}\right) \rho_\iota \omega_{i\iota} \left(\frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}\right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{\iota}}\right)}{2} + \frac{\mathbf{u}_{i\iota} \cdot \mathbf{u}_{i\iota}}{2}\right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \left\langle \frac{\mathbf{e} \cdot \left\{\boldsymbol{\varphi}_\iota - \frac{1}{\theta^{\bar{\iota}}} \left[\mathbf{q}_\iota + \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}\right)\right]\right\}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}.$$

At the microscale make use of

(B.247)
$$\boldsymbol{\varphi}_\iota = \frac{1}{\theta_\iota} \left[\mathbf{q}_\iota + \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota}\right)\right] \quad \text{for } \iota \in \mathcal{I}$$

and

(B.248)
$$\mathbf{t}_\iota = -p_\iota \mathbf{I} + \boldsymbol{\tau}_\iota, \quad \mathbf{t}'_\iota = \gamma_\iota \mathbf{I}' + \boldsymbol{\tau}'_\iota, \quad \text{and} \quad \mathbf{t}''_\iota = -\gamma_\iota \mathbf{I}'' + \boldsymbol{\tau}''_\iota$$

for $\iota \in \mathcal{I}_{\mathrm{f}}, \iota \in \mathcal{I}_{\mathrm{I}}$, and $\iota \in \mathcal{I}_{\mathrm{C}}$ respectively. Substituting in Eq. (B.246) and rearranging, we get

(B.249)

$$
\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta^{\bar{\bar{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot p_{\iota}\mathbf{I}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}'_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta^{\bar{\bar{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{\iota}\mathbf{I}'}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
+\sum_{\iota\in\mathcal{I}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}''_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{C}}}\frac{\mathbf{v}^{\bar{\iota},\bar{s}}}{\theta^{\bar{\bar{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{\iota}\mathbf{I}''}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_{s}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\mu_{i\iota}+\psi_{i\iota}-K^{\bar{\iota}}_{E}-\mu^{\overline{i\iota}}-\psi^{\overline{i\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_{s}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\frac{\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)}{2}+\frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
-\sum_{\iota\in\mathcal{I}}\left\langle\frac{\mathbf{e}\cdot\sum_{i\in\mathcal{I}_{s}}\rho_{\iota}\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_{\iota}}-\frac{\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}}{\theta^{\bar{\bar{\iota}}}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}
$$

$$
+\sum_{\iota\in\mathcal{I}}\left\langle\frac{\left(\frac{1}{\theta^{\bar{\bar{\iota}}}}-\frac{1}{\theta_{\iota}}\right)\mathbf{e}\cdot\left[\mathbf{q}_{\iota}-\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\theta_{\iota}\eta_{\iota}\right]}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}.
$$

B.10. Constrained Entropy Inequality

The AEI given by Eq. (3.29) provides a connection between the system EI and the conservation equations using the thermodynamic relations. The Lagrange multipliers, Eq. (3.30), are chosen in a way to eliminate some of material derivatives to arrive at a final form of the CEI, which will be used to guide the formulation of the closed models. Once these material derivatives are removed, the resultant expression is referenced to a common frame of reference to satisfy the continuum mechanical axiom of objectivity and the resultant terms are placed into the force-flux pairs according to the entropy production postulate.

Substituting Eq. (3.30) into Eq. (3.29) and simplifying by cancelling out material derivatives gives

$$(B.250) \quad \sum_{\iota \in \mathcal{I}} \left[\mathcal{S}_r^\iota - \frac{1}{\theta^{\bar{\bar{\iota}}}} \mathcal{E}_r^\iota + \frac{\mathbf{v}^{\bar{\iota}}}{\theta^{\bar{\bar{\iota}}}} \cdot \boldsymbol{\mathcal{P}}_r^\iota \right.$$

$$\left. + \frac{1}{\theta^{\bar{\bar{\iota}}}} \sum_{i \in \mathcal{I}_s} \left(K_E^{\bar{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} - \frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} \right) \mathcal{M}_r^{i\iota} + \frac{1}{\theta^{\bar{\bar{\iota}}}} \mathcal{T}_r^\iota \right] = \Lambda \geq 0 \quad \text{for } \iota \in \mathcal{I}.$$

Expanding the shorthand expressions for $\mathcal{S}_r^\iota, \mathcal{E}_r^\iota, \boldsymbol{\mathcal{P}}_r^\iota, \mathcal{M}_r^{i\iota}$, and $\mathcal{T}_r^\iota$ leads to the CEI of the form

$$(B.251) \quad \sum_{\iota \in \mathcal{I}} \left[\eta^{\bar{\iota}} \mathbf{I} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}} - \nabla \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\bar{\bar{\iota}}} \right) - \epsilon^\iota b_T^{\bar{\bar{\iota}}} \right] + \sum_{\iota \in \mathcal{I}} \left\langle \frac{\mathbf{e} \cdot \left[(\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}) \eta_\iota - \boldsymbol{\varphi}_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \frac{\mathrm{D}^{\bar{\iota}} \left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}} \right)}{\mathrm{D}t}$$

$$- \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left[E^{\bar{\bar{\iota}}} + \epsilon^\iota \rho^\iota \left(\frac{\mathbf{v}^{\bar{\iota}} \cdot \mathbf{v}^{\bar{\iota}}}{2} + K_E^{\bar{\bar{\iota}}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \psi^{\overline{i\iota}} \right] \mathbf{I} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}}$$

$$+ \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left[\nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \cdot \mathbf{v}^{\bar{\iota}} \right) + \nabla \cdot \left(\epsilon^\iota \mathbf{q}^{\bar{\bar{\iota}}} \right) + \epsilon^\iota h_T^{\bar{\bar{\iota}}} + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \left(\mathbf{g}_T^{\overline{\overline{i\iota}}} - \mathbf{g}^{\overline{i\iota}} \right) \cdot \mathbf{v}^{\bar{\iota}} \right]$$

$$+ \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \sum_{i \in \mathcal{I}_s} \left(\epsilon^\iota \psi^{\overline{i\iota}} r^{i\iota} + \left\langle \rho_\iota \omega_{i\iota} \frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota, \Omega} \right)$$

$$+ \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\sum_{i \in \mathcal{I}_s} \overset{i\kappa \to i\iota}{M_E} + \overset{\kappa \to \iota}{T_v} + \overset{\kappa \to \iota}{Q} \right) + \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left\langle \frac{\mathbf{e} \cdot (\mathbf{t}_\iota \cdot \mathbf{v}_\iota + \mathbf{q}_\iota)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left\langle \frac{\mathbf{e} \cdot (\mathbf{v}_\iota - \mathbf{v}_{\text{ext}}) \left(E_\iota + \sum_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \left(\frac{\mathbf{u}_{i\iota} \cdot \mathbf{u}_{i\iota}}{2} + \psi_{i\iota} \right) + \rho_\iota \frac{\mathbf{v}_\iota \cdot \mathbf{v}_\iota}{2} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}} \frac{\mathbf{v}^{\bar{\iota}}}{\theta^{\bar{\bar{\iota}}}} \cdot \left(\epsilon^\iota \rho^\iota \mathbf{v}^{\bar{\iota}} \mathbf{I} \mathbf{:} \mathbf{d}^{\bar{\bar{\iota}}} - \nabla \cdot \left(\epsilon^\iota \mathbf{t}^{\bar{\bar{\iota}}} \right) - \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \mathbf{g}_T^{\overline{\overline{i\iota}}} \right)$$

260

$$-\sum_{\iota\in\mathcal{I}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\cdot\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\left(\sum_{i\in\mathcal{I}_s}\overset{i\kappa\to i\iota}{\mathbf{M}_v}+\overset{\kappa\to\iota}{\mathbf{T}}\right)$$

$$+\sum_{\iota\in\mathcal{I}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\left[\rho_\iota\mathbf{v}_\iota\left(\mathbf{v}_\iota-\mathbf{v}_{\mathrm{ext}}\right)-\mathbf{t}_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}}{2}\right)\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{I}{:}\mathbf{d}^{\backslash\overline{\iota}}-\epsilon^\iota r^{i\iota}-\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\overset{i\kappa\to i\iota}{M}\right)$$

$$+\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}}{2}\right)\nabla^{\backslash}\cdot\left(\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{u}^{\overline{\overline{i\iota}}}\right)$$

$$+\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}}{2}\right)\left\langle\frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota-\mathbf{v}_{\mathrm{ext}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\left\langle\frac{\mathbf{e}\cdot\rho_\iota\omega_{i\iota}\mathbf{u}_{i\iota}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\eta_\iota\frac{\mathrm{D}^{\overline{s}}\left(\theta_\iota-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)p_\iota\right\rangle_{\Omega_\kappa,\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\overline{s}}\right)p_\iota\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left(\eta^{\overline{\iota}}\nabla^{\backslash}\theta^{\overline{\overline{\iota}}}+\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\iota}\nabla^{\backslash}\mu^{\overline{i\iota}}-\nabla^{\backslash}\left(\epsilon^\iota p^\iota\right)\right)$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\eta_s\frac{\mathrm{D}^{\overline{s}}\left(\theta_s-\theta^{\overline{\overline{s}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_s}\rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}(\mu_{is}-\mu^{\overline{is}})}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\epsilon^s\mathbf{t}^{\backslash s}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}+\frac{\epsilon^s}{\theta^{\overline{\overline{s}}}}\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\frac{\mathbf{C}^s}{j^s}\mathbf{I}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla^{\backslash}\cdot\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{e}\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\frac{\mathbf{C}_s}{j_s}{:}\nabla\boldsymbol{\sigma}_s\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa-\mathbf{v}_s\right)\right\rangle_{\Omega_\kappa,\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}_s\right)\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Gamma_{sM},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\eta_\iota\frac{\mathrm{D}^{\prime\overline{s}}\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{J}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}^{\prime\overline{s}}(\mu_{i\iota}-\mu^{\overline{i\iota}})}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\backslash\overline{\overline{s}}}+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla^{\backprime}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla^{\backprime}\theta^{\bar{\bar{\iota}}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\sum_{i\in\mathcal{J}_s}\frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla^{\backprime}\mu^{\overline{i\iota}}\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\sum_{\kappa\in(\mathcal{J}_{c\iota}\cap\mathcal{J}_{\mathrm{C}})}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\overline{s}}\right)\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\eta^{\bar{\bar{\iota}}}\nabla^{\backprime}\theta^{\bar{\bar{\iota}}}+\sum_{i\in\mathcal{J}_s}\epsilon^\iota\rho^\iota\omega^{i\iota}\nabla^{\backprime}\mu^{\overline{i\iota}}+\nabla^{\backprime}\left(\epsilon^\iota\gamma^\iota\right)\right)$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\eta_\iota\frac{\mathrm{D}^{\prime\prime\overline{s}}\left(\theta_\iota-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{J}_s}\rho_\iota\omega_{i\iota}\frac{\mathrm{D}^{\prime\prime\overline{s}}(\mu_{i\iota}-\mu^{\overline{i\iota}})}{\mathrm{D}t}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla^{\backprime}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\left(\mathbf{l}_\iota\cdot\nabla''\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\gamma_\iota\rangle_{\Omega_\iota,\Omega}:\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\sum_{\kappa\in(\mathcal{J}_{c\iota}\cap\mathcal{J}_{\mathrm{Pt}})}\left\langle\mathbf{n}_\iota\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla^{\backprime}\theta^{\bar{\bar{\iota}}}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\eta_\iota\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\bar{\bar{\iota}}}}\sum_{i\in\mathcal{J}_s}\nabla^{\backprime}\mu^{\overline{i\iota}}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\rho_\iota\omega_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}}}{\theta^{\overline{\overline{\iota}}}} \cdot \left(\eta^{\overline{\overline{\iota}}} \nabla^{\backprime} \theta^{\overline{\overline{\iota}}} + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \nabla^{\backprime} \mu^{\overline{\overline{i\iota}}} - \nabla^{\backprime} \left(\epsilon^\iota \gamma^\iota \right) \right) = \Lambda \geq 0,$$

where $\alpha \in \left(\mathcal{I}_{\mathrm{c}\iota} \cap \mathcal{I}_{\mathrm{P}} \right)$.

We can manipulate Eq. (B.251) to place it in a more convenient form for satisfying our overall goal of having groupings of variables related to non-dissipative processes and groupings of variables related to dissipative processes, which are arranged in flux-force pairs and satisfy the axiom of objectivity. Non-dissipative processes are identified to relate the flux and source of entropy in a system to the flux and source of heat and other thermodynamic quantities.

Eq. (B.251) contains the remaining material derivatives that must be referenced to a common frame to lead to a form that will satisfy the continuum mechanical axiom of objectivity. We select the macroscale solid-phase velocity $\mathbf{v}^{\overline{s}}$ as the reference velocity and write

$$(B.252) \qquad \frac{\mathrm{D}^{\overline{\iota}}}{\mathrm{D}t} = \frac{\partial^{\backprime}}{\partial t} + \mathbf{v}^{\overline{\iota}} \cdot \nabla^{\backprime} = \frac{\partial}{\partial t} + \mathbf{v}^{\overline{\iota}} \cdot \nabla = \frac{\partial^{\backprime}}{\partial t} + \mathbf{v}^{\overline{s}} \cdot \nabla^{\backprime} + \mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \nabla^{\backprime} = \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} + \mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \nabla^{\backprime},$$

then we have

$$(B.253) \quad \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \frac{\mathrm{D}^{\overline{\iota}} \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\overline{i\iota}}} \right)}{\mathrm{D}t} = \sum_{i \in \mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{\mathrm{D}^{\overline{s}} \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\overline{i\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \nabla^{\backprime} \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{\overline{i\iota}}} \right).$$

For the like term applied to an interface ι, if we restrict the material derivative to the microscale surface, then we can group the term inside the averaging operator with those material derivatives remaining from the thermodynamics. To do that we use the following identity

(B.254) $\left\langle \dfrac{\mathrm{D}'^{\bar{s}}}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} = \left\langle \dfrac{\partial'}{\partial t} + \mathbf{v}^{\bar{s}}\!\cdot\!\nabla' \right\rangle_{\Omega_\iota,\Omega}$

$$= \left\langle \frac{\partial}{\partial t} + \mathbf{v}_\iota\!\cdot\!\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla + \mathbf{v}^{\bar{s}}\!\cdot\!\left(\nabla - \mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla\right) \right\rangle_{\Omega_\iota,\Omega}$$

$$= \left\langle \frac{\partial}{\partial t} + \mathbf{v}^{\bar{s}}\!\cdot\!\nabla + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\!\cdot\!\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla \right\rangle_{\Omega_\iota,\Omega}$$

$$= \left\langle \frac{\mathrm{D}^{\bar{s}}}{\mathrm{D}t} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\!\cdot\!\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla \right\rangle_{\Omega_\iota,\Omega} \qquad \text{for } \iota \in \mathfrak{I}_\mathrm{I},$$

where $\alpha \in (\mathfrak{I}_{\mathrm{c}\iota}\cap\mathfrak{I}_\mathrm{P})$ is the outward normal vector from the ι interface. Then we can write

(B.255) $\displaystyle\sum_{i\in\mathfrak{I}_s} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}}\frac{\mathrm{D}^{\bar{\iota}}\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t} = \sum_{i\in\mathfrak{I}_s} \left\langle \rho_\iota\omega_{i\iota}\frac{\mathrm{D}'^{\bar{s}}\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$

$$+ \sum_{i\in\mathfrak{I}_s} \epsilon^\iota\rho^\iota\omega^{i\bar{\iota}}\mathbf{v}^{\bar{\iota},\bar{s}}\!\cdot\!\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)$$

$$- \sum_{i\in\mathfrak{I}_s} \left\langle \rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\!\cdot\!\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right) \right\rangle_{\Omega_\iota,\Omega} \qquad \text{for } \iota \in \mathfrak{I}_\mathrm{I}.$$

The gradient of the macroscale quantities in Eq. (B.255) can be moved outside the averaging operator. Since these macroscale quantities are averaged in the $\mathbf{N}$ direction, it follows that

(B.256) $$\nabla\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right) = \nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)$$

and

(B.257) $\displaystyle\sum_{i\in\mathfrak{I}_s} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}}\frac{\mathrm{D}^{\bar{\iota}}\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t} = \sum_{i\in\mathfrak{I}_s} \left\langle \rho_\iota\omega_{i\iota}\frac{\mathrm{D}'^{\bar{s}}\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$

$$+ \sum_{i\in\mathfrak{I}_s} \epsilon^\iota\rho^\iota\omega^{i\bar{\iota}}\mathbf{v}^{\bar{\iota},\bar{s}}\!\cdot\!\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)$$

$$- \sum_{i\in\mathfrak{I}_s} \nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{\overline{i\iota}}}\right)\cdot\left\langle \rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\!\cdot\!\mathbf{n}_\alpha\mathbf{n}_\alpha \right\rangle_{\Omega_\iota,\Omega} \qquad \text{for } \iota \in \mathfrak{I}_\mathrm{I}.$$

Similarly for a common curve, ι, we have

$$(B.258) \qquad \left\langle \frac{D''\bar{s}}{Dt} \right\rangle_{\Omega_\iota,\Omega} = \left\langle \frac{D\bar{s}}{Dt} + \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right) \cdot (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \cdot \nabla \right\rangle_{\Omega_\iota,\Omega},$$

and thus

$$(B.259) \quad \sum_{i\in\mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \frac{D^{\bar{\iota}}\left(K_E^{\bar{\iota}} + \psi^{\overline{i\iota}}\right)}{Dt} = \sum_{i\in\mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \frac{D''\bar{s}\left(K_E^{\bar{\iota}} + \psi^{\overline{i\iota}}\right)}{Dt} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{i\in\mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mathbf{v}^{\bar{\iota},\bar{s}} \cdot \nabla^{\backprime} \left(K_E^{\bar{\iota}} + \psi^{\overline{i\iota}}\right)$$

$$- \sum_{i\in\mathcal{I}_S} \nabla^{\backprime} \left(K_E^{\bar{\iota}} + \psi^{\overline{i\iota}}\right) \cdot \left\langle \rho_\iota \omega_{i\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right) \cdot (\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota) \right\rangle_{\Omega_\iota,\Omega} \qquad \text{for } \iota \in \mathcal{I}_C.$$

Next we notice that substitution of $\boldsymbol{\mathcal{P}}_r^\iota$ into Eq. (B.250) introduced the product of velocity in non-objective form with several terms arising from the momentum conservation equation. One of these products involves the gravitational acceleration force, $\mathbf{g}_{i\iota}$, which can be put into objective form and combined with the average of the partial time derivative of gravitational potential from the energy equation, $\psi_{i\iota}$. Using the relation between the acceleration vector and its potential, $\mathbf{g}_{i\iota} = -\nabla\psi_{i\iota}$, we can write

$$(B.260) \quad -\mathbf{v}^{\bar{\iota}} \cdot \sum_{i\in\mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mathbf{g}^{\overline{i\iota}} + \sum_{i\in\mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \frac{\partial\psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$$

$$= -\mathbf{v}^{\bar{\iota},\bar{s}} \cdot \sum_{i\in\mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mathbf{g}^{\overline{i\iota}} + \mathbf{v}^{\bar{s}} \cdot \sum_{i\in\mathcal{I}_S} \langle \rho_\iota \omega_{i\iota} \nabla\psi_{i\iota} \rangle_{\Omega_\iota,\Omega} + \sum_{i\in\mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \frac{\partial\psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$$

$$= -\mathbf{v}^{\bar{\iota},\bar{s}} \cdot \sum_{i\in\mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mathbf{g}^{\overline{i\iota}} + \sum_{i\in\mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \frac{D\bar{s}\psi_{i\iota}}{Dt} \right\rangle_{\Omega_\iota,\Omega} \qquad \text{for } \iota \in \mathcal{I}.$$

Note that for the solid-phase the first term on the last line of Eq. (B.260) goes to zero.

Applying Eq. (B.254) to the material derivative in Eq. (B.260), the similar expression for the interfaces is

$$(B.261) \quad -\mathbf{v}^{\bar{\iota}} \cdot \sum_{i\in\mathcal{I}_S} \epsilon^\iota \rho^\iota \omega^{i\bar{\iota}} \mathbf{g}^{\overline{i\iota}} + \sum_{i\in\mathcal{I}_S} \left\langle \rho_\iota \omega_{i\iota} \frac{\partial\psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$$

$$= -\mathbf{v}^{\overline{\iota},\overline{s}} \cdot \sum_{i\in\mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\overline{i\iota}} + \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{\mathrm{D}'^{\overline{s}}\psi_{i\iota}}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{g}_{i\iota} \right\rangle_{\Omega_\iota,\Omega} \quad \text{for } \iota \in \mathcal{I}_\mathrm{I},$$

and with Eq. (B.258) for the common curve

$$(\mathrm{B}.262) \quad -\mathbf{v}^{\overline{\iota}} \cdot \sum_{i\in\mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\overline{i\iota}} + \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega}$$

$$= -\mathbf{v}^{\overline{\iota},\overline{s}} \cdot \sum_{i\in\mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\overline{i\iota}} + \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{\mathrm{D}''^{\overline{s}}\psi_{i\iota}}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \mathbf{g}_{i\iota} \right\rangle_{\Omega_\iota,\Omega} \quad \text{for } \iota \in \mathcal{I}_\mathrm{C}.$$

Using the rearrangement of the end terms as derived in Appendix I and shown in Eq. (B.249), as well as referencing the remaining material derivatives and those velocities multiplying gravitational acceleration terms to the solid phase as in Eq. (B.255), Eq. (B.257), and Eqns (B.259)–(B.262), Eq. (B.251) can be written

$$(\mathrm{B}.263) \quad \sum_{\iota\in\mathcal{I}} \left[\eta^{\overline{\overline{\iota}}} \mathbf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \nabla^\backprime \cdot \left(\epsilon^\iota \boldsymbol{\varphi}^{\overline{\iota}} \right) - \epsilon^\iota b_T^{\overline{\overline{\iota}}} \right]$$

$$- \sum_{\iota\in\mathcal{I}_\mathrm{P}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i\in\mathcal{I}_s} \left[\left\langle \rho_\iota \omega_{i\iota} \frac{\mathrm{D}^{\overline{s}}\left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} + \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \nabla^\backprime \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right) \right]$$

$$- \sum_{\iota\in\mathcal{I}_\mathrm{I}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i\in\mathcal{I}_s} \left[\left\langle \rho_\iota \omega_{i\iota} \frac{\mathrm{D}'^{\overline{s}}\left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} + \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \nabla^\backprime \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right) \right]$$

$$+ \sum_{\iota\in\mathcal{I}_\mathrm{I}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i\in\mathcal{I}_s} \nabla^\backprime \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right) \cdot \left\langle \rho_\iota \omega_{i\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_\alpha \mathbf{n}_\alpha \right\rangle_{\Omega_\iota,\Omega}$$

$$- \sum_{\iota\in\mathcal{I}_\mathrm{C}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i\in\mathcal{I}_s} \left[\left\langle \rho_\iota \omega_{i\iota} \frac{\mathrm{D}''^{\overline{s}}\left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} + \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{v}^{\overline{\iota},\overline{s}} \cdot \nabla^\backprime \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right) \right]$$

$$+ \sum_{\iota\in\mathcal{I}_\mathrm{C}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i\in\mathcal{I}_s} \nabla^\backprime \left(K_E^{\overline{\overline{\iota}}} + \psi^{\overline{i\iota}} \right) \cdot \left\langle \rho_\iota \omega_{i\iota} \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\iota\in\mathfrak{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[E^{\overline{\overline{\iota}}}+\epsilon^{\iota}\rho^{\iota}\left(\frac{\mathbf{v}^{\overline{\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}}}{2}+K_{E}^{\overline{\overline{\iota}}}\right)+\sum_{i\in\mathfrak{I}_{s}}\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\psi^{\overline{i\iota}}\right]\mathbf{l}\boldsymbol{:}\mathbf{d}^{\backslash\overline{\overline{\iota}}}$$

$$+\sum_{\iota\in\mathfrak{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\nabla^{\backslash}\boldsymbol{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\backslash\overline{\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}}\right)+\nabla^{\backslash}\boldsymbol{\cdot}\left(\epsilon^{\iota}\mathbf{q}^{\backslash\overline{\iota}}\right)+\epsilon^{\iota}h_{T}^{\overline{\overline{\iota}}}\right]$$

$$+\sum_{\iota\in\mathfrak{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{i\in\mathfrak{I}_{s}}\epsilon^{\iota}\psi^{\overline{i\iota}}r^{i\iota}+\sum_{\iota\in\mathfrak{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{i\in\mathfrak{I}_{s}}\left\langle\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}^{\overline{s}}\psi_{i\iota}}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\iota}}}\sum_{i\in\mathfrak{I}_{s}}\left\langle\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}'^{\overline{s}}\psi_{i\iota}}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}+\sum_{\iota\in\mathfrak{I}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{i\in\mathfrak{I}_{s}}\left\langle\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}''^{\overline{s}}\psi_{i\iota}}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left(\sum_{i\in\mathfrak{I}_{s}}\overset{i\kappa\to i\iota}{M_{E}}+\overset{\kappa\to\iota}{T_{v}}+\overset{\kappa\to\iota}{Q}\right)$$

$$+\sum_{\iota\in\mathfrak{I}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\boldsymbol{\cdot}\left[\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\overline{\iota}}\mathbf{l}\boldsymbol{:}\mathbf{d}^{\backslash\overline{\overline{\iota}}}-\nabla^{\backslash}\boldsymbol{\cdot}\left(\epsilon^{\iota}\mathbf{t}^{\backslash\overline{\iota}}\right)\right]-\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\boldsymbol{\cdot}\sum_{i\in\mathfrak{I}_{s}}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\mathbf{g}^{\overline{i\iota}}\right)$$

$$-\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\boldsymbol{\cdot}\sum_{i\in\mathfrak{I}_{s}}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\mathbf{g}^{\overline{i\iota}}\right)-\sum_{\iota\in\mathfrak{I}_{\mathrm{C}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\boldsymbol{\cdot}\sum_{i\in\mathfrak{I}_{s}}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\mathbf{g}^{\overline{i\iota}}\right)$$

$$-\sum_{\iota\in\mathfrak{I}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\boldsymbol{\cdot}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left(\sum_{i\in\mathfrak{I}_{s}}\overset{i\kappa\to i\iota}{\mathbf{M}_{v}}+\overset{\kappa\to\iota}{\mathbf{T}}\right)$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{I}}}\sum_{i\in\mathfrak{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\rho_{\iota}\omega_{i\iota}\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\boldsymbol{\cdot}\mathbf{g}_{i\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{C}}}\sum_{i\in\mathfrak{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\rho_{\iota}\omega_{i\iota}\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\boldsymbol{\cdot}\mathbf{g}_{i\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_{E}^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}}}{2}\right)\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\mathbf{l}\boldsymbol{:}\mathbf{d}^{\backslash\overline{\overline{\iota}}}-\epsilon^{\iota}r^{i\iota}\right)$$

$$-\sum_{\iota\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_{E}^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}}}{2}\right)\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\overset{i\kappa\to i\iota}{M}$$

$$+\sum_{\iota\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_{E}^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\iota}}}{2}\right)\nabla^{\backslash}\boldsymbol{\cdot}\left(\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\mathbf{u}^{\overline{\overline{i\iota}}}\right)$$

$$+\sum_{\iota\in\mathfrak{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\eta_{\iota}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathfrak{I}_{s}}\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left(\eta^{\overline{\overline{\iota}}}\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}+\sum_{i\in\mathcal{I}_{s}}\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\nabla^{\backprime}\mu^{\overline{i\iota}}-\nabla^{\backprime}\left(\epsilon^{\iota}p^{\iota}\right)\right)$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\Big\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)p_{\iota}\Big\rangle_{\Omega_{\kappa},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\eta_{s}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{s}-\theta^{\overline{\overline{s}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_{s}}\rho_{s}\omega_{is}\frac{\mathrm{D}^{\overline{s}}(\mu_{is}-\mu^{\overline{is}})}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\epsilon^{s}\mathbf{t}^{\backslash s}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}+\frac{\epsilon^{s}}{\theta^{\overline{\overline{s}}}}\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\frac{\mathbf{C}^{s}}{j^{s}}\mathbf{I}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla^{\backprime}{\cdot}\left\langle\left(\mathbf{t}_{s}-\boldsymbol{\sigma}_{s}{:}\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla{\cdot}\mathbf{t}_{s}-\frac{\mathbf{C}_{s}}{j_{s}}{:}\nabla\boldsymbol{\sigma}_{s}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\Big\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{ss},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\boldsymbol{\sigma}_{s}{:}\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{n}_{s}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}_{s}\right)\right\rangle_{\Omega_{\kappa},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\eta_{\iota}\frac{\mathrm{D}^{\prime\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_{s}}\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}^{\prime\overline{s}}(\mu_{i\iota}-\mu^{\overline{i\iota}})}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\gamma_{\iota}\rangle_{\Omega_{\iota},\Omega}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backprime}{\cdot}\Big\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\Big\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}{\cdot}\Big\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\eta_{\iota}\Big\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\sum_{i\in\mathcal{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backprime}\mu^{\overline{i\iota}}{\cdot}\Big\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\rho_{\iota}\omega_{i\iota}\Big\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\Big\langle\left(\nabla^{\prime}{\cdot}\mathbf{n}_{\alpha}\right)\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\Big\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left(\eta^{\overline{\overline{\iota}}}\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}+\sum_{i\in\mathcal{I}_{s}}\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\nabla^{\backprime}\mu^{\overline{i\iota}}+\nabla^{\backprime}\left(\epsilon^{\iota}\gamma^{\iota}\right)\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in(\mathcal{I}_{\mathrm{c}\iota}\cap\mathcal{I}_{\mathrm{C}})}\Big\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\Big\rangle_{\Omega_{\kappa},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\eta_{\iota}\frac{\mathrm{D}^{\prime\prime\overline{s}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in\mathcal{I}_{s}}\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}^{\prime\prime\overline{s}}(\mu_{i\iota}-\mu^{\overline{i\iota}})}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backprime}\!\cdot\!\left\langle\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\left(\mathbf{l}_{\iota}\!\cdot\!\nabla''\mathbf{l}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\langle\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\gamma_{\iota}\rangle_{\Omega_{\iota},\Omega}\!:\!\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in\left(\mathcal{J}_{\mathrm{c}\iota}\cap\mathcal{J}_{\mathrm{Pt}}\right)}\left\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}\!\cdot\!\left\langle\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\eta_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{i\in\mathcal{J}_{s}}\nabla^{\backprime}\mu^{\overline{i\iota}}\!\cdot\!\left\langle\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\rho_{\iota}\omega_{i\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left(\eta^{\overline{\overline{\iota}}}\nabla^{\backprime}\theta^{\overline{\overline{\iota}}}+\sum_{i\in\mathcal{J}_{s}}\epsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}}\nabla^{\backprime}\mu^{\overline{i\iota}}-\nabla^{\backprime}\left(\epsilon^{\iota}\gamma^{\iota}\right)\right)$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{J}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot p_{\iota}\mathbf{I}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_{\iota}'\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\sum_{\iota\in\mathcal{J}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{\iota}\mathbf{I}'}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_{\iota}''\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{J}_{\mathrm{C}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{\iota}\mathbf{I}''}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}}\sum_{i\in\mathcal{J}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\mu_{i\iota}+\psi_{i\iota}-K_{E}^{\overline{\overline{\iota}}}-\mu^{\overline{i\iota}}-\psi^{\overline{i\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}}\sum_{i\in\mathcal{J}_{s}}\frac{1}{\theta^{\overline{\iota}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\frac{\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{2}+\frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{J}}\left\langle\frac{\mathbf{e}\cdot\sum_{i\in\mathcal{J}_{s}}\rho_{\iota}\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_{\iota}}-\frac{\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}}{\theta^{\overline{\overline{\iota}}}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{J}}\left\langle\frac{\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta_{\iota}}\right)\mathbf{e}\cdot\left[\mathbf{q}_{\iota}-\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\theta_{\iota}\eta_{\iota}\right]}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega},$$

where $\alpha \in (\mathcal{I}_{c\iota} \cap \mathcal{I}_{\mathrm{P}})$.

Within the CIT framework, entropy production is a result of heat conduction, the flow of matter, mechanical dissipation, chemical reactions, and electrical currents leading to irreversible processes. According to the entropy production postulate, the production of entropy can be expressed as a sum of products of a set of thermodynamic fluxes and forces that are zero at equilibrium and independent of all other fluxes and forces in the respective set. Some rearranging is needed to get such a form.

The surficial portion of the non-advective heat flux term may be rearranged using the product rule to obtain

$$(\text{B.264}) \qquad \frac{1}{\theta^{\overline{\overline{\iota}}}} \nabla' \cdot \left(\epsilon^{\iota} \mathbf{q}^{\backslash \overline{\iota}} \right) = \nabla' \cdot \left(\frac{\epsilon^{\iota} \mathbf{q}^{\backslash \overline{\overline{\iota}}}}{\theta^{\overline{\overline{\iota}}}} \right) - \epsilon^{\iota} \mathbf{q}^{\backslash \overline{\iota}} \cdot \nabla' \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} \right).$$

Another application of the product rule that will prove convenient involves rearrangement of the dispersion term that arises from the species mass conservation equation. Looking at only the surficial portion of this term,

$$(\text{B.265}) \quad \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \nabla' \cdot \left(\epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \right)$$

$$= \nabla' \cdot \left[\frac{1}{\theta^{\overline{\overline{\iota}}}} \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \right]$$

$$- \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \cdot \nabla' \left[\frac{1}{\theta^{\overline{\overline{\iota}}}} \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \right]$$

$$= \nabla' \cdot \left[\frac{1}{\theta^{\overline{\overline{\iota}}}} \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \right]$$

$$- \frac{1}{\theta^{\overline{\overline{\iota}}}} \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \cdot \nabla' \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right)$$

$$- \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \cdot \nabla' \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} \right).$$

Summing Eq. (B.265) over all species allows for

$$(\text{B.266}) \quad \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(K_E^{\overline{\overline{i}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \nabla' \cdot \left(\epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \right)$$

$$= \sum_{i \in \mathcal{I}_S} \nabla^{\backslash} \cdot \left[\frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \mathbf{u}^{\overline{\overline{\backslash i\iota}}} \right]$$

$$- \sum_{i \in \mathcal{I}_S} \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \mathbf{u}^{\overline{\overline{\backslash i\iota}}} \cdot \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right)$$

$$- \sum_{i \in \mathcal{I}_S} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\overline{\overline{\backslash i\iota}}} \cdot \nabla^{\backslash} \left(\frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \right).$$

Applying Eq. (B.264) and Eq. (B.266), as well as the thermodynamic relationships found in Eq. (B.148), Eq. (B.168), Eq. (B.197), and Eq. (B.214), and regrouping to combine like terms, Eq. (B.263) can be rewritten as

$$(B.267) \quad - \sum_{\iota \in \mathcal{I}} \nabla^{\backslash} \cdot \left[\epsilon^{\iota} \boldsymbol{\varphi}^{\backslash \overline{\iota}} - \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \left(\epsilon^{\iota} \mathbf{q}^{\backslash \overline{\iota}} + \sum_{i \in \mathcal{I}_S} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\overline{\overline{\backslash i\iota}}} \right) \right]$$

$$+ \sum_{\iota \in \mathcal{I}} \left(\nabla^{\backslash} \cdot \mathbf{N} \right) \mathbf{N} \cdot \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \sum_{i \in \mathcal{I}_S} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\overline{\overline{i\iota}}}$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \left[\epsilon^{\iota} b_T^{\overline{\overline{\iota}}} - \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \left(\epsilon^{\iota} h_T^{\overline{\overline{\iota}}} + \left\langle \eta_{\iota} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\iota} - \theta^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega} \right. \right.$$

$$\left. \left. + \sum_{i \in \mathcal{I}_S} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - K_E^{\overline{\overline{\iota}}} - \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega} \right) \right]$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left[\epsilon^{\iota} b_T^{\overline{\overline{\iota}}} - \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \left(\epsilon^{\iota} h_T^{\overline{\overline{\iota}}} + \left\langle \eta_{\iota} \frac{\mathrm{D}'^{\overline{s}} \left(\theta_{\iota} - \theta^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega} \right. \right.$$

$$\left. \left. + \sum_{i \in \mathcal{I}_S} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}'^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - K_E^{\overline{\overline{\iota}}} - \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega} \right) \right]$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \left[\epsilon^{\iota} b_T^{\overline{\overline{\iota}}} - \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \left(\epsilon^{\iota} h_T^{\overline{\overline{\iota}}} + \left\langle \eta_{\iota} \frac{\mathrm{D}''^{\overline{s}} \left(\theta_{\iota} - \theta^{\overline{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega} \right. \right.$$

$$\left. \left. + \sum_{i \in \mathcal{I}_S} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}''^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - K_E^{\overline{\overline{\iota}}} - \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota},\Omega} \right) \right]$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{1}{\overline{\overline{\theta^{\overline{\iota}}}}} \left(\epsilon^{\iota} p^{\iota} \mathbf{I}^{\backslash} + \epsilon^{\iota} \mathbf{t}^{\backslash \overline{\iota}} \right) : \mathbf{d}^{\backslash \overline{\iota}} - \frac{1}{\overline{\overline{\theta^{\overline{s}}}}} \left(\epsilon^{s} \mathbf{t}^{\backslash s} - \epsilon^{s} \mathbf{t}^{\backslash \overline{s}} \right) : \mathbf{d}^{\backslash \overline{s}}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{I}} \frac{1}{\theta^{\bar{\bar{\iota}}}} \left(\epsilon^\iota\gamma^\iota\mathbf{I'} - \epsilon^\iota\mathbf{t}^{\bar{\iota}}\right) \mathbf{:d}^{\bar{\bar{\iota}}} + \sum_{\iota\in\mathcal{I}_\mathrm{C}} \frac{1}{\theta^{\bar{\iota}}} \left(\epsilon^\iota\gamma^\iota\mathbf{I'} + \epsilon^\iota\mathbf{t}^{\bar{\iota}}\right) \mathbf{:d}^{\bar{\bar{\iota}}}$$

$$-\sum_{\iota\in\mathcal{I}} \sum_{i\in\mathcal{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}}\epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{u}^{\bar{\bar{\backslash i\iota}}}\cdot\nabla'\left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}\right)$$

$$-\sum_{\iota\in\mathcal{I}} \sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}\right)\mathbf{u}^{\bar{\bar{\backslash i\iota}}}\cdot\nabla'\left(\frac{1}{\theta^{\bar{\bar{\iota}}}}\right)$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{f}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\left[\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}}\right) + \mathbf{g}^{\backslash \overline{i\iota}}\right]\right)$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{f}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\eta^{\bar{\bar{\iota}}}\nabla'\theta^{\bar{\bar{\iota}}} + \sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\nabla'\mu^{\overline{i\iota}} - \nabla'\left(\epsilon^\iota p^\iota\right)\right)$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{I}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\left[\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}}\right) + \mathbf{g}^{\backslash \overline{i\iota}}\right]\right)$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{I}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\eta^{\bar{\bar{\iota}}}\nabla'\theta^{\bar{\bar{\iota}}} + \sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\nabla'\mu^{\overline{i\iota}} + \nabla'\left(\epsilon^\iota\gamma^\iota\right)\right)$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{C}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\left[\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}}\right) + \mathbf{g}^{\backslash \overline{i\iota}}\right]\right)$$

$$-\sum_{\iota\in\mathcal{I}} \frac{\mathbf{v}^{\bar{\iota},\bar{s}}\cdot\mathbf{N}}{\theta^{\bar{\bar{\iota}}}}\sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\mathbf{g}^{\overline{i\iota}}\cdot\mathbf{N}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{C}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\bar{\iota}}}}\cdot\left(\eta^{\bar{\bar{\iota}}}\nabla'\theta^{\bar{\bar{\iota}}} + \sum_{i\in\mathcal{I}_s} \epsilon^\iota\rho^\iota\omega^{i\iota}\nabla'\mu^{\overline{i\iota}} - \nabla'\left(\epsilon^\iota\gamma^\iota\right)\right)$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{I}} \sum_{i\in\mathcal{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}}\right)\cdot\left\langle\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{C}} \sum_{i\in\mathcal{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}}\nabla'\left(K_E^{\bar{\bar{\iota}}} + \psi^{\overline{i\iota}}\right)\cdot\left\langle\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\cdot\left(\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota\right)\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{I}} \sum_{i\in\mathcal{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{g}_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{C}} \sum_{i\in\mathcal{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}}\left\langle\rho_\iota\omega_{i\iota}\left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}}\right)\cdot\left(\mathbf{I} - \mathbf{l}_\iota\mathbf{l}_\iota\right)\cdot\mathbf{g}_{i\iota}\right\rangle_{\Omega_\iota,\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\epsilon^{\iota}\mu^{\overline{i\iota}}r^{i\iota}-\sum_{\iota\in\mathcal{I}}\left(\epsilon^{\iota}\mathbf{q}^{\backslash\overline{\iota}}\right)\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}\right)$$

$$+\sum_{\iota\in\mathcal{I}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\sum_{i\in\mathcal{I}_s}\overset{i\kappa\to i\iota}{M_E}+\overset{\kappa\to\iota}{T_v}+\overset{\kappa\to\iota}{Q}\right)$$

$$-\sum_{\iota\in\mathcal{I}}\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\cdot\sum_{\kappa\in\mathcal{I}_{C\iota}}\left(\sum_{i\in\mathcal{I}_s}\overset{i\kappa\to i\iota}{\mathbf{M}_v}+\overset{\kappa\to\iota}{\mathbf{T}}\right)$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}-\frac{\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}}{2}\right)\sum_{\kappa\in\mathcal{I}_{C\iota}}\overset{i\kappa\to i\iota}{M}$$

$$+\sum_{\iota\in\mathcal{I}_f}\sum_{\kappa\in\mathcal{I}_{C\iota}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)p_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{Cs}}\left\langle\left(\frac{\mathbf{C}_s}{j_s}:\boldsymbol{\sigma}_s\right)\left(\mathbf{v}_{\kappa}-\mathbf{v}_s\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{\kappa},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla^{\backslash}\cdot\left\langle\mathbf{I}\cdot\left(\mathbf{t}_s-\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla^{\backslash}\cdot\left\langle\mathbf{NN}\cdot\left(\mathbf{t}_s-\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_I}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backslash}\theta^{\overline{\iota}}\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\eta_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_I}\frac{1}{\theta^{\overline{\overline{\iota}}}}\nabla^{\backslash}\mu^{\overline{i\iota}}\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\rho_{\iota}\omega_{i\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_I}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\nabla^{\backslash}\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}+\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}:\mathbf{d}^{\backslash\overline{\overline{s}}}\right]$$

$$-\sum_{\iota\in\mathcal{I}_I}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\left(\nabla'\cdot\mathbf{n}_{\alpha}\right)\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_I}\frac{1}{\theta^{\overline{\overline{\iota}}}}\sum_{\kappa\in\left(\mathcal{I}_{C\iota}\cap\mathcal{I}_C\right)}\left\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\kappa},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_C}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\nabla^{\backslash}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}+\left\langle\left(\mathbf{I}-\mathbf{l}_{\iota}\mathbf{l}_{\iota}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega}:\mathbf{d}^{\backslash\overline{\overline{s}}}\right]$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \left(\mathbf{l}_\iota \cdot \nabla'' \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \nabla^\backprime \theta^{\overline{\iota}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \eta_\iota \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \nabla^\backprime \mu^{\overline{i\iota}} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_\iota \mathbf{l}_\iota \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \omega_{i\iota} \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \sum_{\kappa \in \left(\mathcal{I}_{\mathrm{c}\iota} \cap \mathcal{I}_{\mathrm{Pt}} \right)} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \gamma_\iota \right\rangle_{\Omega_\kappa, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{1}{\theta^{\overline{\iota}}} \left\langle \frac{\mathbf{e} \cdot \boldsymbol{\tau}_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} + \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash \overline{s}} \right)}{\theta^{\overline{\iota}}} \cdot \left\langle \frac{\mathbf{e} \cdot p_\iota \mathbf{I}^\backprime}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\iota}}} \left\langle \frac{\mathbf{e} \cdot \boldsymbol{\tau}'_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash \overline{s}} \right)}{\theta^{\overline{\iota}}} \cdot \left\langle \frac{\mathbf{e} \cdot \gamma_\iota \mathbf{I}^\backprime}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{1}{\theta^{\overline{\iota}}} \left\langle \frac{\mathbf{e} \cdot \boldsymbol{\tau}''_\iota \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} + \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash \overline{s}} \right)}{\theta^{\overline{\iota}}} \cdot \left\langle \frac{\mathbf{e} \cdot \gamma_\iota \mathbf{I}''}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \mathbf{N}}{\theta^{\overline{\iota}}} \mathbf{N} \cdot \left\langle \frac{\mathbf{e} p_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \mathbf{N}}{\theta^{\overline{\iota}}} \mathbf{N} \cdot \left\langle \frac{\mathbf{e} \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{C}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \mathbf{N}}{\theta^{\overline{\iota}}} \mathbf{N} \cdot \left\langle \frac{\mathbf{e} \gamma_\iota}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} + \sum_{\iota \in \mathcal{I}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}} \right) \eta_\iota \left(\theta^{\overline{\iota}} - \theta_\iota \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}} \right) \rho_\iota \omega_{i\iota} \left(\mu_{i\iota} + \psi_{i\iota} - K_E^{\overline{\overline{\iota}}} - \mu^{\overline{i\iota}} - \psi^{\overline{i\iota}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}} \right) \rho_\iota \omega_{i\iota} \left(\frac{\left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right) \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}} \right)}{2} + \frac{\mathbf{u}_{i\iota} \cdot \mathbf{u}_{i\iota}}{2} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$- \sum_{\iota \in \mathcal{I}} \left\langle \frac{\mathbf{e} \cdot \sum\limits_{i \in \mathcal{I}_s} \rho_\iota \omega_{i\iota} \mathbf{u}_{i\iota} \left(\frac{\mu_{i\iota} + \psi_{i\iota}}{\theta_\iota} - \frac{\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}}{\theta^{\overline{\iota}}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}} \left\langle \frac{\left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta_\iota} \right) \mathbf{e} \cdot \left[\mathbf{q}_\iota - \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}} \right) \theta_\iota \eta_\iota \right]}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} = \Lambda \geq 0.$$

The final set of terms that require some expansion and rearrangement are the inter-entity exchange terms. The objectives of these expansions are to ensure that all velocities that appear are expressed relative to the solid-phase velocity and to gather terms in force-flux pairs.

Terms involving the inter-entity transfer of mass, momentum, and energy need to be rearranged into force-flux form. The straightforward, but somewhat lengthy, manipulations needed to derive this form are guided by the *a priori* knowledge of equilibrium conditions, which can be utilized to derive forms in which the forces are known to be zero at equilibrium. The needed rearrangement is accomplished by extracting all terms involving the transfer of momentum, mass, and energy from Eq. (B.267) and manipulating them to derive the desired form. These manipulations are detailed in turn. The specific two-fluid-phase case is considered at this point rather than including common points, which will not appear in this particular system due to the primary restrictions imposed.

First, consider terms involving the interfacial transport of momentum, which may be written as

$$
\begin{aligned}
\text{(B.268)} \quad T =& -\sum_{\iota \in \mathfrak{I}} \frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}} \cdot \sum_{\kappa \in \mathfrak{I}_{C\iota}} \overset{\kappa \to \iota}{\mathbf{T}} + \sum_{\iota \in \mathfrak{I}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{\kappa \in \mathfrak{I}_{C\iota}} \overset{\kappa \to \iota}{T_v} \\
=& -\frac{\mathbf{v}^{\overline{w}}}{\theta^{\overline{\overline{w}}}} \cdot \left(\overset{wg \to w}{\mathbf{T}} + \overset{ws \to w}{\mathbf{T}} \right) + \frac{1}{\theta^{\overline{\overline{w}}}} \left(\mathbf{v}_w^{\overline{wg}} \cdot \overset{wg \to w}{\mathbf{T}} + \mathbf{v}_w^{\overline{ws}} \cdot \overset{ws \to w}{\mathbf{T}} \right) \\
& -\frac{\mathbf{v}^{\overline{g}}}{\theta^{\overline{\overline{g}}}} \cdot \left(\overset{wg \to g}{\mathbf{T}} + \overset{gs \to g}{\mathbf{T}} \right) + \frac{1}{\theta^{\overline{\overline{g}}}} \left(\mathbf{v}_g^{\overline{wg}} \cdot \overset{wg \to g}{\mathbf{T}} + \mathbf{v}_g^{\overline{gs}} \cdot \overset{gs \to g}{\mathbf{T}} \right) \\
& -\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}} \cdot \left(\overset{ws \to s}{\mathbf{T}} + \overset{gs \to s}{\mathbf{T}} \right) + \frac{1}{\theta^{\overline{\overline{s}}}} \left(\mathbf{v}_s^{\overline{ws}} \cdot \overset{ws \to s}{\mathbf{T}} + \mathbf{v}_s^{\overline{gs}} \cdot \overset{gs \to s}{\mathbf{T}} \right) \\
& -\frac{\mathbf{v}^{\overline{wg}}}{\theta^{\overline{\overline{wg}}}} \cdot \left(-\overset{wg \to w}{\mathbf{T}} - \overset{wg \to g}{\mathbf{T}} + \overset{wgs \to wg}{\mathbf{T}} \right) \\
& +\frac{1}{\theta^{\overline{\overline{wg}}}} \left(-\mathbf{v}_w^{\overline{wg}} \cdot \overset{wg \to w}{\mathbf{T}} - \mathbf{v}_g^{\overline{wg}} \cdot \overset{wg \to g}{\mathbf{T}} + \mathbf{v}_{wg}^{\overline{wgs}} \cdot \overset{wgs \to wg}{\mathbf{T}} \right) \\
& -\frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}} \cdot \left(-\overset{ws \to w}{\mathbf{T}} - \overset{ws \to s}{\mathbf{T}} + \overset{wgs \to ws}{\mathbf{T}} \right)
\end{aligned}
$$

$$+\frac{1}{\theta^{\overline{\overline{ws}}}}\left(-\mathbf{v}_w^{\overline{ws}}\cdot\overset{ws\to w}{\mathbf{T}}-\mathbf{v}_s^{\overline{ws}}\cdot\overset{ws\to s}{\mathbf{T}}+\mathbf{v}_{ws}^{\overline{wgs}}\cdot\overset{wgs\to ws}{\mathbf{T}}\right)$$

$$-\frac{\mathbf{v}^{\overline{gs}}}{\theta^{\overline{\overline{gs}}}}\cdot\left(-\overset{gs\to g}{\mathbf{T}}-\overset{gs\to s}{\mathbf{T}}+\overset{wgs\to gs}{\mathbf{T}}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{gs}}}}\left(-\mathbf{v}_g^{\overline{gs}}\cdot\overset{gs\to g}{\mathbf{T}}-\mathbf{v}_s^{\overline{gs}}\cdot\overset{gs\to s}{\mathbf{T}}+\mathbf{v}_{gs}^{\overline{wgs}}\cdot\overset{wgs\to gs}{\mathbf{T}}\right)$$

$$-\frac{\mathbf{v}^{\overline{wgs}}}{\theta^{\overline{\overline{wgs}}}}\cdot\left(-\overset{wgs\to wg}{\mathbf{T}}-\overset{wgs\to ws}{\mathbf{T}}-\overset{wgs\to gs}{\mathbf{T}}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\left(-\mathbf{v}_{wg}^{\overline{wgs}}\cdot\overset{wgs\to wg}{\mathbf{T}}-\mathbf{v}_{ws}^{\overline{wgs}}\cdot\overset{wgs\to ws}{\mathbf{T}}-\mathbf{v}_{gs}^{\overline{wgs}}\cdot\overset{wgs\to gs}{\mathbf{T}}\right).$$

Putting into objective form by referencing all velocities to $\mathbf{v}^{\overline{s}}$, we arrive at

(B.269)

$$T=-\frac{\mathbf{v}^{\overline{w},\overline{s}}}{\theta^{\overline{\overline{w}}}}\cdot\left(\overset{wg\to w}{\mathbf{T}}+\overset{ws\to w}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{w}}}}\left[\left(\mathbf{v}_w^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wg\to w}{\mathbf{T}}+\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{ws\to w}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{g},\overline{s}}}{\theta^{\overline{\overline{g}}}}\cdot\left(\overset{wg\to g}{\mathbf{T}}+\overset{gs\to g}{\mathbf{T}}\right)+\frac{1}{\theta^{\overline{\overline{g}}}}\left[\left(\mathbf{v}_g^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wg\to g}{\mathbf{T}}+\left(\mathbf{v}_g^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{gs\to g}{\mathbf{T}}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left[\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{ws\to s}{\mathbf{T}}+\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{gs\to s}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{wg},\overline{s}}}{\theta^{\overline{\overline{wg}}}}\cdot\left(-\overset{wg\to w}{\mathbf{T}}-\overset{wg\to g}{\mathbf{T}}+\overset{wgs\to wg}{\mathbf{T}}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\left[-\left(\mathbf{v}_w^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wg\to w}{\mathbf{T}}-\left(\mathbf{v}_g^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wg\to g}{\mathbf{T}}+\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to wg}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{ws},\overline{s}}}{\theta^{\overline{\overline{ws}}}}\cdot\left(-\overset{ws\to w}{\mathbf{T}}-\overset{ws\to s}{\mathbf{T}}+\overset{wgs\to ws}{\mathbf{T}}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{ws}}}}\left[-\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{ws\to w}{\mathbf{T}}-\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{ws\to s}{\mathbf{T}}+\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to ws}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{gs},\overline{s}}}{\theta^{\overline{\overline{gs}}}}\cdot\left(-\overset{gs\to g}{\mathbf{T}}-\overset{gs\to s}{\mathbf{T}}+\overset{wgs\to gs}{\mathbf{T}}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{gs}}}}\left[-\left(\mathbf{v}_g^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{gs\to g}{\mathbf{T}}-\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{gs\to s}{\mathbf{T}}+\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to gs}{\mathbf{T}}\right]$$

$$-\frac{\mathbf{v}^{\overline{wgs},\overline{s}}}{\theta^{\overline{\overline{wgs}}}}\cdot\left(-\overset{wgs\to wg}{\mathbf{T}}-\overset{wgs\to ws}{\mathbf{T}}-\overset{wgs\to gs}{\mathbf{T}}\right)$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\left[-\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to wg}{\mathbf{T}}-\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to ws}{\mathbf{T}}\right.$$

$$- \left(\mathbf{v}_{g\bar{s}}^{\overline{wgs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wgs \to gs}{\mathbf{T}} \Bigg] .$$

Rearranging into force-flux pairs gives

$$(B.270) \quad T = -\frac{\mathbf{v}^{\overline{w},\bar{s}}}{\theta^{\overline{\overline{w}}}} \cdot \overset{wg \to w}{\mathbf{T}} - \frac{\mathbf{v}^{\overline{g},\bar{s}}}{\theta^{\overline{\overline{g}}}} \cdot \overset{wg \to g}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{wg},\bar{s}}}{\theta^{\overline{\overline{wg}}}} \cdot \left(\overset{wg \to w}{\mathbf{T}} + \overset{wg \to g}{\mathbf{T}} \right)$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wg \to w}{\mathbf{T}} + \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wg \to g}{\mathbf{T}}$$

$$- \frac{\mathbf{v}^{\overline{w},\bar{s}}}{\theta^{\overline{\overline{w}}}} \cdot \overset{ws \to w}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{ws},\bar{s}}}{\theta^{\overline{\overline{ws}}}} \cdot \left(\overset{ws \to w}{\mathbf{T}} + \overset{ws \to s}{\mathbf{T}} \right)$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{ws \to w}{\mathbf{T}} + \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{ws \to s}{\mathbf{T}}$$

$$- \frac{\mathbf{v}^{\overline{g},\bar{s}}}{\theta^{\overline{\overline{g}}}} \cdot \overset{gs \to g}{\mathbf{T}} + \frac{\mathbf{v}^{\overline{gs},\bar{s}}}{\theta^{\overline{\overline{gs}}}} \cdot \left(\overset{gs \to g}{\mathbf{T}} + \overset{gs \to s}{\mathbf{T}} \right)$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{gs \to g}{\mathbf{T}} + \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{gs \to s}{\mathbf{T}}$$

$$- \frac{\mathbf{v}^{\overline{wg},\bar{s}}}{\theta^{\overline{\overline{wg}}}} \cdot \overset{wgs \to wg}{\mathbf{T}} - \frac{\mathbf{v}^{\overline{ws},\bar{s}}}{\theta^{\overline{\overline{ws}}}} \cdot \overset{wgs \to ws}{\mathbf{T}} - \frac{\mathbf{v}^{\overline{gs},\bar{s}}}{\theta^{\overline{\overline{gs}}}} \cdot \overset{wgs \to gs}{\mathbf{T}}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{wg}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wgs \to wg}{\mathbf{T}}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wgs \to ws}{\mathbf{T}}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{gs}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wgs \to gs}{\mathbf{T}}$$

$$+ \frac{\mathbf{v}^{\overline{wgs},\bar{s}}}{\theta^{\overline{\overline{wgs}}}} \cdot \left(\overset{wgs \to wg}{\mathbf{T}} + \overset{wgs \to ws}{\mathbf{T}} + \overset{wgs \to gs}{\mathbf{T}} \right)$$

$$= -\sum_{\iota \in \mathfrak{I}} \sum_{\kappa \in \mathfrak{I}_{C\iota}} \frac{\mathbf{v}^{\overline{\iota},\bar{s}}}{\theta^{\overline{\overline{\iota}}}} \cdot \overset{\kappa \to \iota}{\mathbf{T}} + \sum_{\iota \in \mathfrak{I}_{P}} \sum_{\kappa \in \mathfrak{I}_{C\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \left(\mathbf{v}_{\iota}^{\overline{\kappa}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{\kappa \to \iota}{\mathbf{T}}$$

$$+ \sum_{\iota \in \mathfrak{I}_{I}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\mathbf{v}_{\iota}^{\overline{wgs}} - \mathbf{v}^{\bar{s}} \right) \cdot \overset{wgs \to \iota}{\mathbf{T}} .$$

This resultant form is convenient because forces consisting of referenced velocities and differences in the inverse of temperatures are known to be zero at equilibrium. Also, notice that if the velocities with both subscripts and superscripts are replaced by the

higher dimensional macroscale mass averaged entity velocity, that the resulting form reduces to the form used in a previous paper, T6 [110].

Similar manipulations can be performed for the terms involving heat exchange to obtain

$$
\text{(B.271)} \quad Q = \sum_{\iota \in \mathcal{J}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{\kappa \in \mathcal{J}_{C\iota}} \overset{\kappa \to \iota}{Q} = \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \overset{wg \to w}{Q} + \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \overset{ws \to w}{Q}
$$

$$
+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \overset{wg \to g}{Q} + \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \overset{gs \to g}{Q} + \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \overset{ws \to s}{Q}
$$

$$
+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \overset{gs \to s}{Q} + \left(\frac{1}{\theta^{\overline{\overline{wg}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \overset{wgs \to wg}{Q} + \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \overset{wgs \to ws}{Q}
$$

$$
+ \left(\frac{1}{\theta^{\overline{\overline{gs}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \overset{wgs \to gs}{Q}
$$

$$
= \sum_{\iota \in \mathcal{J}_{P}} \sum_{\kappa \in \mathcal{J}_{C\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \overset{\kappa \to \iota}{Q} + \sum_{\iota \in \mathcal{J}_{I}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \overset{wgs \to \iota}{Q} .
$$

Next consider all terms involving the exchange of mass

$$
\text{(B.272)} \quad M = \sum_{\iota \in \mathcal{J}} \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{\kappa \in \mathcal{J}_{C\iota}} \sum_{i \in \mathcal{J}_s} \overset{i\kappa \to i\iota}{M_E} - \sum_{\iota \in \mathcal{J}} \frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}} \cdot \sum_{\kappa \in \mathcal{J}_{C\iota}} \sum_{i \in \mathcal{J}_s} \overset{i\kappa \to i\iota}{\mathbf{M}_v}
$$

$$
- \sum_{\iota \in \mathcal{J}} \sum_{i \in \mathcal{J}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} - \frac{\mathbf{v}^{\overline{\iota}} \cdot \mathbf{v}^{\overline{\iota}}}{2} \right) \sum_{\kappa \in \mathcal{J}_{C\iota}} \overset{i\kappa \to i\iota}{M}
$$

$$
= \frac{1}{\theta^{\overline{\overline{w}}}} \sum_{i \in \mathcal{J}_s} \left(\frac{E_{Tw}^{\overline{\overline{wg}}}}{\epsilon^w \rho_w^{wg}} \overset{iwg \to iw}{M} + \frac{E_{Tw}^{\overline{\overline{ws}}}}{\epsilon^w \rho_w^{ws}} \overset{iws \to iw}{M} \right)
$$

$$
+ \frac{1}{\theta^{\overline{\overline{g}}}} \sum_{i \in \mathcal{J}_s} \left(\frac{E_{Tg}^{\overline{\overline{wg}}}}{\epsilon^g \rho_g^{wg}} \overset{iwg \to ig}{M} + \frac{E_{Tg}^{\overline{\overline{gs}}}}{\epsilon^g \rho_g^{gs}} \overset{igs \to ig}{M} \right)
$$

$$
+ \frac{1}{\theta^{\overline{\overline{s}}}} \sum_{i \in \mathcal{J}_s} \left(\frac{E_{Ts}^{\overline{\overline{ws}}}}{\epsilon^s \rho_s^{ws}} \overset{iws \to is}{M} + \frac{E_{Ts}^{\overline{\overline{gs}}}}{\epsilon^s \rho_s^{gs}} \overset{igs \to is}{M} \right)
$$

$$
- \frac{1}{\theta^{\overline{\overline{wg}}}} \sum_{i \in \mathcal{J}_s} \left(\frac{E_{Tw}^{\overline{\overline{wg}}}}{\epsilon^w \rho_w^{wg}} \overset{iwg \to iw}{M} + \frac{E_{Tg}^{\overline{\overline{wg}}}}{\epsilon^g \rho_g^{wg}} \overset{iwg \to ig}{M} - \frac{E_{Twg}^{\overline{\overline{wgs}}}}{\epsilon^{wg} \rho_{wg}^{wgs}} \overset{iwgs \to iwg}{M} \right)
$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathcal{I}_s}\left(\frac{E_{Tw}^{\overline{\overline{ws}}}}{\epsilon^w\rho_w^{ws}}\overset{iws\to iw}{M}+\frac{E_{Ts}^{\overline{\overline{ws}}}}{\epsilon^s\rho_s^{ws}}\overset{iws\to is}{M}-\frac{E_{Tws}^{\overline{\overline{wgs}}}}{\epsilon^{ws}\rho_{ws}^{wgs}}\overset{iwgs\to iws}{M}\right)$$

$$-\frac{1}{\theta^{\overline{\overline{gs}}}}\sum_{i\in\mathcal{I}_s}\left(\frac{E_{Tg}^{\overline{\overline{gs}}}}{\epsilon^g\rho_g^{gs}}\overset{igs\to ig}{M}+\frac{E_{Ts}^{\overline{\overline{gs}}}}{\epsilon^s\rho_s^{gs}}\overset{igs\to is}{M}-\frac{E_{Tgs}^{\overline{\overline{wgs}}}}{\epsilon^{gs}\rho_{gs}^{wgs}}\overset{iwgs\to igs}{M}\right)$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\sum_{i\in\mathcal{I}_s}\left(\frac{E_{Twg}^{\overline{\overline{wgs}}}}{\epsilon^{wg}\rho_{wg}^{wgs}}\overset{iwgs\to iwg}{M}+\frac{E_{Tws}^{\overline{\overline{wgs}}}}{\epsilon^{ws}\rho_{ws}^{wgs}}\overset{iwgs\to iws}{M}+\frac{E_{Tgs}^{\overline{\overline{wgs}}}}{\epsilon^{gs}\rho_{gs}^{wgs}}\overset{iwgs\to igs}{M}\right)$$

$$-\frac{\mathbf{v}^{\overline{w}}}{\theta^{\overline{\overline{w}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_w^{\overline{wg}}\overset{iwg\to iw}{M}+\mathbf{v}_w^{\overline{ws}}\overset{iws\to iw}{M}\right)$$

$$-\frac{\mathbf{v}^{\overline{g}}}{\theta^{\overline{\overline{g}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_g^{\overline{wg}}\overset{iwg\to ig}{M}+\mathbf{v}_g^{\overline{gs}}\overset{igs\to ig}{M}\right)$$

$$-\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_s^{\overline{ws}}\overset{iws\to is}{M}+\mathbf{v}_s^{\overline{gs}}\overset{igs\to is}{M}\right)$$

$$+\frac{\mathbf{v}^{\overline{wg}}}{\theta^{\overline{\overline{wg}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_w^{\overline{wg}}\overset{iwg\to iw}{M}+\mathbf{v}_g^{\overline{wg}}\overset{iwg\to ig}{M}-\mathbf{v}_{wg}^{\overline{wgs}}\overset{iwgs\to iwg}{M}\right)$$

$$+\frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_w^{\overline{ws}}\overset{iws\to iw}{M}+\mathbf{v}_s^{\overline{ws}}\overset{iws\to is}{M}-\mathbf{v}_{ws}^{\overline{wgs}}\overset{iwgs\to iws}{M}\right)$$

$$+\frac{\mathbf{v}^{\overline{gs}}}{\theta^{\overline{\overline{gs}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_g^{\overline{gs}}\overset{igs\to ig}{M}+\mathbf{v}_s^{\overline{gs}}\overset{igs\to is}{M}-\mathbf{v}_{gs}^{\overline{wgs}}\overset{iwgs\to igs}{M}\right)$$

$$+\frac{\mathbf{v}^{\overline{wgs}}}{\theta^{\overline{\overline{wgs}}}}\cdot\sum_{i\in\mathcal{I}_s}\left(\mathbf{v}_{wg}^{\overline{wgs}}\overset{iwgs\to iwg}{M}+\mathbf{v}_{ws}^{\overline{wgs}}\overset{iwgs\to iws}{M}+\mathbf{v}_{gs}^{\overline{wgs}}\overset{iwgs\to igs}{M}\right)$$

$$-\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{w}}}}\left(K_E^{\overline{\overline{w}}}+\mu^{\overline{iw}}+\psi^{\overline{iw}}-\frac{\mathbf{v}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}}}{2}\right)\left(\overset{iwg\to iw}{M}+\overset{iws\to iw}{M}\right)$$

$$-\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{g}}}}\left(K_E^{\overline{\overline{g}}}+\mu^{\overline{ig}}+\psi^{\overline{ig}}-\frac{\mathbf{v}^{\overline{g}}\cdot\mathbf{v}^{\overline{g}}}{2}\right)\left(\overset{iwg\to ig}{M}+\overset{igs\to ig}{M}\right)$$

$$-\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{s}}}}\left(K_E^{\overline{\overline{s}}}+\mu^{\overline{is}}+\psi^{\overline{is}}-\frac{\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2}\right)\left(\overset{iws\to is}{M}+\overset{igs\to is}{M}\right)$$

$$+\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{wg}}}}\left(K_E^{\overline{\overline{wg}}}+\mu^{\overline{iwg}}+\psi^{\overline{iwg}}-\frac{\mathbf{v}^{\overline{wg}}\cdot\mathbf{v}^{\overline{wg}}}{2}\right)\left(\overset{iwg\to iw}{M}+\overset{iwg\to ig}{M}-\overset{iwgs\to iwg}{M}\right)$$

$$+ \sum_{i \in \mathfrak{I}_s} \frac{1}{\theta^{\overline{\overline{ws}}}} \left(K_E^{\overline{\overline{ws}}} + \mu^{\overline{iws}} + \psi^{\overline{iws}} - \frac{\mathbf{v}^{\overline{ws}} \cdot \mathbf{v}^{\overline{ws}}}{2} \right) \left(\overset{iws \to iw}{M} + \overset{iws \to is}{M} - \overset{iwgs \to iws}{M} \right)$$

$$+ \sum_{i \in \mathfrak{I}_s} \frac{1}{\theta^{\overline{\overline{gs}}}} \left(K_E^{\overline{\overline{gs}}} + \mu^{\overline{igs}} + \psi^{\overline{igs}} - \frac{\mathbf{v}^{\overline{gs}} \cdot \mathbf{v}^{\overline{gs}}}{2} \right) \left(\overset{igs \to ig}{M} + \overset{igs \to is}{M} - \overset{iwgs \to igs}{M} \right)$$

$$+ \sum_{i \in \mathfrak{I}_s} \frac{1}{\theta^{\overline{\overline{wgs}}}} \left(K_E^{\overline{\overline{wgs}}} + \mu^{\overline{iwgs}} + \psi^{\overline{iwgs}} - \frac{\mathbf{v}^{\overline{wgs}} \cdot \mathbf{v}^{\overline{wgs}}}{2} \right)$$

$$\times \left(\overset{iwgs \to iwg}{M} + \overset{iwgs \to iws}{M} + \overset{iwgs \to igs}{M} \right).$$

Substituting for the total energy

$$(B.273) \qquad E_{T\kappa}^{\overline{\overline{\iota}}} = E_{\kappa}^{\overline{\overline{\iota}}} + \epsilon^{\kappa} \rho_{\kappa}^{\iota} \left(\frac{\mathbf{v}_{\kappa}^{\overline{\iota}} \cdot \mathbf{v}_{\kappa}^{\overline{\iota}}}{2} + K_{E\kappa}^{\overline{\overline{\iota}}} + \psi_{\kappa}^{\overline{\iota}} \right)$$

and regrouping, Eq. (B.272) becomes

$$(B.274) \quad M = \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \left(\frac{E_w^{\overline{\overline{wg}}}}{\epsilon^w \rho_w^{wg}} + K_{Ew}^{\overline{\overline{wg}}} + \psi_w^{\overline{wg}} + \frac{\mathbf{v}_w^{\overline{wg}} \cdot \mathbf{v}_w^{\overline{wg}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iwg \to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \left(\frac{E_w^{\overline{\overline{ws}}}}{\epsilon^w \rho_w^{ws}} + K_{Ew}^{\overline{\overline{ws}}} + \psi_w^{\overline{ws}} + \frac{\mathbf{v}_w^{\overline{ws}} \cdot \mathbf{v}_w^{\overline{ws}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iws \to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \left(\frac{E_g^{\overline{\overline{wg}}}}{\epsilon^g \rho_g^{wg}} + K_{Eg}^{\overline{\overline{wg}}} + \psi_g^{\overline{wg}} + \frac{\mathbf{v}_g^{\overline{wg}} \cdot \mathbf{v}_g^{\overline{wg}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iwg \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \left(\frac{E_g^{\overline{\overline{gs}}}}{\epsilon^g \rho_g^{gs}} + K_{Eg}^{\overline{\overline{gs}}} + \psi_g^{\overline{gs}} + \frac{\mathbf{v}_g^{\overline{gs}} \cdot \mathbf{v}_g^{\overline{gs}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{igs \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \left(\frac{E_s^{\overline{\overline{ws}}}}{\epsilon^s \rho_s^{ws}} + K_{Es}^{\overline{\overline{ws}}} + \psi_s^{\overline{ws}} + \frac{\mathbf{v}_s^{\overline{ws}} \cdot \mathbf{v}_s^{\overline{ws}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iws \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \left(\frac{E_s^{\overline{\overline{gs}}}}{\epsilon^s \rho_s^{gs}} + K_{Es}^{\overline{\overline{gs}}} + \psi_s^{\overline{gs}} + \frac{\mathbf{v}_s^{\overline{gs}} \cdot \mathbf{v}_s^{\overline{gs}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{igs \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{wg}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\frac{E_{wg}^{\overline{\overline{wgs}}}}{\epsilon^{wg} \rho_{wg}^{wgs}} + K_{Ewg}^{\overline{\overline{wgs}}} + \psi_{wg}^{\overline{wgs}} + \frac{\mathbf{v}_{wg}^{\overline{wgs}} \cdot \mathbf{v}_{wg}^{\overline{wgs}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iwgs \to iwg}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\frac{E_{ws}^{\overline{\overline{wgs}}}}{\epsilon^{ws} \rho_{ws}^{wgs}} + K_{Ews}^{\overline{\overline{wgs}}} + \psi_{ws}^{\overline{wgs}} + \frac{\mathbf{v}_{ws}^{\overline{wgs}} \cdot \mathbf{v}_{ws}^{\overline{wgs}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iwgs \to iws}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{gs}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left(\frac{E_{gs}^{\overline{\overline{wgs}}}}{\epsilon^{gs} \rho_{gs}^{wgs}} + K_{Egs}^{\overline{\overline{wgs}}} + \psi_{gs}^{\overline{wgs}} + \frac{\mathbf{v}_{gs}^{\overline{wgs}} \cdot \mathbf{v}_{gs}^{\overline{wgs}}}{2} \right) \sum_{i \in \mathfrak{I}_s} \overset{iwgs \to igs}{M}$$

$$- \frac{\mathbf{v}^{\overline{w}}}{\theta^{\overline{\overline{w}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_w^{\overline{wg}} \overset{iwg \to iw}{M} + \mathbf{v}_w^{\overline{ws}} \overset{iws \to iw}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{g}}}{\theta^{\overline{\overline{g}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_g^{\overline{wg}} \overset{iwg \to ig}{M} + \mathbf{v}_g^{\overline{gs}} \overset{igs \to ig}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_s^{\overline{ws}} \overset{iws \to is}{M} + \mathbf{v}_s^{\overline{gs}} \overset{igs \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{wg}}}{\theta^{\overline{\overline{wg}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_w^{\overline{wg}} \overset{iwg \to iw}{M} + \mathbf{v}_g^{\overline{wg}} \overset{iwg \to ig}{M} - \mathbf{v}_{wg}^{\overline{wgs}} \overset{iwgs \to iwg}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_w^{\overline{ws}} \overset{iws \to iw}{M} + \mathbf{v}_s^{\overline{ws}} \overset{iws \to is}{M} - \mathbf{v}_{ws}^{\overline{wgs}} \overset{iwgs \to iws}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{gs}}}{\theta^{\overline{\overline{gs}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_g^{\overline{gs}} \overset{igs \to ig}{M} + \mathbf{v}_s^{\overline{gs}} \overset{igs \to is}{M} - \mathbf{v}_{gs}^{\overline{wgs}} \overset{iwgs \to igs}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{wgs}}}{\theta^{\overline{\overline{wgs}}}} \cdot \sum_{i \in \mathfrak{I}_s} \left(\mathbf{v}_{wg}^{\overline{wgs}} \overset{iwgs \to iwg}{M} + \mathbf{v}_{ws}^{\overline{wgs}} \overset{iwgs \to iws}{M} + \mathbf{v}_{gs}^{\overline{wgs}} \overset{iwgs \to igs}{M} \right)$$

$$- \sum_{i \in \mathfrak{I}_s} \left[\frac{1}{\theta^{\overline{\overline{w}}}} \left(K_E^{\overline{\overline{w}}} + \mu^{\overline{iw}} + \psi^{\overline{iw}} - \frac{\mathbf{v}^{\overline{w}} \cdot \mathbf{v}^{\overline{w}}}{2} \right) \right.$$

$$\left. - \frac{1}{\theta^{\overline{\overline{wg}}}} \left(K_E^{\overline{\overline{wg}}} + \mu^{\overline{iwg}} + \psi^{\overline{iwg}} - \frac{\mathbf{v}^{\overline{wg}} \cdot \mathbf{v}^{\overline{wg}}}{2} \right) \right] \overset{iwg \to iw}{M}$$

$$- \sum_{i \in \mathfrak{I}_s} \left[\frac{1}{\theta^{\overline{\overline{w}}}} \left(K_E^{\overline{\overline{w}}} + \mu^{\overline{iw}} + \psi^{\overline{iw}} - \frac{\mathbf{v}^{\overline{w}} \cdot \mathbf{v}^{\overline{w}}}{2} \right) \right.$$

$$\left. - \frac{1}{\theta^{\overline{\overline{ws}}}} \left(K_E^{\overline{\overline{ws}}} + \mu^{\overline{iws}} + \psi^{\overline{iws}} - \frac{\mathbf{v}^{\overline{ws}} \cdot \mathbf{v}^{\overline{ws}}}{2} \right) \right] \overset{iws \to iw}{M}$$

$$- \sum_{i \in \mathfrak{I}_s} \left[\frac{1}{\theta^{\overline{\overline{g}}}} \left(K_E^{\overline{\overline{g}}} + \mu^{\overline{ig}} + \psi^{\overline{ig}} - \frac{\mathbf{v}^{\overline{g}} \cdot \mathbf{v}^{\overline{g}}}{2} \right) \right.$$

$$\left. - \frac{1}{\theta^{\overline{\overline{wg}}}} \left(K_E^{\overline{\overline{wg}}} + \mu^{\overline{iwg}} + \psi^{\overline{iwg}} - \frac{\mathbf{v}^{\overline{wg}} \cdot \mathbf{v}^{\overline{wg}}}{2} \right) \right] \overset{iwg \to ig}{M}$$

$$-\sum_{i\in\mathcal{I}_s}\left[\frac{1}{\theta^{\overline{\overline{g}}}}\left(K_E^{\overline{\overline{g}}}+\mu^{\overline{ig}}+\psi^{\overline{ig}}-\frac{\mathbf{v}^{\overline{g}}\boldsymbol{\cdot}\mathbf{v}^{\overline{g}}}{2}\right)\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{gs}}}}\left(K_E^{\overline{\overline{gs}}}+\mu^{\overline{igs}}+\psi^{\overline{igs}}-\frac{\mathbf{v}^{\overline{gs}}\boldsymbol{\cdot}\mathbf{v}^{\overline{gs}}}{2}\right)\right]\overset{igs\to ig}{M}$$

$$-\sum_{i\in\mathcal{I}_s}\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left(K_E^{\overline{\overline{s}}}+\mu^{\overline{is}}+\psi^{\overline{is}}-\frac{\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2}\right)\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(K_E^{\overline{\overline{ws}}}+\mu^{\overline{iws}}+\psi^{\overline{iws}}-\frac{\mathbf{v}^{\overline{ws}}\boldsymbol{\cdot}\mathbf{v}^{\overline{ws}}}{2}\right)\right]\overset{iws\to is}{M}$$

$$-\sum_{i\in\mathcal{I}_s}\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left(K_E^{\overline{\overline{s}}}+\mu^{\overline{is}}+\psi^{\overline{is}}-\frac{\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2}\right)\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{gs}}}}\left(K_E^{\overline{\overline{gs}}}+\mu^{\overline{igs}}+\psi^{\overline{igs}}-\frac{\mathbf{v}^{\overline{gs}}\boldsymbol{\cdot}\mathbf{v}^{\overline{gs}}}{2}\right)\right]\overset{igs\to is}{M}$$

$$-\sum_{i\in\mathcal{I}_s}\left[\frac{1}{\theta^{\overline{\overline{wg}}}}\left(K_E^{\overline{\overline{wg}}}+\mu^{\overline{iwg}}+\psi^{\overline{iwg}}-\frac{\mathbf{v}^{\overline{wg}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wg}}}{2}\right)\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}-\frac{\mathbf{v}^{\overline{wgs}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wgs}}}{2}\right)\right]\overset{iwgs\to iwg}{M}$$

$$-\sum_{i\in\mathcal{I}_s}\left[\frac{1}{\theta^{\overline{\overline{ws}}}}\left(K_E^{\overline{\overline{ws}}}+\mu^{\overline{iws}}+\psi^{\overline{iws}}-\frac{\mathbf{v}^{\overline{ws}}\boldsymbol{\cdot}\mathbf{v}^{\overline{ws}}}{2}\right)\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}-\frac{\mathbf{v}^{\overline{wgs}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wgs}}}{2}\right)\right]\overset{iwgs\to iws}{M}$$

$$-\sum_{i\in\mathcal{I}_s}\left[\frac{1}{\theta^{\overline{\overline{gs}}}}\left(K_E^{\overline{\overline{gs}}}+\mu^{\overline{igs}}+\psi^{\overline{igs}}-\frac{\mathbf{v}^{\overline{gs}}\boldsymbol{\cdot}\mathbf{v}^{\overline{gs}}}{2}\right)\right.$$

$$\left.-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}-\frac{\mathbf{v}^{\overline{wgs}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wgs}}}{2}\right)\right]\overset{iwgs\to igs}{M}.$$

Simplifying terms involving kinetic energy and gravitational potential, and grouping terms involving products with velocities gives

$$(\text{B.275})\quad M=\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{wg}}}}\right)\sum_{i\in\mathcal{I}_s}\left(\frac{E_w^{\overline{\overline{wg}}}}{\epsilon^w\rho_w^{\overline{wg}}}-\mu_{iw}^{\overline{wg}}\right)\overset{iwg\to iw}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\sum_{i\in\mathcal{I}_s}\left(\frac{E_w^{\overline{\overline{ws}}}}{\epsilon^w\rho_w^{\overline{ws}}}-\mu_{iw}^{\overline{ws}}\right)\overset{iws\to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_g^{\overline{\overline{wg}}}}{\epsilon^g \rho_g^{\overline{wg}}} - \mu_{ig}^{\overline{wg}} \right) \overset{iwg \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_g^{\overline{\overline{gs}}}}{\epsilon^g \rho_g^{gs}} - \mu_{ig}^{\overline{gs}} \right) \overset{igs \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_s^{\overline{\overline{ws}}}}{\epsilon^s \rho_s^{ws}} - \mu_{is}^{\overline{ws}} \right) \overset{iws \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_s^{\overline{\overline{gs}}}}{\epsilon^s \rho_s^{gs}} - \mu_{is}^{\overline{gs}} \right) \overset{igs \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{wg}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_{wg}^{\overline{\overline{wgs}}}}{\epsilon^{wg} \rho_{wg}^{wgs}} - \mu_{iwg}^{\overline{wgs}} \right) \overset{iwgs \to iwg}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_{ws}^{\overline{\overline{wgs}}}}{\epsilon^{ws} \rho_{ws}^{wgs}} - \mu_{iws}^{\overline{wgs}} \right) \overset{iwgs \to iws}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{gs}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathfrak{I}_s} \quad \left(\frac{E_{gs}^{\overline{\overline{wgs}}}}{\epsilon^{gs} \rho_{gs}^{wgs}} - \mu_{igs}^{\overline{wgs}} \right) \overset{iwgs \to igs}{M}$$

$$- \frac{\mathbf{v}^{\overline{w}}}{\theta^{\overline{\overline{w}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_w^{\overline{wg}} \overset{iwg \to iw}{M} + \mathbf{v}_w^{\overline{ws}} \overset{iws \to iw}{M} \right) - \frac{\mathbf{v}^{\overline{g}}}{\theta^{\overline{\overline{g}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_g^{\overline{wg}} \overset{iwg \to ig}{M} + \mathbf{v}_g^{\overline{gs}} \overset{igs \to ig}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_s^{\overline{ws}} \overset{iws \to is}{M} + \mathbf{v}_s^{\overline{gs}} \overset{igs \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{wg}}}{\theta^{\overline{\overline{wg}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_w^{\overline{wg}} \overset{iwg \to iw}{M} + \mathbf{v}_g^{\overline{wg}} \overset{iwg \to ig}{M} - \mathbf{v}_{wg}^{\overline{wgs}} \overset{iwgs \to iwg}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{ws}}}{\theta^{\overline{\overline{ws}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_w^{\overline{ws}} \overset{iws \to iw}{M} + \mathbf{v}_s^{\overline{ws}} \overset{iws \to is}{M} - \mathbf{v}_{ws}^{\overline{wgs}} \overset{iwgs \to iws}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{gs}}}{\theta^{\overline{\overline{gs}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_g^{\overline{gs}} \overset{igs \to ig}{M} + \mathbf{v}_s^{\overline{gs}} \overset{igs \to is}{M} - \mathbf{v}_{gs}^{\overline{wgs}} \overset{iwgs \to igs}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{wgs}}}{\theta^{\overline{\overline{wgs}}}} \cdot \sum_{i \in \mathfrak{I}_s} \quad \left(\mathbf{v}_{wg}^{\overline{wgs}} \overset{iwgs \to iwg}{M} + \mathbf{v}_{ws}^{\overline{wgs}} \overset{iwgs \to iws}{M} + \mathbf{v}_{gs}^{\overline{wgs}} \overset{iwgs \to igs}{M} \right)$$

$$- \frac{1}{\theta^{\overline{\overline{w}}}} \sum_{i \in \mathfrak{I}_s} \quad \left[\left(K_E^{\overline{\overline{w}}} + \mu^{\overline{iw}} + \psi^{\overline{iw}} \right) - \left(K_{Ew}^{\overline{\overline{wg}}} + \mu_{iw}^{\overline{wg}} + \psi_w^{\overline{wg}} \right) \right] \overset{iwg \to iw}{M}$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{wg}}}+\mu^{\overline{iwg}}+\psi^{\overline{iwg}}\right)-\left(K_{Ew}^{\overline{\overline{wg}}}+\mu_{iw}^{\overline{wg}}+\psi_w^{\overline{wg}}\right)\right]{}^{iwg\to iw}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{w}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{w}}}+\mu^{\overline{iw}}+\psi^{\overline{iw}}\right)-\left(K_{Ew}^{\overline{\overline{ws}}}+\mu_{iw}^{\overline{ws}}+\psi_w^{\overline{ws}}\right)\right]{}^{iws\to iw}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{ws}}}+\mu^{\overline{iws}}+\psi^{\overline{iws}}\right)-\left(K_{Ew}^{\overline{\overline{ws}}}+\mu_{iw}^{\overline{ws}}+\psi_w^{\overline{ws}}\right)\right]{}^{iws\to iw}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{g}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{g}}}+\mu^{\overline{ig}}+\psi^{\overline{ig}}\right)-\left(K_{Eg}^{\overline{\overline{wg}}}+\mu_{ig}^{\overline{wg}}+\psi_g^{\overline{wg}}\right)\right]{}^{iwg\to ig}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{wg}}}+\mu^{\overline{iwg}}+\psi^{\overline{iwg}}\right)-\left(K_{Eg}^{\overline{\overline{wg}}}+\mu_{ig}^{\overline{wg}}+\psi_g^{\overline{wg}}\right)\right]{}^{iwg\to ig}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{g}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{g}}}+\mu^{\overline{ig}}+\psi^{\overline{ig}}\right)-\left(K_{Eg}^{\overline{\overline{gs}}}+\mu_{ig}^{\overline{gs}}+\psi_g^{\overline{gs}}\right)\right]{}^{igs\to ig}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{gs}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{gs}}}+\mu^{\overline{igs}}+\psi^{\overline{igs}}\right)-\left(K_{Eg}^{\overline{\overline{gs}}}+\mu_{ig}^{\overline{gs}}+\psi_g^{\overline{gs}}\right)\right]{}^{igs\to ig}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{s}}}+\mu^{\overline{is}}+\psi^{\overline{is}}\right)-\left(K_{Es}^{\overline{\overline{ws}}}+\mu_{is}^{\overline{ws}}+\psi_s^{\overline{ws}}\right)\right]{}^{iws\to is}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{ws}}}+\mu^{\overline{iws}}+\psi^{\overline{iws}}\right)-\left(K_{Es}^{\overline{\overline{ws}}}+\mu_{is}^{\overline{ws}}+\psi_s^{\overline{ws}}\right)\right]{}^{iws\to is}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{s}}}+\mu^{\overline{is}}+\psi^{\overline{is}}\right)-\left(K_{Es}^{\overline{\overline{gs}}}+\mu_{is}^{\overline{gs}}+\psi_s^{\overline{gs}}\right)\right]{}^{igs\to is}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{gs}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{gs}}}+\mu^{\overline{igs}}+\psi^{\overline{igs}}\right)-\left(K_{Es}^{\overline{\overline{gs}}}+\mu_{is}^{\overline{gs}}+\psi_s^{\overline{gs}}\right)\right]{}^{igs\to is}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{wg}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{wg}}}+\mu^{\overline{iwg}}+\psi^{\overline{iwg}}\right)-\left(K_{Ewg}^{\overline{\overline{wgs}}}+\mu_{iwg}^{\overline{wgs}}+\psi_{wg}^{\overline{wgs}}\right)\right]{}^{iwgs\to iwg}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)-\left(K_{Ewg}^{\overline{\overline{wgs}}}+\mu_{iwg}^{\overline{wgs}}+\psi_{wg}^{\overline{wgs}}\right)\right]{}^{iwgs\to iwg}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{ws}}}+\mu^{\overline{iws}}+\psi^{\overline{iws}}\right)-\left(K_{Ews}^{\overline{\overline{wgs}}}+\mu_{iws}^{\overline{wgs}}+\psi_{ws}^{\overline{wgs}}\right)\right]{}^{iwgs\to iws}\!M$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\sum_{i\in\mathfrak{I}_s}\ \left[\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)-\left(K_{Ews}^{\overline{\overline{wgs}}}+\mu_{iws}^{\overline{wgs}}+\psi_{ws}^{\overline{wgs}}\right)\right]{}^{iwgs\to iws}\!M$$

$$-\frac{1}{\theta^{\overline{\overline{gs}}}}\sum_{i\in\mathcal{I}_s}\left[\left(K_E^{\overline{\overline{gs}}}+\mu^{\overline{igs}}+\psi^{\overline{igs}}\right)-\left(K_{Egs}^{\overline{wgs}}+\mu_{igs}^{\overline{wgs}}+\psi_{gs}^{\overline{wgs}}\right)\right]\overset{iwgs\to igs}{M}$$

$$+\frac{1}{\theta^{\overline{wgs}}}\sum_{i\in\mathcal{I}_s}\left[\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)-\left(K_{Egs}^{\overline{wgs}}+\mu_{igs}^{\overline{wgs}}+\psi_{gs}^{\overline{wgs}}\right)\right]\overset{iwgs\to igs}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{wg}}}}\right)\frac{\mathbf{v}_w^{\overline{wg}}\cdot\mathbf{v}_w^{\overline{wg}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iwg\to iw}{M}+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\frac{\mathbf{v}_w^{\overline{ws}}\cdot\mathbf{v}_w^{\overline{ws}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iws\to iw}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{g}}}}-\frac{1}{\theta^{\overline{\overline{wg}}}}\right)\frac{\mathbf{v}_g^{\overline{wg}}\cdot\mathbf{v}_g^{\overline{wg}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iwg\to ig}{M}+\left(\frac{1}{\theta^{\overline{\overline{g}}}}-\frac{1}{\theta^{\overline{\overline{gs}}}}\right)\frac{\mathbf{v}_g^{\overline{gs}}\cdot\mathbf{v}_g^{\overline{gs}}}{2}\sum_{i\in\mathcal{I}_s}\overset{igs\to ig}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\frac{\mathbf{v}_s^{\overline{ws}}\cdot\mathbf{v}_s^{\overline{ws}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iws\to is}{M}+\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{gs}}}}\right)\frac{\mathbf{v}_s^{\overline{gs}}\cdot\mathbf{v}_s^{\overline{gs}}}{2}\sum_{i\in\mathcal{I}_s}\overset{igs\to is}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{wg}}}}-\frac{1}{\theta^{\overline{wgs}}}\right)\frac{\mathbf{v}_{wg}^{\overline{wgs}}\cdot\mathbf{v}_{wg}^{\overline{wgs}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iwgs\to iwg}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{ws}}}}-\frac{1}{\theta^{\overline{wgs}}}\right)\frac{\mathbf{v}_{ws}^{\overline{wgs}}\cdot\mathbf{v}_{ws}^{\overline{wgs}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iwgs\to iws}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{gs}}}}-\frac{1}{\theta^{\overline{wgs}}}\right)\frac{\mathbf{v}_{gs}^{\overline{wgs}}\cdot\mathbf{v}_{gs}^{\overline{wgs}}}{2}\sum_{i\in\mathcal{I}_s}\overset{iwgs\to igs}{M}$$

$$+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}}}{2\theta^{\overline{\overline{w}}}}-\frac{\mathbf{v}^{\overline{wg}}\cdot\mathbf{v}^{\overline{wg}}}{2\theta^{\overline{\overline{wg}}}}\right)\overset{iwg\to iw}{M}+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{g}}\cdot\mathbf{v}^{\overline{g}}}{2\theta^{\overline{\overline{g}}}}-\frac{\mathbf{v}^{\overline{wg}}\cdot\mathbf{v}^{\overline{wg}}}{2\theta^{\overline{\overline{wg}}}}\right)\overset{iwg\to ig}{M}$$

$$+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}}}{2\theta^{\overline{\overline{w}}}}-\frac{\mathbf{v}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}}{2\theta^{\overline{\overline{ws}}}}\right)\overset{iws\to iw}{M}+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{s}}}}-\frac{\mathbf{v}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}}{2\theta^{\overline{\overline{ws}}}}\right)\overset{iws\to is}{M}$$

$$+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{g}}\cdot\mathbf{v}^{\overline{g}}}{2\theta^{\overline{\overline{g}}}}-\frac{\mathbf{v}^{\overline{gs}}\cdot\mathbf{v}^{\overline{gs}}}{2\theta^{\overline{\overline{gs}}}}\right)\overset{igs\to ig}{M}+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{s}}}}-\frac{\mathbf{v}^{\overline{gs}}\cdot\mathbf{v}^{\overline{gs}}}{2\theta^{\overline{\overline{gs}}}}\right)\overset{igs\to is}{M}$$

$$+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{wg}}\cdot\mathbf{v}^{\overline{wg}}}{2\theta^{\overline{\overline{wg}}}}-\frac{\mathbf{v}^{\overline{wgs}}\cdot\mathbf{v}^{\overline{wgs}}}{2\theta^{\overline{\overline{wgs}}}}\right)\overset{iwgs\to iwg}{M}$$

$$+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}}{2\theta^{\overline{\overline{ws}}}}-\frac{\mathbf{v}^{\overline{wgs}}\cdot\mathbf{v}^{\overline{wgs}}}{2\theta^{\overline{\overline{wgs}}}}\right)\overset{iwgs\to iws}{M}$$

$$+\sum_{i\in\mathcal{I}_s}\left(\frac{\mathbf{v}^{\overline{gs}}\cdot\mathbf{v}^{\overline{gs}}}{2\theta^{\overline{\overline{gs}}}}-\frac{\mathbf{v}^{\overline{wgs}}\cdot\mathbf{v}^{\overline{wgs}}}{2\theta^{\overline{\overline{wgs}}}}\right)\overset{iwgs\to igs}{M},$$

which can be written in objective form and simplified to give

$$(B.276) \quad M = \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa} - \mu_{i\iota}^{\overline{\kappa}} \right) \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{wgs}}}}{\epsilon^\iota \rho_\iota^{wgs}} - \mu_{i\iota}^{\overline{wgs}} \right) \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \frac{1}{\theta^{\overline{\overline{\kappa}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\overline{\kappa}}} + \mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}} \right) - \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{wgs}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\overline{wgs}}} + \mu^{\overline{iwgs}} + \psi^{\overline{iwgs}} \right) - \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\overline{\kappa}}} + \mu_{i\iota}^{\overline{\kappa}} + \psi_\iota^{\overline{\kappa}} \right) - \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\overline{wgs}}} + \mu_{i\iota}^{\overline{wgs}} + \psi_\iota^{\overline{wgs}} \right) \right.$$

$$\left. - \left(K_E^{\overline{\overline{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$+ \frac{\mathbf{v}^{\overline{wg,s}}}{\theta^{\overline{\overline{wg}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \overset{iwg \to iw}{M} + \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \overset{iwg \to ig}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{ws,s}}}{\theta^{\overline{\overline{ws}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \overset{iws \to iw}{M} + \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \overset{iws \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{gs,s}}}{\theta^{\overline{\overline{gs}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) \overset{igs \to ig}{M} + \left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) \overset{igs \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{wgs,s}}}{\theta^{\overline{\overline{wgs}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \overset{iwgs \to iwg}{M} + \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \overset{iwgs \to iws}{M} \right.$$

$$\left. + \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \overset{iwgs \to igs}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{wg}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \overset{iwg \to iw}{M} + \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \overset{iwg \to ig}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{ws}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \overset{iws \to iw}{M} + \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \overset{iws \to is}{M} \right)$$

286

$$+ \frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{gs}}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) \overset{igs \to ig}{M} + \left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) \overset{igs \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{wgs}}} \cdot \sum_{i \in \mathcal{I}_s} \left(\left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \overset{iwgs \to iwg}{M} + \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \overset{iwgs \to iws}{M} \right.$$

$$\left. + \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \overset{iwgs \to igs}{M} \right)$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{wg}}} \right) \left(\frac{\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right)}{2} \right.$$

$$\left. + \frac{2 \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2} \right) \sum_{i \in \mathcal{I}_s} \overset{iwg \to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \left(\frac{\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)}{2} \right.$$

$$\left. + \frac{2 \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2} \right) \sum_{i \in \mathcal{I}_s} \overset{iws \to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{wg}}} \right) \left(\frac{\left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right)}{2} \right.$$

$$\left. + \frac{2 \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2} \right) \sum_{i \in \mathcal{I}_s} \overset{iwg \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{gs}}} \right) \left(\frac{\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right)}{2} \right.$$

$$\left. + \frac{2 \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2} \right) \sum_{i \in \mathcal{I}_s} \overset{igs \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \left(\frac{\left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)}{2} \right.$$

$$\left. + \frac{2 \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2} \right) \sum_{i \in \mathcal{I}_s} \overset{iws \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}}\right) \left(\frac{\left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right)}{2}\right.$$

$$\left. + \frac{2\left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2}\right) \sum_{i \in \mathfrak{I}_s} \overset{igs \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{wg}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}}\right) \left(\frac{\left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right)}{2}\right.$$

$$\left. + \frac{2\left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2}\right) \sum_{i \in \mathfrak{I}_s} \overset{iwgs \to iwg}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}}\right) \left(\frac{\left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right)}{2}\right.$$

$$\left. + \frac{2\left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2}\right) \sum_{i \in \mathfrak{I}_s} \overset{iwgs \to iws}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{gs}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}}\right) \left(\frac{\left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right)}{2}\right.$$

$$\left. + \frac{2\left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{v}^{\overline{s}} - \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2}\right) \sum_{i \in \mathfrak{I}_s} \overset{iwgs \to igs}{M}$$

$$- \left(\frac{\mathbf{v}^{\overline{w},\overline{s}} \cdot \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right) + \mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{s}} + \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{w}}}}\right) \sum_{i \in \mathfrak{I}_s} \overset{iwg \to iw}{M}$$

$$+ \left(\frac{\mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{w},\overline{s}} + 2\mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{s}} + \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{w}}}}\right) \sum_{i \in \mathfrak{I}_s} \overset{iwg \to iw}{M}$$

$$- \left(\frac{\mathbf{v}^{\overline{wg},\overline{s}} \cdot \mathbf{v}^{\overline{wg},\overline{s}} + \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{wg}}}}\right) \sum_{i \in \mathfrak{I}_s} \overset{iwg \to iw}{M}$$

$$- \left(\frac{\mathbf{v}^{\overline{w},\overline{s}} \cdot \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) + \mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{s}} + \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{w}}}}\right) \sum_{i \in \mathfrak{I}_s} \overset{iws \to iw}{M}$$

$$+ \left(\frac{\mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{w},\overline{s}} + 2\mathbf{v}^{\overline{w},\overline{s}} \cdot \mathbf{v}^{\overline{s}} + \mathbf{v}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{w}}}}\right) \sum_{i \in \mathfrak{I}_s} \overset{iws \to iw}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{ws},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{ws},\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{ws}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iws\to iw}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\left(\mathbf{v}_g^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)+\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}+\left(\mathbf{v}_g^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{g}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwg\to ig}{M}$$

$$+\left(\frac{\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{g},\overline{s}}+2\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{g}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwg\to ig}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{wg},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wg},\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{wg}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwg\to ig}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\left(\mathbf{v}_g^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)+\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}+\left(\mathbf{v}_g^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{g}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{igs\to ig}{M}$$

$$+\left(\frac{\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{g},\overline{s}}+2\mathbf{v}^{\overline{g},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{g}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{igs\to ig}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{gs},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{gs},\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{gs}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{igs\to ig}{M}$$

$$-\frac{\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{I}_s}\overset{iws\to is}{M}+\frac{\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{I}_s}\overset{iws\to is}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{ws},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{ws},\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{ws}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iws\to is}{M}$$

$$-\frac{\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)}{\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{I}_s}\overset{igs\to is}{M}+\frac{\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{I}_s}\overset{igs\to is}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{gs},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{gs},\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{gs}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{igs\to is}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{wg},\overline{s}}\boldsymbol{\cdot}\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)+\mathbf{v}^{\overline{wg},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}+\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{wg}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\to iwg}{M}$$

$$+\left(\frac{\mathbf{v}^{\overline{wg},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wg},\overline{s}}+2\mathbf{v}^{\overline{wg},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{wg}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\to iwg}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{wgs},\overline{s}}+\mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{wgs}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\to iwg}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{ws},\overline{s}}\cdot\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)+\mathbf{v}^{\overline{ws},\overline{s}}\cdot\mathbf{v}^{\overline{s}}+\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{v}^{\overline{s}}}{\theta^{\overline{ws}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\rightarrow iws}{M}$$

$$+\left(\frac{\mathbf{v}^{\overline{ws},\overline{s}}\cdot\mathbf{v}^{\overline{ws},\overline{s}}+2\mathbf{v}^{\overline{ws},\overline{s}}\cdot\mathbf{v}^{\overline{s}}+\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{ws}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\rightarrow iws}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\cdot\mathbf{v}^{\overline{wgs},\overline{s}}+\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{wgs}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\rightarrow iws}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{gs},\overline{s}}\cdot\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)+\mathbf{v}^{\overline{gs},\overline{s}}\cdot\mathbf{v}^{\overline{s}}+\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{v}^{\overline{s}}}{\theta^{\overline{gs}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\rightarrow igs}{M}$$

$$+\left(\frac{\mathbf{v}^{\overline{gs},\overline{s}}\cdot\mathbf{v}^{\overline{gs},\overline{s}}+2\mathbf{v}^{\overline{gs},\overline{s}}\cdot\mathbf{v}^{\overline{s}}+\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{gs}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\rightarrow igs}{M}$$

$$-\left(\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\cdot\mathbf{v}^{\overline{wgs},\overline{s}}+\mathbf{v}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}}}{2\theta^{\overline{\overline{wgs}}}}\right)\sum_{i\in\mathfrak{I}_s}\overset{iwgs\rightarrow igs}{M}.$$

Noting that products with solid-phase velocities squared cancel out and canceling other products of solid-phase velocities yields

$$(B.277)\quad M=\sum_{\iota\in\mathfrak{I}_\mathrm{P}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\sum_{i\in\mathfrak{I}_s}\left(\frac{E_\iota^{\overline{\overline{\kappa}}}}{\epsilon^\iota\rho_\iota^\kappa}-\mu_{i\iota}^{\overline{\kappa}}\right)\overset{i\kappa\rightarrow i\iota}{M}$$

$$+\sum_{\iota\in\mathfrak{I}_\mathrm{I}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)\sum_{i\in\mathfrak{I}_s}\left(\frac{E_\iota^{\overline{wgs}}}{\epsilon^\iota\rho_\iota^{wgs}}-\mu_{i\iota}^{\overline{wgs}}\right)\overset{iwgs\rightarrow i\iota}{M}$$

$$+\sum_{\iota\in\mathfrak{I}_\mathrm{P}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\frac{1}{\theta^{\overline{\overline{\kappa}}}}\sum_{i\in\mathfrak{I}_s}\left[\left(K_E^{\overline{\overline{\kappa}}}+\mu^{\overline{i\kappa}}+\psi^{\overline{i\kappa}}\right)-\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\right]\overset{i\kappa\rightarrow i\iota}{M}$$

$$+\sum_{\iota\in\mathfrak{I}_\mathrm{I}}\frac{1}{\theta^{\overline{wgs}}}\sum_{i\in\mathfrak{I}_s}\left[\left(K_E^{\overline{wgs}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)-\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\right]\overset{iwgs\rightarrow i\iota}{M}$$

$$+\sum_{\iota\in\mathfrak{I}_\mathrm{P}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{C}\iota}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\sum_{i\in\mathfrak{I}_s}\left[\left(K_{E\iota}^{\overline{\kappa}}+\mu_{i\iota}^{\overline{\kappa}}+\psi_\iota^{\overline{\kappa}}\right)-\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\right]\overset{i\kappa\rightarrow i\iota}{M}$$

$$+\sum_{\iota\in\mathfrak{I}_\mathrm{I}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{wgs}}}\right)\sum_{i\in\mathfrak{I}_s}\left[\left(K_{E\iota}^{\overline{wgs}}+\mu_{i\iota}^{\overline{wgs}}+\psi_\iota^{\overline{wgs}}\right)\right.$$

$$\left.-\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\right]\overset{iwgs\rightarrow i\iota}{M}$$

$$+ \frac{\mathbf{v}^{\overline{wg},\overline{s}}}{\theta^{\overline{\overline{wg}}}} \cdot \sum_{i \in \mathbb{J}_s} \left(\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right) \overset{iwg \to iw}{M} + \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right) \overset{iwg \to ig}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{\theta^{\overline{\overline{ws}}}} \cdot \sum_{i \in \mathbb{J}_s} \left(\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \overset{iws \to iw}{M} + \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \overset{iws \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{gs},\overline{s}}}{\theta^{\overline{\overline{gs}}}} \cdot \sum_{i \in \mathbb{J}_s} \left(\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right) \overset{igs \to ig}{M} + \left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right) \overset{igs \to is}{M} \right)$$

$$+ \frac{\mathbf{v}^{\overline{wgs},\overline{s}}}{\theta^{\overline{\overline{wgs}}}} \cdot \sum_{i \in \mathbb{J}_s} \left(\left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \overset{iwgs \to iwg}{M} + \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \overset{iwgs \to iws}{M} \right.$$

$$\left. + \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \overset{iwgs \to igs}{M} \right)$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \frac{\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{iwg \to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{wg}}}} \right) \frac{\left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{iwg \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \frac{\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{iws \to iw}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{g}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \frac{\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{igs \to ig}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) \frac{\left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{iws \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{gs}}}} \right) \frac{\left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_s^{\overline{gs}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{igs \to is}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{wg}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \frac{\left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{iwgs \to iwg}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{ws}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \frac{\left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right)}{2} \sum_{i \in \mathbb{J}_s} \overset{iwgs \to iws}{M}$$

$$+ \left(\frac{1}{\theta^{\overline{\overline{\overline{gs}}}}} - \frac{1}{\theta^{\overline{\overline{\overline{wgs}}}}} \right) \frac{\left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right)}{2} \sum_{i \in \mathcal{I}_S} \overset{iwgs \to igs}{M}$$

$$- \sum_{i \in \mathcal{I}_S} \frac{\mathbf{v}^{\overline{w,\overline{s}}}}{2\theta^{\overline{\overline{w}}}} \cdot \left(\left[2 \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{w,\overline{s}}} \right] \overset{iwg \to iw}{M} \right.$$

$$\left. + \left[2 \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{w,\overline{s}}} \right] \overset{iws \to iw}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{wg,\overline{s}}} \cdot \mathbf{v}^{\overline{wg,\overline{s}}}}{2\theta^{\overline{\overline{wg}}}} \sum_{i \in \mathcal{I}_S} \left(\overset{iwg \to iw}{M} + \overset{iwg \to ig}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{wg,\overline{s}}}}{2\theta^{\overline{\overline{\overline{wg}}}}} \cdot \left[2 \left(\mathbf{v}_{wg}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{wg,\overline{s}}} \right] \sum_{i \in \mathcal{I}_S} \overset{iwgs \to iwg}{M}$$

$$- \sum_{i \in \mathcal{I}_S} \frac{\mathbf{v}^{\overline{g,\overline{s}}}}{2\theta^{\overline{\overline{g}}}} \cdot \left(\left[2 \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{g,\overline{s}}} \right] \overset{iwg \to ig}{M} \right.$$

$$\left. + \left[2 \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{g,\overline{s}}} \right] \overset{igs \to ig}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{ws,\overline{s}}} \cdot \mathbf{v}^{\overline{ws,\overline{s}}}}{2\theta^{\overline{\overline{ws}}}} \sum_{i \in \mathcal{I}_S} \left(\overset{iws \to iw}{M} + \overset{iws \to is}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{ws,\overline{s}}}}{2\theta^{\overline{\overline{\overline{ws}}}}} \cdot \left[2 \left(\mathbf{v}_{ws}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{ws,\overline{s}}} \right] \sum_{i \in \mathcal{I}_S} \overset{iwgs \to iws}{M}$$

$$- \frac{\mathbf{v}^{\overline{gs,\overline{s}}} \cdot \mathbf{v}^{\overline{gs,\overline{s}}}}{2\theta^{\overline{\overline{gs}}}} \sum_{i \in \mathcal{I}_S} \left(\overset{igs \to ig}{M} + \overset{igs \to is}{M} \right)$$

$$- \frac{\mathbf{v}^{\overline{gs,\overline{s}}}}{2\theta^{\overline{\overline{\overline{gs}}}}} \cdot \left[2 \left(\mathbf{v}_{gs}^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) - \mathbf{v}^{\overline{gs,\overline{s}}} \right] \sum_{i \in \mathcal{I}_S} \overset{iwgs \to igs}{M}$$

$$- \frac{\mathbf{v}^{\overline{wgs,\overline{s}}} \cdot \mathbf{v}^{\overline{wgs,\overline{s}}}}{2\theta^{\overline{\overline{wgs}}}} \sum_{i \in \mathcal{I}_S} \left(\overset{iwgs \to iwg}{M} + \overset{iwgs \to iws}{M} + \overset{iwgs \to igs}{M} \right).$$

For the collection of mass exchange quantities, the expansion and regrouping of terms leads to

$$\text{(B.278)} \quad M = \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \sum_{i \in \mathcal{I}_S} \left(\frac{E_\iota^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa} - \mu_{i\iota}^{\overline{\kappa}} \right) \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{wgs}}}}{\epsilon^\iota \rho_\iota^{\overline{wgs}}} - \mu_{i\iota}^{\overline{wgs}} \right) \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \frac{1}{\theta^{\overline{\bar{\kappa}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\bar{\kappa}}} + \mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}} \right) - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{wgs}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\overline{wgs}}} + \mu^{\overline{iwgs}} + \psi^{\overline{iwgs}} \right) - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\bar{\kappa}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\bar{\kappa}}} + \mu_{i\iota}^{\overline{\kappa}} + \psi_\iota^{\overline{\kappa}} \right) - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\bar{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\overline{wgs}}} + \mu_{i\iota}^{\overline{wgs}} + \psi_\iota^{\overline{wgs}} \right) \right.$$

$$\left. - \left(K_E^{\overline{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$- \frac{\mathbf{v}^{\overline{w},\overline{s}}}{2\theta^{\overline{\overline{w}}}} \cdot \left[\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{wg}} \right) + \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{w}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iwg \to iw}{M}$$

$$- \frac{\mathbf{v}^{\overline{w},\overline{s}}}{2\theta^{\overline{\overline{w}}}} \cdot \left[\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{ws}} \right) + \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{w}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iws \to iw}{M}$$

$$- \frac{\mathbf{v}^{\overline{g},\overline{s}}}{2\theta^{\overline{\overline{g}}}} \cdot \left[\left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{wg}} \right) + \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{g}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iwg \to ig}{M}$$

$$- \frac{\mathbf{v}^{\overline{g},\overline{s}}}{2\theta^{\overline{\overline{g}}}} \cdot \left[\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{gs}} \right) + \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{g}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{igs \to ig}{M}$$

$$+ \frac{\mathbf{v}^{\overline{wg},\overline{s}}}{2\theta^{\overline{\overline{wg}}}} \cdot \left[\left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{w}} \right) + \left(\mathbf{v}_w^{\overline{wg}} - \mathbf{v}^{\overline{wg}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iwg \to iw}{M}$$

$$+ \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{2\theta^{\overline{\overline{ws}}}} \cdot \left[\left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{w}} \right) + \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{ws}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iws \to iw}{M}$$

$$+ \frac{\mathbf{v}^{\overline{wg},\overline{s}}}{2\theta^{\overline{\overline{wg}}}} \cdot \left[\left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{g}} \right) + \left(\mathbf{v}_g^{\overline{wg}} - \mathbf{v}^{\overline{wg}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iwg \to ig}{M}$$

$$+ \frac{\mathbf{v}^{\overline{gs},\overline{s}}}{2\theta^{\overline{\overline{gs}}}} \cdot \left[\left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{g}} \right) + \left(\mathbf{v}_g^{\overline{gs}} - \mathbf{v}^{\overline{gs}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{igs \to ig}{M}$$

$$+ \frac{\mathbf{v}^{\overline{ws},\overline{s}}}{2\theta^{\overline{\overline{ws}}}} \cdot \left[\left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) + \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{ws}} \right) \right] \sum_{i \in \mathcal{I}_s} \overset{iws \to is}{M}$$

$$+\frac{\mathbf{v}^{\overline{gs},\overline{s}}}{2\theta^{\overline{\overline{gs}}}}\cdot\left[\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)+\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{gs}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{igs\to is}{M}$$

$$-\frac{\mathbf{v}^{\overline{wg},\overline{s}}}{2\theta^{\overline{\overline{wg}}}}\cdot\left[\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)+\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{wg}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{iwgs\to iwg}{M}$$

$$-\frac{\mathbf{v}^{\overline{ws},\overline{s}}}{2\theta^{\overline{\overline{ws}}}}\cdot\left[\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)+\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{ws}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{iwgs\to iws}{M}$$

$$-\frac{\mathbf{v}^{\overline{gs},\overline{s}}}{2\theta^{\overline{\overline{gs}}}}\cdot\left[\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)+\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{gs}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{iwgs\to igs}{M}$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}}{2\theta^{\overline{\overline{wgs}}}}\cdot\left[\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{wg}}\right)+\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{iwgs\to iwg}{M}$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}}{2\theta^{\overline{\overline{wgs}}}}\cdot\left[\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{ws}}\right)+\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{iwgs\to iws}{M}$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}}{2\theta^{\overline{\overline{wgs}}}}\cdot\left[\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{gs}}\right)+\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)\right]\sum_{i\in\mathcal{I}_s}\overset{iwgs\to igs}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{wg}}}}\right)\left(\frac{\left(\mathbf{v}_w^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_w^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)}{2}-\frac{\mathbf{v}^{\overline{w},\overline{s}}\cdot\mathbf{v}^{\overline{wg},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_s}\overset{iwg\to iw}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\left(\frac{\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}-\frac{\mathbf{v}^{\overline{w},\overline{s}}\cdot\mathbf{v}^{\overline{ws},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_s}\overset{iws\to iw}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{g}}}}-\frac{1}{\theta^{\overline{\overline{wg}}}}\right)\left(\frac{\left(\mathbf{v}_g^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_g^{\overline{wg}}-\mathbf{v}^{\overline{s}}\right)}{2}-\frac{\mathbf{v}^{\overline{g},\overline{s}}\cdot\mathbf{v}^{\overline{wg},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_s}\overset{iwg\to ig}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{g}}}}-\frac{1}{\theta^{\overline{\overline{gs}}}}\right)\left(\frac{\left(\mathbf{v}_g^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_g^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)}{2}-\frac{\mathbf{v}^{\overline{g},\overline{s}}\cdot\mathbf{v}^{\overline{gs},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_s}\overset{igs\to ig}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\frac{\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{iws\to is}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{gs}}}}\right)\frac{\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_s^{\overline{gs}}-\mathbf{v}^{\overline{s}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{igs\to is}{M}$$

$$+\left(\frac{1}{\theta^{\overline{\overline{wg}}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)\left(\frac{\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_{wg}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)}{2}\right.$$

$$
\left. -\frac{\mathbf{v}^{\overline{wg},\overline{s}}\cdot\mathbf{v}^{\overline{wgs},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_S}\overset{iwgs\rightarrow iwg}{M}
$$

$$
+\left(\frac{1}{\theta^{\overline{\overline{ws}}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)\left(\frac{\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_{ws}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)}{2}\right.
$$

$$
\left. -\frac{\mathbf{v}^{\overline{ws},\overline{s}}\cdot\mathbf{v}^{\overline{wgs},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_S}\overset{iwgs\rightarrow iws}{M}
$$

$$
+\left(\frac{1}{\theta^{\overline{\overline{gs}}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)\left(\frac{\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_{gs}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)}{2}\right.
$$

$$
\left. -\frac{\mathbf{v}^{\overline{gs},\overline{s}}\cdot\mathbf{v}^{\overline{wgs},\overline{s}}}{2}\right)\sum_{i\in\mathcal{I}_S}\overset{iwgs\rightarrow igs}{M}.
$$

This form is attractive because each grouping of terms matches a flux-force pair and this formulation reduces to the form found in previous TCAT papers when the velocities that are both subscripted and superscripted are replaced by the higher dimensional macroscale mass averaged velocity.

Eqs. (B.270), (B.271), and (B.278) can be substituted into Eq. (B.267) to yield, after expanding some of the summations over entities and regrouping of terms,

$$
\text{(B.279)}\quad -\sum_{\iota\in\left(\mathcal{I}_{\mathrm{f}}\cup\mathcal{I}_{\mathrm{I}}\cup\mathcal{I}_{\mathrm{C}}\right)}\nabla'\cdot\left[\epsilon^{\iota}\boldsymbol{\varphi}^{\backslash\overline{\iota}}-\frac{1}{\theta^{\overline{\iota}}}\left(\epsilon^{\iota}\mathbf{q}^{\overline{\iota}}+\sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}}\left(\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{i\iota}}\right)\mathbf{u}^{\backslash\overline{\overline{i\iota}}}\right)\right]
$$

$$
+\sum_{\iota\in\left(\mathcal{I}_{\mathrm{f}}\cup\mathcal{I}_{\mathrm{I}}\cup\mathcal{I}_{\mathrm{C}}\right)}\left(\nabla'\cdot\mathbf{N}\right)\mathbf{N}\cdot\frac{1}{\theta^{\overline{\iota}}}\sum_{i\in\mathcal{I}_S}\epsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}}\left(\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{i\iota}}\right)\mathbf{u}^{\overline{\overline{i\iota}}}
$$

$$
-\nabla'\cdot\left\{\epsilon^s\boldsymbol{\varphi}^{\backslash\overline{s}}-\frac{1}{\theta^{\overline{\overline{s}}}}\left[\epsilon^s\mathbf{q}^{\backslash\overline{s}}+\sum_{i\in\mathcal{I}_S}\epsilon^s\rho^s\omega^{\overline{is}}\left(\mu^{\overline{\overline{is}}}+\psi^{\overline{is}}\right)\mathbf{u}^{\backslash\overline{\overline{is}}}\right.\right.
$$

$$
\left.\left.-\left\langle\mathbf{I}'\cdot\left(\mathbf{t}_s-\boldsymbol{\sigma}_s\colon\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\right\}
$$

$$
+\left(\nabla'\cdot\mathbf{N}\right)\mathbf{N}\cdot\left[\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{i\in\mathcal{I}_S}\epsilon^s\rho^s\omega^{\overline{is}}\left(\mu^{\overline{\overline{is}}}+\psi^{\overline{is}}\right)\mathbf{u}^{\overline{\overline{is}}}\right.
$$

$$
\left.+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s\colon\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]
$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \left[\epsilon^{\iota} b_T^{\bar{\bar{\iota}}} - \frac{1}{\theta^{\bar{\bar{\iota}}}} \left(\epsilon^{\iota} h_T^{\bar{\bar{\iota}}} + \left\langle \eta_{\iota} \frac{\mathrm{D}^{\bar{s}} \left(\theta_{\iota} - \theta^{\bar{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right) \right.$$

$$\left. - \frac{1}{\theta^{\bar{\bar{\iota}}}} \sum_{i \in \mathcal{I}_s} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}^{\bar{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - \psi^{\overline{i\iota}} - K_E^{\bar{\bar{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right]$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left[\epsilon^{\iota} b_T^{\bar{\bar{\iota}}} - \frac{1}{\theta^{\bar{\bar{\iota}}}} \left(\epsilon^{\iota} h_T^{\bar{\bar{\iota}}} + \left\langle \eta_{\iota} \frac{\mathrm{D}'^{\bar{s}} \left(\theta_{\iota} - \theta^{\bar{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right) \right.$$

$$\left. - \frac{1}{\theta^{\bar{\bar{\iota}}}} \sum_{i \in \mathcal{I}_s} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}'^{\bar{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - \psi^{\overline{i\iota}} - K_E^{\bar{\bar{\iota}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right]$$

$$- \epsilon^{wgs} b_T^{\overline{\overline{wgs}}} + \frac{1}{\theta^{\overline{\overline{wgs}}}} \left(\epsilon^{wgs} h_T^{\overline{\overline{wgs}}} + \left\langle \eta_{wgs} \frac{\mathrm{D}''^{\bar{s}} \left(\theta_{wgs} - \theta^{\overline{wgs}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wgs}, \Omega} \right)$$

$$+ \frac{1}{\theta^{\overline{\overline{wgs}}}} \sum_{i \in \mathcal{I}_s} \left\langle \rho_{wgs} \omega_{iwgs} \frac{\mathrm{D}''^{\bar{s}} \left(\mu_{iwgs} + \psi_{iwgs} - \mu^{\overline{iwgs}} - \psi^{\overline{iwgs}} - K_E^{\overline{wgs}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wgs}, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\epsilon^{\iota}}{\theta^{\bar{\bar{\iota}}}} \left(\mathbf{t}^{\backslash \bar{\iota}} + p^{\iota} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \bar{\iota}} + \frac{\epsilon^{s}}{\theta^{\bar{\bar{s}}}} \left(\mathbf{t}^{\backslash \bar{s}} - \mathbf{t}^{\backslash s} \right) : \mathbf{d}^{\backslash \bar{s}}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\epsilon^{\iota}}{\theta^{\bar{\bar{\iota}}}} \left(\mathbf{t}^{\backslash \bar{\iota}} - \gamma^{\iota} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \bar{\iota}} + \frac{\epsilon^{wgs}}{\theta^{\overline{\overline{wgs}}}} \left(\mathbf{t}^{\backslash \overline{\overline{wgs}}} + \gamma^{wgs} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \overline{\overline{wgs}}}$$

$$- \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\bar{\bar{\iota}}}} \epsilon^{\iota} \rho^{\iota} \omega^{i\bar{\iota}} \mathbf{u}^{\backslash \overline{\bar{i\iota}}} \cdot \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right)$$

$$- \sum_{\iota \in \left(\mathcal{I}_{\mathrm{f}} \cup \mathcal{I}_{\mathrm{I}} \cup \mathcal{I}_{\mathrm{C}} \right)} \left(\epsilon^{\iota} \mathbf{q}^{\backslash \bar{\iota}} + \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\bar{\iota}} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\backslash \overline{i\iota}} \right) \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\bar{\bar{\iota}}}} \right)$$

$$- \left[\epsilon^{s} \mathbf{q}^{\backslash \bar{s}} + \sum_{i \in \mathcal{I}_s} \epsilon^{s} \rho^{s} \omega^{i\bar{s}} \left(\mu^{\overline{i s}} + \psi^{\overline{i s}} \right) \mathbf{u}^{\backslash \overline{\bar{i s}}} \right.$$

$$\left. - \left\langle \mathbf{I}^{\backslash} \cdot \left(\mathbf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_s, \Omega} \right] \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\bar{\bar{s}}}} \right)$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\left(\mathbf{v}^{\backslash \bar{\iota}} - \mathbf{v}^{\backslash \bar{s}} \right)}{\theta^{\bar{\bar{\iota}}}} \cdot \left[\sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\bar{\iota}} \nabla^{\backslash} \left(K_E^{\bar{\bar{\iota}}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right.$$

$$+\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\mathbf{g}^{\backslash\overline{i\iota}}+\eta^{\overline{\overline{\iota}}}\nabla^\backslash\theta^{\overline{\overline{\iota}}}-\nabla^\backslash(\epsilon^\iota p^\iota)$$

$$+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left(\overset{\kappa\rightarrow\iota}{\mathbf{T}}\cdot\mathbf{I}^\backslash+\frac{\left(\mathbf{v}_\iota^{\backslash\overline{\kappa}}-\mathbf{v}^{\backslash\overline{\kappa}}\right)+\left(\mathbf{v}_\iota^{\backslash\overline{\kappa}}-\mathbf{v}^{\backslash\overline{\iota}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{i\kappa\rightarrow i\iota}{M}\right)\Bigg]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\Bigg[\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\mathbf{g}^{\overline{\overline{i\iota}}}\cdot\mathbf{N}$$

$$+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\mathbf{N}\cdot\left(\overset{\kappa\rightarrow\iota}{\mathbf{T}}+\frac{\left(\mathbf{v}_\iota^{\overline{\kappa}}-\mathbf{v}^{\overline{\kappa}}\right)+\left(\mathbf{v}_\iota^{\overline{\kappa}}-\mathbf{v}^{\overline{\iota}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{i\kappa\rightarrow i\iota}{M}\right)\Bigg]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\Bigg[\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\nabla^\backslash\left(K_E^{\overline{\overline{\iota}}}+\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)$$

$$+\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\mathbf{g}^{\backslash\overline{i\iota}}+\eta^{\overline{\overline{\iota}}}\nabla^\backslash\theta^{\overline{\overline{\iota}}}+\nabla^\backslash(\epsilon^\iota\gamma^\iota)$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{\mathrm{C}\iota}\cap\mathcal{I}_{\mathrm{P}}\right)}\left(\overset{\iota\rightarrow\kappa}{\mathbf{T}}\cdot\mathbf{I}^\backslash+\frac{\left(\mathbf{v}_\kappa^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{\kappa}}\right)+\left(\mathbf{v}_\kappa^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{\iota}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{i\iota\rightarrow i\kappa}{M}\right)$$

$$+\left(\overset{wgs\rightarrow\iota}{\mathbf{T}}\cdot\mathbf{I}^\backslash+\frac{\left(\mathbf{v}_\iota^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{wgs}}\right)+\left(\mathbf{v}_\iota^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{\iota}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{iwgs\rightarrow i\iota}{M}\right)\Bigg]$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\Bigg[\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{i\overline{\iota}}\mathbf{g}^{\overline{\overline{i\iota}}}\cdot\mathbf{N}$$

$$-\sum_{\kappa\in\left(\mathcal{I}_{\mathrm{C}\iota}\cap\mathcal{I}_{\mathrm{P}}\right)}\mathbf{N}\cdot\left(\overset{\iota\rightarrow\kappa}{\mathbf{T}}+\frac{\left(\mathbf{v}_\kappa^{\overline{\iota}}-\mathbf{v}^{\overline{\kappa}}\right)+\left(\mathbf{v}_\kappa^{\overline{\iota}}-\mathbf{v}^{\overline{\iota}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{i\iota\rightarrow i\kappa}{M}\right)$$

$$+\mathbf{N}\cdot\left(\overset{wgs\rightarrow\iota}{\mathbf{T}}+\frac{\left(\mathbf{v}_\iota^{\overline{wgs}}-\mathbf{v}^{\overline{wgs}}\right)+\left(\mathbf{v}_\iota^{\overline{wgs}}-\mathbf{v}^{\overline{\iota}}\right)}{2}\sum_{i\in\mathcal{I}_s}\overset{iwgs\rightarrow i\iota}{M}\right)\Bigg]$$

$$-\frac{\left(\mathbf{v}^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\cdot\Bigg[\sum_{i\in\mathcal{I}_s}\epsilon^{wgs}\rho^{wgs}\omega^{i\overline{wgs}}\nabla^\backslash\left(K_E^{\overline{\overline{wgs}}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)$$

$$+\sum_{i\in\mathcal{I}_s}\epsilon^{wgs}\rho^{wgs}\omega^{i\overline{wgs}}\mathbf{g}^{\backslash\overline{iwgs}}+\eta^{\overline{\overline{wgs}}}\nabla^\backslash\theta^{\overline{\overline{wgs}}}-\nabla^\backslash(\epsilon^{wgs}\gamma^{wgs})$$

$$- \sum_{\kappa \in \mathcal{I}_{cwgs}} \left(\overset{wgs \to \kappa}{\mathbf{T}} \cdot \mathbf{I}^{\backslash} + \frac{\left(\mathbf{v}_\kappa^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{\kappa}} \right) + \left(\mathbf{v}_\kappa^{\backslash \overline{wgs}} - \mathbf{v}^{\backslash \overline{wgs}} \right)}{2} \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\kappa}{M} \right) \Bigg]$$

$$- \frac{\mathbf{v}^{\overline{wgs},\overline{s}} \cdot \mathbf{N}}{\theta^{\overline{wgs}}} \Bigg[\sum_{i \in \mathcal{I}_s} \epsilon^{wgs} \rho^{wgs} \omega^{i\overline{wgs}} \mathbf{g}^{\overline{iwgs}} \cdot \mathbf{N}$$

$$- \sum_{\kappa \in \mathcal{I}_{cwgs}} \mathbf{N} \cdot \left(\overset{wgs \to \kappa}{\mathbf{T}} + \frac{\left(\mathbf{v}_\kappa^{\overline{wgs}} - \mathbf{v}^{\overline{\kappa}} \right) + \left(\mathbf{v}_\kappa^{\overline{wgs}} - \mathbf{v}^{\overline{wgs}} \right)}{2} \sum_{i \in \mathcal{I}_s} \overset{iwgs \to i\kappa}{M} \right) \Bigg]$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\iota}}} \nabla^{\backslash} \left(K_E^{\overline{\iota}} + \psi^{\overline{i\iota}} + \mu^{\overline{i\iota}} \right) \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \rho_\iota \omega_{i\iota} \right\rangle_{\Omega_\iota, \Omega}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\iota}}} \nabla^{\backslash} \theta^{\overline{\iota}} \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \eta_\iota \right\rangle_{\Omega_\iota, \Omega} - \sum_{\iota \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\iota}}} \mu^{\overline{i\iota}} \epsilon^\iota r^{i\iota}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{c\iota}} \frac{1}{\theta^{\overline{\overline{\kappa}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{\overline{\kappa}}} + \mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}} \right) - \left(K_E^{\overline{\iota}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{wgs}}}} \sum_{i \in \mathcal{I}_s} \left[\left(K_E^{\overline{wgs}} + \mu^{\overline{iwgs}} + \psi^{\overline{iwgs}} \right) - \left(K_E^{\overline{\iota}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \sum_{i \in \mathcal{I}_s} \left[\left(K_{E\iota}^{\overline{\overline{\kappa}}} + \mu_{i\iota}^{\overline{\kappa}} + \psi_\iota^{\overline{\kappa}} \right) - \left(K_E^{\overline{\iota}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \right] \overset{i\kappa \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \sum_{i \in \mathcal{I}_s} \Bigg[\left(K_{E\iota}^{\overline{wgs}} + \mu_{i\iota}^{\overline{wgs}} + \psi_\iota^{\overline{wgs}} \right)$$

$$- \left(K_E^{\overline{\iota}} + \mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \Bigg] \overset{iwgs \to i\iota}{M}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \sum_{\kappa \in \mathcal{I}_{c\iota}} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \left\{ \overset{\kappa \to \iota}{Q} + \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{\kappa}}}}{\epsilon^\iota \rho_\iota^\kappa} - \mu_{i\iota}^{\overline{\kappa}} \right) \overset{i\kappa \to i\iota}{M} + \left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{\kappa \to \iota}{\mathbf{T}} \right.$$

$$\left. + \left[\frac{\left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right)}{2} - \frac{\mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{v}^{\overline{\kappa},\overline{s}}}{2} \right] \sum_{i \in \mathcal{I}_s} \overset{i\kappa \to i\iota}{M} \right\}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \right) \left\{ \overset{wgs \to \iota}{Q} + \sum_{i \in \mathcal{I}_s} \left(\frac{E_\iota^{\overline{wgs}}}{\epsilon^\iota \rho_\iota^{wgs}} - \mu_{i\iota}^{\overline{wgs}} \right) \overset{iwgs \to i\iota}{M} \right.$$

$$+ \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}} \right) \cdot \overset{wgs \to \iota}{\mathbf{T}}$$

$$+\left[\frac{\left(\mathbf{v}_\iota^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_\iota^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)}{2}-\frac{\mathbf{v}^{\overline{\iota,s}}\cdot\mathbf{v}^{\overline{wgs,s}}}{2}\right]\sum_{i\in\mathcal{I}_S}\overset{iwgs\to i\iota}{M}\Bigg\}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\left\langle p_\iota\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\iota\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{\kappa\in\mathcal{I}_{cs}}\left\langle\left(\frac{\mathbf{C}_s}{j_s}{:}\boldsymbol{\sigma}_s\right)(\mathbf{v}_\kappa-\mathbf{v}_s)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left[\nabla'\cdot\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\iota-\mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}+\left\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\gamma_\iota\right\rangle_{\Omega_\iota,\Omega}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\left\langle\left(p_w-p_g-\gamma_{wg}\nabla'\cdot\mathbf{n}_w+\sum_{i\in\mathcal{I}_S}\rho_{wg}\omega_{iwg}\mathbf{n}_w\cdot\mathbf{g}_{iwg}\right)\right.$$

$$\left.\left(\mathbf{v}_{wg}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_w\right\rangle_{\Omega_{wg},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle\left(p_w+\gamma_{ws}\nabla'\cdot\mathbf{n}_s-\sum_{i\in\mathcal{I}_S}\rho_{ws}\omega_{iws}\mathbf{n}_s\cdot\mathbf{g}_{iws}\right)\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{gs}}}}\left\langle\left(p_g+\gamma_{gs}\nabla'\cdot\mathbf{n}_s-\sum_{i\in\mathcal{I}_S}\rho_{gs}\omega_{igs}\mathbf{n}_s\cdot\mathbf{g}_{igs}\right)\left(\mathbf{v}_{gs}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{gs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla'\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}{:}\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\mathbf{l}_{wgs}\cdot\nabla''\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{i\in\mathcal{I}_S}\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla'\left(K_E^{\overline{wgs}}+\mu^{\overline{iwgs}}+\psi^{\overline{iwgs}}\right)$$

$$\cdot\left\langle\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\rho_{wgs}\omega_{iwgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\sum_{i\in\mathcal{I}_s}\left\langle\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\rho_{wgs}\omega_{iwgs}\mathbf{g}_{iwgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla^{\backprime}\theta^{\overline{\overline{wgs}}}\cdot\left\langle\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\eta_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot p_{\iota}\mathbf{I}^{\backprime}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}'_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{\iota}\mathbf{I}^{\backprime}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}''_{wgs}\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{wgs}}\right)}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$+\frac{\left(\mathbf{v}^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{wgs}\mathbf{I}''}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}p_{\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{wgs}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{wgs}}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\mu_{i\iota}+\psi_{i\iota}-K_E^{\overline{\overline{\iota}}}-\mu^{\overline{i\iota}}-\psi^{\overline{i\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\frac{\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{2}+\frac{\mathbf{u}_{i\iota}\cdot\mathbf{u}_{i\iota}}{2}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}}\left\langle\frac{\mathbf{e}\cdot\sum\limits_{i\in\mathcal{I}_s}\rho_{\iota}\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_{\iota}}-\frac{\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}}{\theta^{\overline{\overline{\iota}}}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\left\langle\frac{\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta_{\iota}}\right)\mathbf{e}\cdot\left[\mathbf{q}_{\iota}-\left(\mathbf{v}_{\iota}-\mathbf{v}_{\mathrm{ext}}\right)\theta_{\iota}\eta_{\iota}\right]}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=\Lambda\geq0.$$

B.11. Simplified Entropy Inequality

The CEI is exact given the set of primary restrictions. Because of this exact nature, it is an important expression for archival purposes. However, the CEI is not in a force-flux form where all forces and fluxes vanish at equilibrium. We seek such a force-flux form to guide the development of closure relations, and we call this form the simplified entropy inequality (SEI). The SEI is derived from the CEI given a set of secondary restrictions and approximations, which are non-unique and subject to change if the class of system of focus changes in the future or if improved approximations are developed. Secondary restrictions limit the system being considered to a subset of the general system for which the CEI was derived. Approximations are explicit statements of non-exact, but reasonable, approaches used to simplify expressions that are otherwise non-reducible. While not exact, the derivation of the SEI is done systematically and the restrictions and approximations are explicit. The validity of these assumptions can be checked using microscale experimental or simulation approaches. We will formulate the SEI by systematically examining the secondary restrictions and approximations and their resultant consequences on the CEI. The final result that we seek is an inequality consisting of a sum of force-flux pair products that vanish at equilibrium.

Secondary Restriction 1 states that no deformation takes place and thus the Green's deformation tensor becomes the identity tensor and the Lagrangian stress tensor is the zero tensor, which allows several solid-phase terms to be simplified. Secondary Restriction 2 means $r^{i\iota} = 0$, which allows all products with this term to be dropped from the CEI. Secondary Restriction 3 states that the interfaces and common curves are massless and frictionless, which implies that their mass density is zero and there is no viscous stress. This restriction reduces the conservation of mass equations for an interface to a jump condition, eliminates the conservation of mass equation for the common curve, and all other terms involving mass exchange with the common curve. Approximation 1 is a statement that terms involving K_E and $\mathbf{u}\cdot\mathbf{u}$ can be neglected, because they are second-order products of velocity fluctuations that are expected to be small.

Secondary Restrictions 1–3 and SEI Approximations 1 and 2 can be applied to the CEI, Eq. (B.279), to yield

$$
\text{(B.280)} \quad -\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \nabla^{\backslash} \cdot \left[\epsilon^{\iota} \boldsymbol{\varphi}^{\backslash \bar{\iota}} - \frac{1}{\theta^{\bar{\iota}}} \left(\epsilon^{\iota} \mathbf{q}^{\backslash \bar{\iota}} + \sum_{i \in \mathcal{I}_S} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\backslash \overline{i\iota}} \right) \right]
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} (\nabla^{\backslash} \cdot \mathbf{N}) \, \mathbf{N} \cdot \frac{1}{\theta^{\bar{\iota}}} \sum_{i \in \mathcal{I}_S} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\overline{i\iota}}
$$

$$
- \nabla^{\backslash} \cdot \left(\epsilon^{s} \boldsymbol{\varphi}^{\backslash \bar{s}} - \frac{\epsilon^{s} \mathbf{q}^{\backslash \bar{s}}}{\theta^{\bar{s}}} \right) - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \nabla^{\backslash} \cdot \left(\epsilon^{\iota} \boldsymbol{\varphi}^{\backslash \bar{\iota}} - \frac{\epsilon^{\iota} \mathbf{q}^{\backslash \bar{\iota}}}{\theta^{\bar{\iota}}} \right)
$$

$$
- \nabla^{\backslash} \cdot \left(\epsilon^{wgs} \boldsymbol{\varphi}^{\backslash \overline{wgs}} - \frac{\epsilon^{wgs} \mathbf{q}^{\backslash \overline{wgs}}}{\theta^{\overline{wgs}}} \right)
$$

$$
- \sum_{\iota \in \mathcal{I}_{\mathrm{P}}} \left[\epsilon^{\iota} b_T^{\bar{\iota}} - \frac{1}{\theta^{\bar{\iota}}} \left(\epsilon^{\iota} h_T^{\bar{\iota}} + \left\langle \eta_{\iota} \frac{\mathrm{D}^{\bar{s}} \left(\theta_{\iota} - \theta^{\bar{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right) \right.
$$

$$
\left. - \frac{1}{\theta^{\bar{\iota}}} \sum_{i \in \mathcal{I}_S} \left\langle \rho_{\iota} \omega_{i\iota} \frac{\mathrm{D}^{\bar{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{i\iota}} - \psi^{\overline{i\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right]
$$

$$
- \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left[\epsilon^{\iota} b_T^{\bar{\iota}} - \frac{1}{\theta^{\bar{\iota}}} \left(\epsilon^{\iota} h_T^{\bar{\iota}} + \left\langle \eta_{\iota} \frac{\mathrm{D}'^{\bar{s}} \left(\theta_{\iota} - \theta^{\bar{\iota}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\iota}, \Omega} \right) \right]
$$

$$
- \epsilon^{wgs} b_T^{\overline{wgs}} + \frac{1}{\theta^{\overline{wgs}}} \left(\epsilon^{wgs} h_T^{\overline{wgs}} + \left\langle \eta_{wgs} \frac{\mathrm{D}''^{\bar{s}} \left(\theta_{wgs} - \theta^{\overline{wgs}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wgs}, \Omega} \right)
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\epsilon^{\iota}}{\theta^{\bar{\iota}}} \left(\mathbf{t}^{\backslash \bar{\iota}} + p^{\iota} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \bar{\iota}} + \frac{\epsilon^{s}}{\theta^{\bar{s}}} \left(\mathbf{t}^{\backslash \bar{s}} - \mathbf{t}^{\backslash s} \right) : \mathbf{d}^{\backslash \bar{s}}
$$

$$
+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\epsilon^{\iota}}{\theta^{\bar{\iota}}} \left(\mathbf{t}^{\backslash \bar{\iota}} - \gamma^{\iota} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \bar{\iota}} + \frac{\epsilon^{wgs}}{\theta^{\overline{wgs}}} \left(\mathbf{t}^{\backslash \overline{wgs}} + \gamma^{wgs} \mathbf{I}^{\backslash} \right) : \mathbf{d}^{\backslash \overline{wgs}}
$$

$$
- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{i \in \mathcal{I}_S} \frac{1}{\theta^{\bar{\iota}}} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \mathbf{u}^{\backslash \overline{i\iota}} \cdot \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right)
$$

$$
- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \left(\epsilon^{\iota} \mathbf{q}^{\backslash \bar{\iota}} + \sum_{i \in \mathcal{I}_S} \epsilon^{\iota} \rho^{\iota} \omega^{i\iota} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}} \right) \mathbf{u}^{\overline{i\iota}} \right) \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\bar{\iota}}} \right)
$$

$$-\epsilon^s \mathbf{q}^{\backslash\overline{\overline{s}}} \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\overline{s}}}}\right) - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\epsilon^{\iota} \mathbf{q}^{\backslash\overline{\iota}}\right) \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\iota}}}\right) - \epsilon^{wgs} \mathbf{q}^{\backslash\overline{\overline{wgs}}} \cdot \nabla^{\backslash} \left(\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)$$

$$-\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\iota}}} \cdot \left(\sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \nabla^{\backslash} \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}\right)\right.$$

$$\left. + \sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{g}^{\backslash\overline{i\iota}} - \nabla^{\backslash} \left(\epsilon^{\iota} p^{\iota}\right) + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{I}^{\backslash}\right)$$

$$-\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{N}}{\theta^{\overline{\iota}}} \left(\sum_{i \in \mathcal{I}_s} \epsilon^{\iota} \rho^{\iota} \omega^{i\overline{\iota}} \mathbf{g}^{\overline{i\iota}} \cdot \mathbf{N} + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{N}\right)$$

$$-\sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\left(\mathbf{v}^{\backslash\iota} - \mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\iota}}} \cdot \left(\nabla^{\backslash} \left(\epsilon^{\iota} \gamma^{\iota}\right) + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{I}^{\backslash}\right) - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\mathbf{v}^{\overline{\iota},\overline{s}} \cdot \mathbf{N}}{\theta^{\overline{\iota}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{N}$$

$$-\frac{\left(\mathbf{v}^{\backslash\overline{wgs}} - \mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{wgs}}} \cdot \left(-\nabla^{\backslash} \left(\epsilon^{wgs} \gamma^{wgs}\right) - \sum_{\kappa \in \mathcal{I}_{\mathrm{C}wgs}} \overset{wgs \to \kappa}{\mathbf{T}} \cdot \mathbf{I}^{\backslash}\right)$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}} \cdot \mathbf{N}}{\theta^{\overline{wgs}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}wgs}} \overset{wgs \to \kappa}{\mathbf{T}} \cdot \mathbf{N}$$

$$+\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \frac{1}{\theta^{\overline{\overline{\kappa}}}} \sum_{i \in \mathcal{I}_s} \left[\left(\mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}}\right) - \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}\right)\right] \overset{i\kappa \to i\iota}{M}$$

$$+\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\right) \left[\overset{\kappa \to \iota}{Q} + \sum_{i \in \mathcal{I}_s} \left(\frac{E_{\iota}^{\overline{\overline{\kappa}}}}{\epsilon^{\iota} \rho_{\iota}^{\kappa}} - \mu_{i\iota}^{\overline{\kappa}}\right) \overset{i\kappa \to i\iota}{M}\right.$$

$$\left. + \left(\mathbf{v}_{\iota}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right) \cdot \overset{\kappa \to \iota}{\mathbf{T}}\right] + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}s}} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\right) \left[\overset{\kappa \to s}{Q} + \left(\mathbf{v}_s^{\overline{\kappa}} - \mathbf{v}^{\overline{\overline{s}}}\right) \cdot \overset{\kappa \to s}{\mathbf{T}}\right]$$

$$+\sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\iota}}} - \frac{1}{\theta^{\overline{wgs}}}\right) \left[\overset{wgs \to \iota}{Q} + \left(\mathbf{v}_{\iota}^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right) \cdot \overset{wgs \to \iota}{\mathbf{T}}\right]$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{I}^{\backslash} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega} - \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \left(\nabla \cdot \mathbf{t}_s - \nabla \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s}\right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$+\sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\iota}}} \left[\nabla^{\backslash} \cdot \left\langle \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \cdot \left(\mathbf{v}_{\iota} - \mathbf{v}^{\overline{s}}\right) \gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega} + \left\langle \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega} : \mathbf{d}^{\backslash\overline{\overline{s}}}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\left\langle \left(p_w - p_g - \gamma_{wg}\nabla'\!\cdot\!\mathbf{n}_w\right)\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_w\right\rangle_{\Omega_{wg},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \left(p_w + \gamma_{ws}\nabla'\!\cdot\!\mathbf{n}_s\right)\left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{gs}}}}\left\langle \left(p_g + \gamma_{gs}\nabla'\!\cdot\!\mathbf{n}_s\right)\left(\mathbf{v}_{gs} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{gs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\nabla`\!\cdot\!\left\langle \left(\mathbf{I} - \mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle \left(\mathbf{I} - \mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}\!:\!\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle \left(\mathbf{l}_{wgs}\!\cdot\!\nabla''\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle \mathbf{n}_\iota\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\gamma_\iota\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle \frac{\mathbf{e}\!\cdot\!\boldsymbol{\tau}_\iota\!\cdot\!\left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} + \sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}} - \mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\!\cdot\!\left\langle \frac{\mathbf{e}\!\cdot\!p_\iota\mathbf{I}\backslash}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}} - \mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\!\cdot\!\left\langle \frac{\mathbf{e}\!\cdot\!\gamma_\iota\mathbf{I}'}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} + \frac{\left(\mathbf{v}^{\backslash\overline{wgs}} - \mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\!\cdot\!\left\langle \frac{\mathbf{e}\!\cdot\!\gamma_{wgs}\mathbf{I}''}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\!\cdot\!\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle \frac{\mathbf{e}p_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} - \sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\!\cdot\!\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle \frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\!\cdot\!\mathbf{N}}{\theta^{\overline{\overline{wgs}}}}\mathbf{N}\cdot\left\langle \frac{\mathbf{e}\gamma_{wgs}}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{P}}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle \frac{\mathbf{e}\!\cdot\!\left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}}\right)\rho_\iota\omega_{i\iota}\left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\left\langle \frac{\mathbf{e}\!\cdot\!\sum\limits_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_\iota} - \frac{\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{\overline{i\iota}}}}{\theta^{\overline{\overline{\iota}}}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\left\langle \frac{\left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta_\iota}\right)\mathbf{e}\!\cdot\!\left[\mathbf{q}_\iota - \left(\mathbf{v}_\iota - \mathbf{v}_{\mathrm{ext}}\right)\theta_\iota\eta_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} = \Lambda \geq 0.$$

Combining the fluid phase portion of line 2 of Eq. (B.280) with the grouping on lines 5 and 6 we can write

(B.281)

$$\sum_{\iota \in \mathcal{I}_f} \left(\nabla^\backprime \cdot \mathbf{N} \right) \mathbf{N} \cdot \frac{1}{\theta^{\overline{\overline{\iota}}}} \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\iota} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\overline{\overline{i\iota}}}$$

$$- \sum_{\iota \in \mathcal{I}_f} \left[\epsilon^\iota b_T^{\overline{\overline{\iota}}} - \frac{1}{\theta^{\overline{\iota}}} \left(\epsilon^\iota h_T^{\overline{\overline{\iota}}} + \left\langle \eta_\iota \frac{D^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\iota}} \right)}{Dt} \right\rangle_{\Omega_\iota, \Omega} \right) \right.$$

$$\left. - \frac{1}{\theta^{\overline{\iota}}} \sum_{i \in \mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{D^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota, \Omega} \right]$$

$$= - \sum_{\iota \in \mathcal{I}_f} \left[\epsilon^\iota b_T^{\overline{\overline{\iota}}} - \frac{1}{\theta^{\overline{\overline{\iota}}}} \left(\epsilon^\iota h_T^{\overline{\overline{\iota}}} + \left(\nabla^\backprime \cdot \mathbf{N} \right) \mathbf{N} \cdot \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\iota} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\overline{\overline{i\iota}}} \right. \right.$$

$$\left. + \left\langle \eta_\iota \frac{D^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\iota}} \right)}{Dt} \right\rangle_{\Omega_\iota, \Omega} \right.$$

$$\left. \left. + \sum_{i \in \mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{D^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota, \Omega} \right) \right].$$

SEI Approximation 3 states that the system is macroscopically simple, which according to the approximation, means that the relationship among entropy fluxes, heat fluxes, and dispersive fluxes may be equated as

(B.282)
$$\epsilon^\iota \boldsymbol{\varphi}^{\overline{\iota}} - \frac{1}{\theta^{\overline{\iota}}} \left[\epsilon^\iota \mathbf{q}^{\overline{\iota}} + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\iota} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\overline{\overline{i\iota}}} \right] = 0 \quad \text{for } \iota \in \mathcal{I}_f,$$

(B.283)
$$\epsilon^s \boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}} \epsilon^s \mathbf{q}^{\overline{\overline{s}}} = 0,$$

(B.284)
$$\epsilon^\iota \boldsymbol{\varphi}^{\overline{\iota}} - \frac{1}{\theta^{\overline{\iota}}} \epsilon^\iota \mathbf{q}^{\overline{\iota}} = 0 \quad \text{for } \iota \in \mathcal{I}_I,$$

and

(B.285)
$$\epsilon^{wgs} \boldsymbol{\varphi}^{\overline{\overline{wgs}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}} \epsilon^{wgs} \mathbf{q}^{\overline{\overline{wgs}}} = 0.$$

Also from SEI Approximation 3, the entropy source, the heat source, and material derivatives of the deviations in temperature and potential terms may be equated. If we expand the terms of these types that are grouped together we can write

(B.286)

$$
-\epsilon^\iota b_T^{\overline{\overline{\iota}}} + \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\epsilon^\iota h_T^{\overline{\overline{\iota}}} + \left\langle \eta_\iota \frac{D^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} \right.
$$

$$
+ \left(\nabla^{\backprime}{\cdot}\mathbf{N} \right) \mathbf{N}{\cdot} \sum_{i\in\mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\overline{\overline{i\iota}}}
$$

$$
\left. + \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{D^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} \right]
$$

$$
= -\epsilon^\iota b^\iota - \epsilon^\iota \left(\nabla^{\backprime}{\cdot}\mathbf{N} \right) \left(\mathbf{N}{\cdot}\boldsymbol{\varphi}^{\overline{\overline{\iota}}} \right) + \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\epsilon^\iota h^{\overline{\overline{\iota}}} + \epsilon^\iota \left(\nabla^{\backprime}{\cdot}\mathbf{N} \right) \left(\mathbf{N}{\cdot}\mathbf{q}^{\overline{\overline{\iota}}} \right) \right.
$$

$$
+ \left(\nabla^{\backprime}{\cdot}\mathbf{N} \right) \mathbf{N}{\cdot} \sum_{i\in\mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\overline{\overline{i\iota}}} + \left\langle \eta_\iota \frac{D^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota,\Omega}
$$

$$
\left. + \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{D^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} \right]
$$

$$
= -\epsilon^\iota b^\iota + \frac{1}{\theta^{\overline{\overline{\iota}}}} \left[\epsilon^\iota h^{\overline{\overline{\iota}}} + \left\langle \eta_\iota \frac{D^{\overline{s}} \left(\theta_\iota - \theta^{\overline{\overline{\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} \right.
$$

$$
\left. + \sum_{i\in\mathcal{I}_s} \left\langle \rho_\iota \omega_{i\iota} \frac{D^{\overline{s}} \left(\mu_{i\iota} + \psi_{i\iota} - \mu^{\overline{\overline{i\iota}}} - \psi^{\overline{\overline{i\iota}}} \right)}{Dt} \right\rangle_{\Omega_\iota,\Omega} \right] = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{f}}.
$$

Similar expansion of the total entropy source and heat flux terms and use of Eq. (B.283), Eq. (B.284), and Eq. (B.285) yields

$$
\text{(B.287)} \quad -\epsilon^s b^s + \frac{1}{\theta^{\overline{\overline{s}}}} \left(\epsilon^s h^{\overline{\overline{s}}} + \left\langle \eta_s \frac{D^{\overline{s}} \left(\theta_s - \theta^{\overline{\overline{s}}} \right)}{Dt} \right\rangle_{\Omega_s,\Omega} \right.
$$

$$
\left. + \left\langle \rho_s \frac{D^{\overline{s}} \left(\mu_s + \psi_s - \mu^{\overline{s}} - \psi^{\overline{s}} \right)}{Dt} \right\rangle_{\Omega_s,\Omega} \right) = 0,
$$

$$(\text{B.288}) \qquad -\epsilon^{\iota}b^{\iota} + \frac{1}{\theta^{\bar{\bar{\iota}}}}\left(\epsilon^{\iota}h^{\bar{\bar{\iota}}} + \left\langle \eta_{\iota}\frac{\mathrm{D}^{\prime\bar{s}}\left(\theta_{\iota} - \theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\right) = 0 \quad \text{for } \iota \in \mathcal{I}_{\mathrm{I}},$$

and

$$(\text{B.289}) \qquad -\epsilon^{wgs}b^{wgs} + \frac{1}{\theta^{\overline{\overline{wgs}}}}\left(\epsilon^{wgs}h^{\overline{\overline{wgs}}} + \left\langle \eta_{wgs}\frac{\mathrm{D}^{\prime\prime\bar{s}}\left(\theta_{wgs} - \theta^{\overline{\overline{wgs}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{wgs},\Omega}\right) = 0.$$

Many of the remaining microscale quantities found within averaging operators include dyadic products of orientation vectors. These quantities are referred to as geometric orientation tensors and can be written as

$$(\text{B.290}) \qquad \mathbf{G}^{\iota} = \langle \mathbf{G}_{\iota}\rangle_{\Omega_{\iota},\Omega_{\iota}} = \langle \mathbf{n}_{\kappa}\mathbf{n}_{\kappa}\rangle_{\Omega_{\iota},\Omega_{\iota}} \quad \text{for } \iota \in \mathcal{I}_{\mathrm{I}} \text{ and } \kappa \in \left(\mathcal{I}_{c\iota} \cap \mathcal{I}_{\mathrm{P}}\right),$$

and

$$(\text{B.291}) \qquad \mathbf{G}^{wgs} = \langle \mathbf{G}_{wgs}\rangle_{\Omega_{wgs},\Omega_{wgs}} = \langle \mathbf{I} - \mathbf{l}_{wgs}\mathbf{l}_{wgs}\rangle_{\Omega_{wgs},\Omega_{wgs}}.$$

While Eq. (B.290) and Eq. (B.291) are exact and accessible given detailed knowledge of the microscale, these terms appear within averaging operators as products with other microscale variables. As a result of SEI Approximation 4, we approximate these terms by assuming independence among certain groupings of variables, allowing integrals of products to be expressed as products of integrals as in

$$(\text{B.292}) \qquad \left\langle \mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota} - \mathbf{v}^{\bar{s}}\right)\gamma_{\iota}\right\rangle_{\Omega_{\iota},\Omega} \approx \epsilon^{\iota}\mathbf{G}^{\iota}\cdot\mathbf{v}^{\bar{\iota},\bar{s}}\gamma^{\iota},$$

$$(\text{B.293}) \qquad \langle \mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\gamma_{\iota}\rangle_{\Omega_{\iota},\Omega} \approx \epsilon^{\iota}\mathbf{G}^{\iota}\gamma^{\iota},$$

$$(\text{B.294}) \qquad \left\langle \left(\mathbf{I} - \mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\bar{s}}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega} \approx \epsilon^{wgs}\mathbf{G}^{wgs}\cdot\mathbf{v}^{\overline{wgs},\bar{s}}\gamma^{wgs},$$

and

$$(\text{B.295}) \qquad \left\langle \left(\mathbf{I} - \mathbf{l}_{wgs}\mathbf{l}_{wgs}\right)\gamma_{wgs}\right\rangle_{\Omega_{wgs},\Omega} \approx \epsilon^{wgs}\mathbf{G}^{wgs}\gamma^{wgs},$$

where $\iota \in \mathcal{I}_{\mathrm{I}}$, $\alpha \in (\mathcal{I}_{\mathrm{c}\iota} \cap \mathcal{I}_{\mathrm{P}})$, and $\mathbf{G}^{\backslash \iota} = \mathbf{G}^\iota - \mathbf{NN} \cdot \mathbf{G}^\iota \cdot \mathbf{NN}$.

Note that

$$(\text{B.296}) \quad \frac{1}{\theta^{\bar{\bar{\iota}}}} \nabla^\backslash \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\bar{s}} \right) \gamma_\iota \right\rangle_{\Omega_\iota, \Omega} = \frac{1}{\theta^{\bar{\bar{\iota}}}} \nabla^\backslash \cdot \left(\epsilon^\iota \mathbf{G}^\iota \cdot \mathbf{v}^{\overline{\iota, \bar{s}}} \gamma^\iota \right)$$

$$= \frac{\mathbf{v}^{\overline{\iota, \bar{s}}}}{\theta^{\bar{\bar{\iota}}}} \cdot \nabla^\backslash \cdot \left(\epsilon^\iota \mathbf{G}^\iota \gamma^\iota \right) + \frac{1}{\theta^{\bar{\bar{\iota}}}} \epsilon^\iota \mathbf{G}^\iota \gamma^\iota : \mathbf{d}^{\backslash \overline{\overline{\iota, \bar{s}}}}$$

$$= \frac{\mathbf{v}^{\backslash \bar{\iota}} - \mathbf{v}^{\backslash \bar{s}}}{\theta^{\bar{\bar{\iota}}}} \cdot \nabla^\backslash \cdot \left(\epsilon^\iota \mathbf{G}^{\backslash \iota} \gamma^\iota \right) + \frac{\mathbf{v}^{\overline{\iota, \bar{s}}}}{\theta^{\bar{\bar{\iota}}}} \cdot \left(\nabla^\backslash \cdot \mathbf{N} \right) \mathbf{NN} \cdot \left(\epsilon^\iota \mathbf{G}^\iota \cdot \mathbf{N} \gamma^\iota \right)$$

$$+ \frac{\epsilon^\iota}{\theta^{\bar{\bar{\iota}}}} \mathbf{G}^{\backslash \iota} \gamma^\iota : \mathbf{d}^{\backslash \overline{\overline{\iota, \bar{s}}}},$$

where $\mathbf{d}^{\backslash \overline{\overline{\iota, \bar{s}}}} = \mathbf{d}^{\backslash \bar{\iota}} - \mathbf{d}^{\backslash \bar{s}}$, and

$$(\text{B.297}) \quad \frac{1}{\theta^{\bar{\bar{\iota}}}} \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \gamma_\iota \rangle_{\Omega_\iota, \Omega} : \mathbf{d}^{\backslash \bar{\bar{s}}} = \frac{1}{\theta^{\bar{\bar{\iota}}}} \epsilon^\iota \mathbf{G}^\iota \gamma^\iota : \mathbf{d}^{\backslash \bar{\bar{s}}} = \frac{\epsilon^\iota}{\theta^{\bar{\bar{\iota}}}} \mathbf{G}^{\backslash \iota} \gamma^\iota : \mathbf{d}^{\backslash \bar{\bar{s}}}.$$

The same type of manipulations can be done for similar terms which arise averaged over the common curves.

For a three-phase system, the following relationships between the unit vectors are valid along the common curve at the smooth solid surface with normal $\mathbf{n}_s$,

$$(\text{B.298}) \quad \mathbf{n}_{wg} = \cos \varphi_{ws,wg} \mathbf{n}_{ws} - \sin \varphi_{ws,wg} \mathbf{n}_s,$$

and

$$(\text{B.299}) \quad \mathbf{n}_{gs} = -\mathbf{n}_{ws}.$$

Also along the wgs common curve exists the identity

$$(\text{B.300}) \quad \mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} = \mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} \cdot \mathbf{n}_s \mathbf{n}_s + \mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} \cdot \mathbf{n}_{ws} \mathbf{n}_{ws}.$$

Then the normal curvature, κ_{Nwgs}, and the geodesic curvature, κ_{Gwgs} are defined, respectively, as

$$(\text{B.301}) \quad \kappa_{Nwgs} = \mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} \cdot \mathbf{n}_s,$$

and

(B.302)
$$\kappa_{Gwgs} = \mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} \cdot \mathbf{n}_{ws},$$

so that Eqn (B.300) may be written

(B.303)
$$\mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} = \kappa_{Nwgs} \mathbf{n}_s + \kappa_{Gwgs} \mathbf{n}_{ws}.$$

Applying the approximations given by Eqs. (B.282)–(B.303), the CEI can be simplified such that the SEI is written as

(B.304)

$$\sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\epsilon^\iota}{\theta^{\overline{\overline{\iota}}}} \left(\mathbf{t}^{\backslash \overline{\overline{\iota}}} + p^\iota \mathbf{I}^\backslash \right) : \mathbf{d}^{\backslash \overline{\overline{\iota}}} + \frac{\epsilon^s}{\theta^{\overline{\overline{s}}}} \left(\mathbf{t}^{\backslash \overline{s}} - \mathbf{t}^{\backslash s} \right) : \mathbf{d}^{\backslash \overline{\overline{s}}}$$

$$+ \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\epsilon^\iota}{\theta^{\overline{\overline{\iota}}}} \left[\mathbf{t}^{\backslash \overline{\iota}} - \gamma^\iota \left(\mathbf{I}^\backslash - \mathbf{G}^{\backslash \iota} \right) \right] : \mathbf{d}^{\backslash \overline{\overline{\iota}}} + \frac{\epsilon^{wgs}}{\theta^{\overline{\overline{wgs}}}} \left[\mathbf{t}^{\overline{\backslash wgs}} + \gamma^{wgs} \left(\mathbf{I}^\backslash - \mathbf{G}^{\backslash wgs} \right) \right] : \mathbf{d}^{\backslash \overline{\overline{wgs}}}$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \sum_{i \in \mathcal{I}_s} \frac{1}{\theta^{\overline{\overline{\iota}}}} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \cdot \nabla^\backslash \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right)$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \left(\epsilon^\iota \mathbf{q}^{\backslash \overline{\overline{\iota}}} + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) \mathbf{u}^{\backslash \overline{\overline{i\iota}}} \right) \cdot \nabla^\backslash \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} \right)$$

$$- \epsilon^s \mathbf{q}^{\backslash \overline{s}} \cdot \nabla^\backslash \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right) - \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \left(\epsilon^\iota \mathbf{q}^{\backslash \overline{\iota}} \right) \cdot \nabla^\backslash \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} \right) - \epsilon^{wgs} \mathbf{q}^{\overline{\backslash wgs}} \cdot \nabla^\backslash \left(\frac{1}{\theta^{\overline{\overline{wgs}}}} \right)$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash \overline{s}} \right)}{\theta^{\overline{\overline{\iota}}}} \cdot \left(\sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \nabla^\backslash \left(\mu^{\overline{\overline{i\iota}}} + \psi^{\overline{\overline{i\iota}}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\backslash \overline{\overline{i\iota}}} \right.$$

$$\left. - \nabla^\backslash \left(\epsilon^\iota p^\iota \right) + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{I}^\backslash \right)$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{f}}} \frac{\mathbf{v}^{\overline{\iota}, \overline{s}} \cdot \mathbf{N}}{\theta^{\overline{\overline{\iota}}}} \left(\sum_{i \in \mathcal{I}_s} \epsilon^\iota \rho^\iota \omega^{i\overline{\iota}} \mathbf{g}^{\overline{\overline{i\iota}}} \cdot \mathbf{N} + \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{N} \right)$$

$$- \sum_{\iota \in \mathcal{I}_{\mathrm{I}}} \frac{\left(\mathbf{v}^{\backslash \iota} - \mathbf{v}^{\backslash \overline{s}} \right)}{\theta^{\overline{\overline{\iota}}}} \cdot \left(\nabla^\backslash \cdot \left[\epsilon^\iota \gamma^\iota \left(\mathbf{I}^\backslash - \mathbf{G}^{\backslash \iota} \right) \right] + \overset{\kappa \to \iota}{\mathbf{T}} \cdot \mathbf{I}^\backslash \right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}} \frac{\mathbf{v}^{\overline{\iota,\overline{s}}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\left(\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}} \overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{N} - \left(\nabla^{\backprime}\cdot\mathbf{N}\right)\mathbf{N}\cdot\epsilon^\iota\mathbf{G}^\iota\cdot\mathbf{N}\gamma^\iota\right)$$

$$-\frac{\left(\mathbf{v}^{\backprime\overline{wgs}} - \mathbf{v}^{\backprime\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\cdot\left(-\nabla^{\backprime}\cdot\left[\epsilon^{wgs}\gamma^{wgs}\left(\mathbf{I}^{\backprime} - \mathbf{G}^{\backprime wgs}\right)\right] - \sum_{\kappa\in\mathcal{I}_{Cwgs}} \overset{wgs\to\kappa}{\mathbf{T}}\cdot\mathbf{I}^{\backprime}\right)$$

$$+\frac{\mathbf{v}^{\overline{wgs,\overline{s}}}\cdot\mathbf{N}}{\theta^{\overline{\overline{wgs}}}}\left(\sum_{\kappa\in\mathcal{I}_{Cwgs}} \overset{wgs\to\kappa}{\mathbf{T}}\cdot\mathbf{N} - \left(\nabla'\cdot\mathbf{N}\right)\mathbf{N}\cdot\epsilon^{wgs}\mathbf{G}^{wgs}\cdot\mathbf{N}\gamma^{wgs}\right)$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}} \frac{1}{\theta^{\overline{\overline{\kappa}}}}\sum_{i\in\mathcal{I}_s} \left[\left(\mu^{\overline{i\kappa}} + \psi^{\overline{i\kappa}}\right) - \left(\mu^{\overline{i\iota}} + \psi^{\overline{i\iota}}\right)\right]\overset{i\kappa\to i\iota}{M}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\left[\overset{\kappa\to\iota}{Q} + \sum_{i\in\mathcal{I}_s} \left(\frac{E_\iota^{\overline{\overline{\kappa}}}}{\epsilon^\iota\rho_\iota^\kappa} - \mu_{i\iota}^{\overline{\kappa}}\right)\overset{i\kappa\to i\iota}{M}\right.$$

$$\left.+\left(\mathbf{v}_\iota^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right)\cdot\overset{\kappa\to\iota}{\mathbf{T}}\right] + \sum_{\kappa\in\mathcal{I}_{Cs}} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\left[\overset{\kappa\to s}{Q} + \left(\mathbf{v}_s^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right)\cdot\overset{\kappa\to s}{\mathbf{T}}\right]$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}} \left(\frac{1}{\theta^{\overline{\overline{\iota}}}} - \frac{1}{\theta^{\overline{\overline{wgs}}}}\right)\left[\overset{wgs\to\iota}{Q} + \left(\mathbf{v}_\iota^{\overline{wgs}} - \mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to\iota}{\mathbf{T}}\right]$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega} - \frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s - \nabla\boldsymbol{\sigma}_s\colon\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\left\langle\left(p_w - p_g - \gamma_{wg}\nabla'\cdot\mathbf{n}_w\right)\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_w\right\rangle_{\Omega_{wg},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle\left(p_w + \gamma_{ws}\nabla'\cdot\mathbf{n}_s\right)\left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{gs}}}}\left\langle\left(p_g + \gamma_{gs}\nabla'\cdot\mathbf{n}_s\right)\left(\mathbf{v}_{gs} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{gs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\gamma_{wgs}\kappa_{Gwgs} + \gamma_{ws} - \gamma_{gs} + \gamma_{wg}\cos\varphi_{ws,wg}\right)\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega}$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\gamma_{wgs}\kappa_{Nwgs} - \gamma_{wg}\sin\varphi_{ws,wg}\right)\mathbf{n}_s\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_\iota\cdot\left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega} + \sum_{\iota\in\mathcal{I}_{\mathrm{f}}} \frac{\left(\mathbf{v}^{\backprime\overline{\iota}} - \mathbf{v}^{\backprime\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\cdot p_\iota\mathbf{I}^{\backprime}}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{I}}\frac{\left(\mathbf{v}^{\backslash\iota}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left\langle\frac{\mathbf{e}\!\cdot\!\gamma_\iota\mathbf{I}'}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\frac{\left(\mathbf{v}^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\cdot\left\langle\frac{\mathbf{e}\!\cdot\!\gamma_{wgs}\mathbf{I}''}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_\mathrm{f}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\!\cdot\!\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}p_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\sum_{\iota\in\mathcal{I}_\mathrm{I}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\!\cdot\!\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_\iota}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\!\cdot\!\mathbf{N}}{\theta^{\overline{\overline{wgs}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{wgs}}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{P}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\!\cdot\!\left(\mathbf{v}_\iota-\mathbf{v}_\mathrm{ext}\right)\rho_\iota\omega_{i\iota}\left(\mu_{i\iota}+\psi_{i\iota}-\mu^{\overline{i\iota}}-\psi^{\overline{i\iota}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_\mathrm{f}}\left\langle\frac{\mathbf{e}\!\cdot\!\sum\limits_{i\in\mathcal{I}_s}\rho_\iota\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_\iota}-\frac{\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}}{\theta^{\overline{\iota}}}\right)}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\left\langle\frac{\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta_\iota}\right)\mathbf{e}\!\cdot\!\left[\mathbf{q}_\iota-\left(\mathbf{v}_\iota-\mathbf{v}_\mathrm{ext}\right)\theta_\iota\eta_\iota\right]}{\mathbf{n}_\iota\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=\Lambda\geq0.$$

Several terms remain in Eq. (B.304) that are not in a strict force-flux form. For these terms, we must either make approximations and rearrangements such that these terms are in a strict force-flux form, or we can exclude a term if it can be concluded to be essentially zero based upon our secondary restrictions and SEI approximations. Because the solid phase does not deform (Secondary Restriction 1), and the velocity of the solid particles is small (SEI Approximation 6), we will assume that

(B.305) $$\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\!\cdot\!\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s\!:\!\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\approx0.$$

Next consider the term

(B.306) $$T_s=-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\!\cdot\!\mathbf{I}'\!\cdot\!\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}.$$

A first-order closure scheme for this expression would be

(B.307) $$\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\!\cdot\!\mathbf{I}'\right\rangle_{\Omega_{ss},\Omega}\approx\hat{\mathbf{R}}_t\!\cdot\!\mathbf{I}'\!\cdot\!\left\langle\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right\rangle_{\Omega_{ss},\Omega}.$$

Because both terms within the averaging operators are zero, we can neglect this term. Note this is not as complete as deriving an expression that reduces to the equilibrium condition that applies to this case, but we haven't succeeded in extracting this condition from the CEI.

The next set of terms from Eq. (B.304) that we will deal with involve averages over interfaces and common curves. These terms may be written as

$$
\begin{aligned}
\text{(B.308)} \quad T_{\text{avg}} = & -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ss},\Omega} \\
& + \frac{1}{\theta^{\overline{\overline{wg}}}} \left\langle \left(p_w - p_g - \gamma_{wg} \nabla' \cdot \mathbf{n}_w \right) \left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_w \right\rangle_{\Omega_{wg},\Omega} \\
& - \frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \left(p_w + \gamma_{ws} \nabla' \cdot \mathbf{n}_s \right) \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega} \\
& - \frac{1}{\theta^{\overline{\overline{gs}}}} \left\langle \left(p_g + \gamma_{gs} \nabla' \cdot \mathbf{n}_s \right) \left(\mathbf{v}_{gs} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_{gs},\Omega} \\
& - \frac{1}{\theta^{\overline{\overline{wgs}}}} \left\langle \left(\gamma_{wgs} \kappa_{Gwgs} + \gamma_{ws} - \gamma_{gs} + \gamma_{wg} \cos \varphi_{ws,wg} \right) \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \\
& - \frac{1}{\theta^{\overline{\overline{wgs}}}} \left\langle \left(\gamma_{wgs} \kappa_{Nwgs} - \gamma_{wg} \sin \varphi_{ws,wg} \right) \mathbf{n}_s \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}.
\end{aligned}
$$

The terms in Eq. (B.308) that involve fluid pressures need to be manipulated into force-flux form. We have previously considered terms of a similar form [89, 90]. The derivation of evolution equations is based upon averaging theorems and approximations of residual error terms. The situation at hand is somewhat different due to the domain being megascale in one dimension, thus the averaging theorem formulation must be re-examined.

Averaging the normal and geodesic curvature over the common curve we have

$$
\text{(B.309)} \qquad \kappa_N^{\overline{\overline{wgs}}} = \left\langle \kappa_{Nwgs} \right\rangle_{\Omega_{wgs},\Omega}, \text{ and}
$$

$$
\text{(B.310)} \qquad \kappa_G^{\overline{\overline{wgs}}} = \left\langle \kappa_{Gwgs} \right\rangle_{\Omega_{wgs},\Omega}.
$$

Next we define the macroscale contact angle such that

$$(\text{B.311}) \qquad \cos\varphi^{\overline{\overline{ws,wg}}} = \frac{\langle\cos\left(\varphi_{ws,wg}\right)\rangle_{\Omega_{wgs},\Omega_{wgs}}}{[\langle\cos\left(\varphi_{ws,wg}\right)\rangle^2_{\Omega_{wgs},\Omega_{wgs}} + \langle\sin\left(\varphi_{ws,wg}\right)\rangle^2_{\Omega_{wgs},\Omega_{wgs}}]^{1/2}},$$

and similarly

$$(\text{B.312}) \qquad \sin\varphi^{\overline{\overline{ws,wg}}} = \frac{\langle\sin\left(\varphi_{ws,wg}\right)\rangle_{\Omega_{wgs},\Omega_{wgs}}}{[\langle\cos\left(\varphi_{ws,wg}\right)\rangle^2_{\Omega_{wgs},\Omega_{wgs},} + \langle\sin\left(\varphi_{ws,wg}\right)\rangle^2_{\Omega_{wgs},\Omega_{wgs},}]^{1/2}}.$$

The macroscale surface curvature, J_ι^κ, obtained as the divergence of $\mathbf{n}_\iota$ averaged over the κ interface, is defined by

$$(\text{B.313}) \qquad J_\iota^\kappa = \langle\nabla'\cdot\mathbf{n}_\iota\rangle_{\Omega_\kappa,\Omega_\kappa},$$

while the surface curvature weighted by the interfacial tension is defined as

$$(\text{B.314}) \qquad J_\iota^{\overline{\overline{\kappa}}} = \langle\nabla'\cdot\mathbf{n}_\iota\rangle_{\Omega_\kappa,\Omega_\kappa,\gamma_\kappa},$$

where $\Omega_\kappa = \bar\Omega_\iota \cap \bar\Omega_\alpha$, ι and α are phase qualifiers, and $\kappa \in \mathfrak{I}_{\mathrm{I}}$.

We can write

$$(\text{B.315}) \qquad \langle\gamma_\kappa\nabla'\cdot\mathbf{n}_\iota\rangle_{\Omega_\kappa,\Omega_\kappa} = \gamma^\kappa J_\iota^\kappa + \langle(\gamma_\kappa - \gamma^\kappa)\nabla'\cdot\mathbf{n}_\iota\rangle_{\Omega_\kappa,\Omega_\kappa}.$$

The macroscale pressure of phase ι averaged over an interface κ is denoted p_ι^κ where

$$(\text{B.316}) \qquad p_\iota^\kappa = \langle p_\iota\rangle_{\Omega_\kappa,\Omega_\kappa} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{f}} \text{ and } \kappa \in \mathfrak{I}_{\mathrm{c}\iota},$$

and the macroscale tension of surface ι averaged over the common curve wgs is defined by

$$(\text{B.317}) \qquad \gamma_\iota^{wgs} = \langle\gamma_\iota\rangle_{\Omega_{wgs},\Omega_{wgs}} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}.$$

Define the fractional entity measure as

$$(\text{B.318}) \qquad \chi_\iota^\kappa = \frac{\epsilon^\iota}{\epsilon^\kappa} \quad \text{for } \iota, \kappa \in \mathfrak{I}.$$

A common instance of the χ operator occurs when ss denotes the entire surface of the solid phase and the fraction of the solid surface in contact with the κ phase is

(B.319)
$$\chi_{\kappa s}^{ss} = \frac{\epsilon^{\kappa s}}{\epsilon^{ss}} \quad \text{for } \kappa \in \mathcal{I}_\mathrm{f},$$

where ϵ^{ss} is the specific surface area of the solid surface.

We can derive geometric density approximations by extending the formulation of [89] in accordance with SEI Approximation 8. Because the transport and gradient theorems for the system under consideration in this work are different than the transport and gradient theorem for the three-dimensional macroscale system that was previously considered [89], it will be necessary to reconsider expressions that may be derived based upon the averaging theorems.

Applying Theorem 3.4.2 and Theorem 3.4.3 to $f_\iota = 1$, we get

(B.320)
$$\nabla'\epsilon^\iota = -\sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \langle \mathbf{n}_\iota \rangle_{\Omega_\kappa,\Omega} - \langle \mathbf{e} \rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathcal{I}_\mathrm{P},$$

and

(B.321)
$$\frac{\partial'\epsilon^\iota}{\partial t} = \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa \rangle_{\Omega_\kappa,\Omega} + \langle \mathbf{e}\cdot\mathbf{v}_{\mathrm{ext}} \rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathcal{I}_\mathrm{P}.$$

Adding the dot product of Eq. (B.320) with the macroscale velocity of the solid phase $\mathbf{v}^{\bar{s}}$ to Eq. (B.321) provides

(B.322)
$$\frac{\mathrm{D}^{\bar{s}}\epsilon^\iota}{\mathrm{D}t} = \sum_{\kappa \in \mathcal{I}_{\mathrm{C}\iota}} \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_\kappa,\Omega} + \left\langle \mathbf{e}\cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathcal{I}_\mathrm{P}.$$

For the solid phase, Eq. (B.322) yields

(B.323)
$$\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t} = \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{ws},\Omega} + \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{gs} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{gs},\Omega}$$
$$+ \left\langle \mathbf{e}\cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Gamma_{sM},\Omega}.$$

When there is no mass transfer to or from the solid phase, the normal velocity of the solid phase is equal to the velocity of the fluid-solid interfaces normal to the solid surface. Because the solid surface ss is equal to the sum of the ws and gs surfaces, we get

$$\text{(B.324)} \qquad \frac{D^{\overline{s}}\epsilon^s}{Dt} = \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ss},\Omega} + \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega},$$

and as a result of SEI Approximation 5, we can write

$$\text{(B.325)} \qquad \chi_{\kappa s}^{ss} \frac{D^{\overline{s}}\epsilon^s}{Dt} \approx \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{\kappa s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{\kappa s},\Omega} + \chi_{\kappa s}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega},$$

where $\kappa \in \mathfrak{I}_{\text{f}}$.

Eq. (B.325) can be rearranged to give

$$\text{(B.326)} \qquad \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{\kappa s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{\kappa s},\Omega} \approx \chi_{\kappa s}^{ss} \frac{D^{\overline{s}}\epsilon^s}{Dt} - \chi_{\kappa s}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega},$$

where $\kappa \in \mathfrak{I}_{\text{f}}$.

Taking into account $\mathbf{n}_w = -\mathbf{n}_s$ on the ws interface, we get from Eq. (B.322) for the w phase

$$\text{(B.327)} \qquad \frac{D^{\overline{s}}\epsilon^w}{Dt} = -\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} + \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wg},\Omega}$$

$$+ \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{wM},\Omega}.$$

Substitution of Eq. (B.325) into Eq. (B.327) gives us

$$\text{(B.328)} \qquad \frac{D^{\overline{s}}\epsilon^w}{Dt} + \chi_{ws}^{ss} \frac{D^{\overline{s}}\epsilon^s}{Dt} \approx \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wg},\Omega} + \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{wM},\Omega}$$

$$+ \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega},$$

and rearranging yields the approximation

$$\text{(B.329)} \qquad \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wg},\Omega} \approx \frac{D^{\overline{s}}\epsilon^w}{Dt} + \chi_{ws}^{ss} \frac{D^{\overline{s}}\epsilon^s}{Dt} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{wM},\Omega}$$

$$- \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega}.$$

A capillary pressure term that arises in the constrained entropy inequality can be written for the case of a massless interface as

$$(B.330) \qquad \theta^{\overline{\overline{wg}}} T_\eta = \left\langle \left(p_w - p_g - \gamma_{wg} \nabla' \cdot \mathbf{n}_w \right) \left(\mathbf{v}_{wg} - \mathbf{v}^{\bar{s}} \right) \cdot \mathbf{n}_w \right\rangle_{\Omega_{wg}, \Omega}.$$

[90] derived an approximation to Eqn (B.330), which can be written as

$$(B.331) \qquad \theta^{\overline{\overline{wg}}} T_\eta \approx \left(A^{\overline{\overline{wg}}} - \frac{\gamma^{wg}}{\left(p_w^{wg} - p_g^{wg} \right)} \hat{k}_1^{wg} \left(\epsilon^{wg} - \epsilon_{eq}^{wg} \right) \right) \left(p_w^{wg} - p_g^{wg} - J_w^{wg} \gamma^{wg} \right),$$

where

$$(B.332) \qquad A^{\overline{\overline{wg}}} = \left\langle \left(\mathbf{v}_{wg} - \mathbf{v}^{\bar{s}} \right) \cdot \mathbf{n}_w \right\rangle_{\Omega_{wg}, \Omega},$$

is approximated by Eq. (B.329), the equilibrium specific interfacial area of the wg interface is parameterized in general form as

$$(B.333) \qquad \epsilon_{eq}^{wg} = \epsilon_{eq}^{wg} \left(s^w, J_w^{wg} \right),$$

and the coefficient $\hat{k}_1^{wg}$ is defined as

$$(B.334) \qquad \hat{k}^{wg} = \left(\frac{J_w^{wg} \gamma^{wg}}{p_w^{wg} - p_g^{wg}} - 1 \right) \hat{k}_1^{wg},$$

where s^w is the wetting phase saturation, and $\hat{k}^{wg}$ is a function of system variables. The approximation in Eq. (B.331) is based on the assumption that the difference between microscale and macroscale values of interfacial tension and fluid pressures at the interface are less important than changes in the curvature of the interface. This assumption is documented in SEI Approximation 9.

Similarly we can apply Theorem 3.4.5 and Theorem 3.4.6 to $f_\iota = 1$, and we get

$$(B.335) \quad \nabla' \epsilon^\iota = \nabla' \cdot \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \rangle_{\Omega_\iota, \Omega} - \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha \right) \mathbf{n}_\alpha \right\rangle_{\Omega_\iota, \Omega}$$

$$- \langle \mathbf{n}_\iota \rangle_{\Omega_{wgs}, \Omega} - \left\langle \frac{\mathbf{e}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M}, \Omega} \qquad \text{for } \iota \in \mathbb{J}_\mathbf{I}, \alpha \in (\mathbb{J}_{c\iota} \cap \mathbb{J}_\mathbf{P})$$

and

$$(\text{B.336}) \quad \frac{\partial^{\backslash} \epsilon^{\iota}}{\partial t} = -\nabla^{\backslash} \cdot \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{v}_\iota \rangle_{\Omega_\iota,\Omega} + \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha \right) \mathbf{n}_\alpha \cdot \mathbf{v}_\iota \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \langle \mathbf{n}_\iota \cdot \mathbf{v}_{wgs} \rangle_{\Omega_{wgs},\Omega} + \left\langle \frac{\mathbf{e} \cdot \mathbf{v}_{\text{ext}}}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}, \alpha \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{P}}).$$

Adding the dot product of Eq. (B.335) with the macroscale solid-phase velocity $\mathbf{v}^{\overline{s}}$ to Eq. (B.336) provides

$$(\text{B.337}) \quad \frac{\mathrm{D}^{\overline{s}} \epsilon^{\iota}}{\mathrm{D}t} = -\nabla^{\backslash} \cdot \left\langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\iota,\Omega} - \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \rangle_{\Omega_\iota,\Omega} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha \right) \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\iota,\Omega} + \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

$$+ \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} .$$

Following [89], we can define the average macroscale interface velocity normal to the interface as

$$(\text{B.338}) \qquad \mathbf{w}^{\overline{\overline{\iota}}} = \langle \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \mathbf{v}_\iota \rangle_{\Omega_\iota,\Omega_\iota} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}}, \alpha \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{P}}).$$

Eqs. (B.337) and (B.338) can be combined, the curvature term can be decomposed, and the geometric orientation tensor can be used to yield

$$(\text{B.339}) \quad \frac{\mathrm{D}^{\overline{s}} \epsilon^{\iota}}{\mathrm{D}t} = -\nabla^{\backslash} \cdot \left[\epsilon^{\iota} \left(\mathbf{w}^{\overline{\overline{\iota}}} - \mathbf{G}^{\iota} \cdot \mathbf{v}^{\overline{s}} \right) \right] - \epsilon^{\iota} \mathbf{G}^{\iota} : \mathbf{d}^{\overline{\overline{s}}} + J_\alpha^{\iota} \left\langle \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\iota,\Omega}$$

$$+ \left\langle \left(\nabla' \cdot \mathbf{n}_\alpha - J_\alpha^{\iota} \right) \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\iota,\Omega} + \left\langle \mathbf{n}_\iota \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

$$+ \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_\iota \cdot \mathbf{e}} \right\rangle_{\Gamma_{\iota M},\Omega} \quad \text{for } \iota \in \mathfrak{I}_{\mathrm{I}} \text{ and } \alpha \in (\mathfrak{I}_{\mathrm{c}\iota} \cap \mathfrak{I}_{\mathrm{P}}).$$

We are seeking expressions for the averages of the normal components of $\mathbf{v}_{wgs}$ relative to $\mathbf{v}^{\overline{s}}$. Eq. (B.339) applies to any interface. Let's consider the fluid-solid interface

instances of Eq. (B.339) and let $\alpha = s$. According to SEI Approximation 7, we note that

(B.340) $\qquad \left\langle \left(\nabla' \cdot \mathbf{n}_s - J_s^\iota \right) \mathbf{n}_s \cdot \left(\mathbf{v}_\iota - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\iota,\Omega} \approx 0 \quad \text{for } \iota \in \{ws, gs\}.$

Combining Eqs. (B.339) and (B.340) for the ws interface yields

(B.341) $\quad \dfrac{\mathrm{D}^{\overline{s}} \epsilon^{ws}}{\mathrm{D}t} \approx -\nabla' \cdot \left[\epsilon^{ws} \left(\mathbf{w}^{\overline{\overline{ws}}} - \mathbf{G}^{ws} \cdot \mathbf{v}^{\overline{s}} \right) \right] - \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\backslash \overline{s}}$

$\qquad + J_s^{ws} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} + \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$

$\qquad + \left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega}.$

Substituting Eq. (B.326) into Eq. (B.341) yields

(B.342) $\quad \dfrac{\mathrm{D}^{\overline{s}} \epsilon^{ws}}{\mathrm{D}t} \approx -\nabla' \cdot \left[\epsilon^{ws} \left(\mathbf{w}^{\overline{\overline{ws}}} - \mathbf{G}^{ws} \cdot \mathbf{v}^{\overline{s}} \right) \right] - \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\backslash \overline{s}}$

$\qquad + J_s^{ws} \left[\chi_{ws}^{ss} \dfrac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$

$\qquad + \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} + \left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega},$

or

(B.343) $\quad \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \dfrac{\mathrm{D}^{\overline{s}} \epsilon^{ws}}{\mathrm{D}t} + \nabla' \cdot \left[\epsilon^{ws} \left(\mathbf{w}^{\overline{\overline{ws}}} - \mathbf{G}^{ws} \cdot \mathbf{v}^{\overline{s}} \right) \right]$

$\qquad + \epsilon^{ws} \mathbf{G}^{ws} : \mathbf{d}^{\backslash \overline{s}} - J_s^{ws} \left[\chi_{ws}^{ss} \dfrac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$

$\qquad - \left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega}.$

Because of SEI Approximation 5, we can write

(B.344) $\qquad\qquad\qquad\qquad \mathbf{G}^{ws} \approx \mathbf{G}^{gs} \approx \mathbf{G}^{ss},$

and

(B.345) $$\mathbf{n}_s \cdot \mathbf{v}_s \approx \mathbf{n}_s \cdot \mathbf{v}_{ss} \approx \mathbf{n}_s \cdot \mathbf{v}_{ws} \approx \mathbf{n}_s \cdot \mathbf{v}_{gs} \approx \mathbf{n}_s \cdot \mathbf{v}_{wgs},$$

which allows Eq. (B.343) to be written as

(B.346) $\left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \dfrac{\mathrm{D}^{\bar{s}} \epsilon^{ws}}{\mathrm{D}t} + \nabla^{\backprime} \cdot \left[\epsilon^{ws} \left(\mathbf{w}^{\overline{\overline{ws}}} - \mathbf{G}^{ss} \cdot \mathbf{v}^{\bar{s}} \right) \right]$

$$+\epsilon^{ws} \mathbf{G}^{ss} : \mathbf{d}^{\backprime \bar{\bar{s}}} - J_s^{ws} \left[\chi_{ws}^{ss} \dfrac{\mathrm{D}^{\bar{s}} \epsilon^s}{\mathrm{D}t} - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$$

$$-\left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega}.$$

As a result of SEI Approximations 4 and 5 the second term on the RHS of Eq. (B.346) vanishes giving

(B.347) $\left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \dfrac{\mathrm{D}^{\bar{s}} \epsilon^{ws}}{\mathrm{D}t} + \epsilon^{ws} \mathbf{G}^{ss} : \mathbf{d}^{\backprime \bar{\bar{s}}}$

$$-J_s^{ws} \left[\chi_{ws}^{ss} \dfrac{\mathrm{D}^{\bar{s}} \epsilon^s}{\mathrm{D}t} - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$$

$$-\left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega}.$$

Eq. (B.347) may also be written as

(B.348) $\left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \chi_{ws}^{ss} \dfrac{\mathrm{D}^{\bar{s}} \epsilon^{ss}}{\mathrm{D}t} + \epsilon^{ss} \dfrac{\mathrm{D}^{\bar{s}} \chi_{ws}^{ss}}{\mathrm{D}t} + \chi_{ws}^{ss} \epsilon^{ss} \mathbf{G}^{ss} : \mathbf{d}^{\backprime \bar{\bar{s}}}$

$$-J_s^{ws} \left[\chi_{ws}^{ss} \dfrac{\mathrm{D}^{\bar{s}} \epsilon^s}{\mathrm{D}t} - \chi_{ws}^{ss} \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$$

$$-\left\langle \dfrac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega}.$$

A similar set of manipulations for the gs interface yields

(B.349) $\left\langle \mathbf{n}_{gs} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \chi_{gs}^{ss} \dfrac{\mathrm{D}^{\bar{s}} \epsilon^{ss}}{\mathrm{D}t} + \epsilon^{ss} \dfrac{\mathrm{D}^{\bar{s}} \chi_{gs}^{ss}}{\mathrm{D}t} + \chi_{gs}^{ss} \epsilon^{ss} \mathbf{G}^{ss} : \mathbf{d}^{\backprime \bar{\bar{s}}}$

$$-J_s^{gs}\left[\chi_{gs}^{ss}\frac{D^{\overline{s}}\epsilon^s}{Dt} - \chi_{gs}^{ss}\left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}.$$

Adding Eqs. (B.348) and (B.349) we get

$$(\text{B.350}) \quad 0 \approx \frac{D^{\overline{s}}\epsilon^{ss}}{Dt} + \epsilon^{ss}\mathbf{G}^{ss}{:}\mathbf{d}^{\backslash\overline{\overline{s}}} - J_s^{ss}\left[\frac{D^{\overline{s}}\epsilon^s}{Dt} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega} - \left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega},$$

where $J_s^{ss} = J_s^{ws}\chi_{ws}^{ss} + J_s^{gs}\chi_{gs}^{ss}$, which can also be written as

$$(\text{B.351}) \quad \frac{D^{\overline{s}}\epsilon^{ss}}{Dt} + \epsilon^{ss}\mathbf{G}^{ss}{:}\mathbf{d}^{\backslash\overline{\overline{s}}} - J_s^{ss}\left[\frac{D^{\overline{s}}\epsilon^s}{Dt} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$\approx\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega} + \left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}.$$

Combining Eqs. (B.348) and (B.351) and assuming $J_s^{ws} \approx J_s^{gs} \approx J_s^{ss}$ yields

$$(\text{B.352}) \quad \left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega} \approx \epsilon^{ss}\frac{D^{\overline{s}}\chi_{ws}^{ss}}{Dt}$$

$$-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega} + \chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}.$$

Using Eq. (B.345), the normal velocity component of the common curve can be written as

$$(\text{B.353}) \qquad\qquad \left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega} \approx \frac{\epsilon^{wgs}}{\epsilon^{ss}}\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ss},\Omega}.$$

Substituting Eq. (B.324) into Eq. (B.353), we get

$$(\text{B.354}) \qquad \left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega} \approx \frac{\epsilon^{wgs}}{\epsilon^{ss}}\left(\frac{D^{\overline{s}}\epsilon^s}{Dt} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right).$$

Using Eq. (B.324), we can write the first term in the right hand side of Eq. (B.308) as

(B.355) $\quad -\dfrac{1}{\theta^{\overline{\overline{s}}}}\Big\langle \mathbf{n}_s \cdot \mathbf{t}_s{\cdot}\mathbf{n}_s\mathbf{n}_s{\cdot}\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{ss},\Omega}$

$\approx -\dfrac{1}{\theta^{\overline{\overline{s}}}}\langle \mathbf{n}_s \cdot \mathbf{t}_s{\cdot}\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}}\Big\langle \mathbf{n}_s{\cdot}\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{ss},\Omega}$

$= -\dfrac{1}{\theta^{\overline{\overline{s}}}}\langle \mathbf{n}_s \cdot \mathbf{t}_s{\cdot}\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}}\left(\dfrac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} - \Big\langle \mathbf{e}{\cdot}\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Gamma_{sM},\Omega}\right).$

The second term of Eq. (B.308) is approximated in Eqns (B.331)–(B.334). Substituting Eq. (B.315) into the third and the fourth terms of Eq. (B.308) yields

(B.356) $\quad -\dfrac{1}{\theta^{\overline{\overline{\iota s}}}}\Big\langle \left(p_\iota + \gamma_{\iota s}\nabla'{\cdot}\mathbf{n}_s\right)\left(\mathbf{v}_{\iota s} - \mathbf{v}^{\overline{s}}\right){\cdot}\mathbf{n}_s\Big\rangle_{\Omega_{\iota s},\Omega}$

$\approx -\dfrac{1}{\theta^{\overline{\overline{\iota s}}}}\langle p_\iota + \gamma_{\iota s}\nabla'{\cdot}\mathbf{n}_s\rangle_{\Omega_{\iota s},\Omega_{\iota s}}\Big\langle \left(\mathbf{v}_{\iota s} - \mathbf{v}^{\overline{s}}\right){\cdot}\mathbf{n}_s\Big\rangle_{\Omega_{\iota s},\Omega}$

$\approx -\dfrac{1}{\theta^{\overline{\overline{\iota s}}}}\left(p_\iota^{\iota s} + \gamma^{\iota s}J_s^{\iota s} + \langle(\gamma_{\iota s} - \gamma^{\iota s})\nabla'{\cdot}\mathbf{n}_s\rangle_{\Omega_{\iota s},\Omega_{\iota s}}\right)\Big\langle \left(\mathbf{v}_{\iota s} - \mathbf{v}^{\overline{s}}\right){\cdot}\mathbf{n}_s\Big\rangle_{\Omega_{\iota s},\Omega}.$

According to SEI Approximation 7 the third term in Eq. (B.356) is negligibly small. So, applying Eq. (B.326) we have

(B.357) $\quad -\dfrac{1}{\theta^{\overline{\overline{\iota s}}}}\Big\langle \left(p_\iota + \gamma_{\iota s}\nabla'{\cdot}\mathbf{n}_s\right)\left(\mathbf{v}_{\iota s} - \mathbf{v}^{\overline{s}}\right){\cdot}\mathbf{n}_s\Big\rangle_{\Omega_{\iota s},\Omega}$

$-\dfrac{\chi_{\iota s}^{ss}}{\theta^{\overline{\overline{\iota s}}}}\left(p_\iota^{\iota s} + \gamma^{\iota s}J_s^{\iota s}\right)\left(\dfrac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} - \Big\langle \mathbf{e}{\cdot}\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Gamma_{sM},\Omega}\right).$

Using Eq. (B.352) and Eq. (B.354) as well as assuming separability of variables, the last two terms in the right hand side of Eqn (B.308) can be approximated as

(B.358)

$-\dfrac{1}{\theta^{\overline{\overline{wgs}}}}\langle\left(\gamma_{wgs}\kappa_{Gwgs} + \gamma_{ws} - \gamma_{gs} + \gamma_{wg}\cos\varphi_{ws,wg}\right)\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\rangle_{\Omega_{wgs},\Omega}$

$\approx -\dfrac{1}{\theta^{\overline{\overline{wgs}}}}\left(\gamma^{wgs}\kappa_G^{\overline{\overline{wgs}}} + \gamma_{ws}^{wgs} - \gamma_{gs}^{wgs} + \gamma_{wg}^{wgs}\cos\varphi^{\overline{\overline{ws,wg}}}\right)\left(\epsilon^{ss}\dfrac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}\right.$

$$-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\bar{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}+\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\bar{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\Bigg),$$

and

$$(B.359)\quad -\frac{1}{\theta^{\overline{\overline{wgs}}}}\left\langle\left(\gamma_{wgs}\kappa_{Nwgs}-\gamma_{wg}\sin\varphi_{ws,wg}\right)\mathbf{n}_s\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wgs},\Omega}$$

$$\approx-\frac{\chi_{wgs}^{ss}}{\theta^{\overline{\overline{wgs}}}}\left(\gamma^{wgs}\kappa_N^{\overline{\overline{wgs}}}-\gamma_{wg}^{wgs}\sin\varphi^{\overline{\overline{ws}},\overline{\overline{wg}}}\right)\left(\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t}-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right).$$

Finally, we say that the velocities of the phases averaged over the solid-fluid interface surface, $\mathbf{v}_w^{\overline{ws}}, \mathbf{v}_s^{\overline{ws}}, \mathbf{v}_g^{\overline{gs}}$, and $\mathbf{v}_s^{\overline{gs}}$ are small and will be assumed to be equal to the macroscale solid-phase velocity itself, $\mathbf{v}^{\bar{s}}$. With these changes, the final SEI can be written as

(B.360)

$$\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\epsilon^\iota}{\theta^{\bar{\iota}}}\left(\mathbf{t}^{\backslash\bar{\iota}}+p^\iota\mathbf{I}\right):\mathbf{d}^{\backslash\bar{\iota}}+\frac{\epsilon^s}{\theta^{\bar{\bar{s}}}}\left(\mathbf{t}^{\backslash\bar{s}}-\mathbf{t}^{\backslash s}\right):\mathbf{d}^{\backslash\bar{s}}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\epsilon^\iota}{\theta^{\bar{\iota}}}\left[\mathbf{t}^{\backslash\bar{\iota}}-\gamma^\iota\left(\mathbf{I}-\mathbf{G}^{\backslash\iota}\right)\right]:\mathbf{d}^{\backslash\bar{\iota}}+\frac{\epsilon^{wgs}}{\theta^{\overline{\overline{wgs}}}}\left[\mathbf{t}^{\backslash\overline{\overline{wgs}}}+\gamma^{wgs}\left(\mathbf{I}-\mathbf{G}^{\backslash wgs}\right)\right]:\mathbf{d}^{\backslash\overline{\overline{wgs}}}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{i\in\mathcal{I}_s}\frac{1}{\theta^{\bar{\iota}}}\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mathbf{u}^{\backslash\overline{\overline{i\iota}}}\cdot\nabla^{\backslash}\left(\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{\overline{i\iota}}}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\left(\epsilon^\iota\mathbf{q}^{\backslash\bar{\iota}}+\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\left(\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{\overline{i\iota}}}\right)\mathbf{u}^{\backslash\overline{\overline{i\iota}}}\right)\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\bar{\iota}}}\right)$$

$$-\epsilon^s\mathbf{q}^{\backslash\bar{s}}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\bar{\bar{s}}}}\right)-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\epsilon^\iota\mathbf{q}^{\backslash\bar{\iota}}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\bar{\iota}}}\right)-\epsilon^{wgs}\mathbf{q}^{\backslash\overline{\overline{wgs}}}\cdot\nabla^{\backslash}\left(\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\left(\mathbf{v}^{\backslash\iota}-\mathbf{v}^{\backslash\bar{s}}\right)}{\theta^{\bar{\iota}}}\cdot\left(\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\nabla^{\backslash}\left(\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{\overline{i\iota}}}\right)\right.$$

$$\left.+\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mathbf{g}^{\backslash\overline{i\iota}}-\nabla^{\backslash}\left(\epsilon^\iota p^\iota\right)+\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{I}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota,\bar{s}}}\cdot\mathbf{N}}{\theta^{\bar{\iota}}}\left(\sum_{i\in\mathcal{I}_s}\epsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mathbf{g}^{\overline{i\iota}}\cdot\mathbf{N}+\sum_{\kappa\in\mathcal{I}_{\mathrm{c}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{N}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\backslash\iota}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{\iota}}}}\cdot\left(\nabla^{\backslash}\cdot\left[\epsilon^{\iota}\gamma^{\iota}\left(\mathbf{I}^{\backslash}-\mathbf{G}^{\backslash\iota}\right)\right]+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{I}^{\backslash}\right)$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\left(\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\overset{\kappa\to\iota}{\mathbf{T}}\cdot\mathbf{N}-\left(\nabla^{\backslash}\cdot\mathbf{N}\right)\mathbf{N}\cdot\epsilon^{\iota}\mathbf{G}^{\iota}\cdot\mathbf{N}\gamma^{\iota}\right)$$

$$+\frac{\left(\mathbf{v}^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\cdot\left(\nabla^{\backslash}\cdot\left[\epsilon^{wgs}\gamma^{wgs}\left(\mathbf{I}^{\backslash}-\mathbf{G}^{\backslash wgs}\right)\right]+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}wgs}}\overset{wgs\to\kappa}{\mathbf{T}}\cdot\mathbf{I}^{\backslash}\right)$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{wgs}}}}\left(\sum_{\kappa\in\mathcal{I}_{\mathrm{C}wgs}}\overset{wgs\to\kappa}{\mathbf{T}}\cdot\mathbf{N}-\left(\nabla^{\backslash}\cdot\mathbf{N}\right)\mathbf{N}\cdot\epsilon^{wgs}\mathbf{G}^{wgs}\cdot\mathbf{N}\gamma^{wgs}\right)$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\frac{1}{\theta^{\overline{\overline{\kappa}}}}\sum_{i\in\mathcal{I}_s}\left[\left(\mu^{\overline{i\kappa}}+\psi^{\overline{i\kappa}}\right)-\left(\mu^{\overline{i\iota}}+\psi^{\overline{i\iota}}\right)\right]\overset{i\kappa\to i\iota}{M}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{I}_{\mathrm{C}\iota}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\left[\overset{\kappa\to\iota}{Q}+\sum_{i\in\mathcal{I}_s}\left(\frac{E_{\iota}^{\overline{\overline{\kappa}}}}{\epsilon^{\iota}\rho_{\iota}^{\kappa}}-\mu_{i\iota}^{\overline{\kappa}}\right)\overset{i\kappa\to i\iota}{M}\right.$$

$$\left.+\left(\mathbf{v}_{\iota}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{\kappa\to\iota}{\mathbf{T}}\right]+\sum_{\kappa\in\mathcal{I}_{\mathrm{C}s}}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\overset{\kappa\to s}{Q}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta^{\overline{\overline{wgs}}}}\right)\left[\overset{wgs\to\iota}{Q}+\left(\mathbf{v}_{\iota}^{\overline{wgs}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{wgs\to\iota}{\mathbf{T}}\right]$$

$$+\frac{1}{\theta^{\overline{\overline{wg}}}}\left(p_w^{wg}-p_g^{wg}-\gamma^{wg}J_w^{wg}\right)\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^w}{\mathrm{D}t}+\chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{wM},\Omega}\right.$$

$$\left.-\chi_{ws}^{ss}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}-\frac{\gamma^{wg}}{\left(p_w^{wg}-p_g^{wg}\right)}\hat{k}_1^{wg}\left(\epsilon^{wg}-\epsilon_{\mathrm{eq}}^{wg}\right)\right]$$

$$-\left[\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\chi_{\iota s}^{ss}}{\theta^{\overline{\overline{\iota s}}}}\left(p_{\iota}^{\iota s}+\gamma^{\iota s}J_s^{\iota s}\right)+\frac{1}{\theta^{\overline{\overline{s}}}}\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ss},\Omega_{ss}}\right.$$

$$\left.+\frac{\chi_{wgs}^{ss}}{\theta^{\overline{\overline{wgs}}}}\left(\gamma^{wgs}\kappa_N^{\overline{\overline{wgs}}}-\gamma_{wg}^{wgs}\sin\varphi^{\overline{\overline{ws}},\overline{\overline{wg}}}\right)\right]$$

$$\times\left(\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)$$

$$-\frac{1}{\theta^{\overline{\overline{wgs}}}}\left(\gamma^{wgs}\kappa_G^{\overline{\overline{wgs}}}+\gamma_{ws}^{wgs}-\gamma_{gs}^{wgs}+\gamma_{wg}^{wgs}\cos\varphi^{\overline{\overline{ws},\overline{wg}}}\right)\left(\epsilon^{ss}\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}\right.$$

$$-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}+\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\Bigg)$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\boldsymbol{\tau}_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\iota}}}\cdot\left\langle\frac{\mathbf{e}\cdot p_{\iota}\mathbf{l'}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\backslash\overline{\iota}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\iota}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{\iota}\mathbf{l'}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}+\frac{\left(\mathbf{v}^{\backslash\overline{wgs}}-\mathbf{v}^{\backslash\overline{s}}\right)}{\theta^{\overline{\overline{wgs}}}}\cdot\left\langle\frac{\mathbf{e}\cdot\gamma_{wgs}\mathbf{l''}}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}p_{\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}-\sum_{\iota\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\iota},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{\iota}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{\iota}}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\frac{\mathbf{v}^{\overline{wgs},\overline{s}}\cdot\mathbf{N}}{\theta^{\overline{\overline{wgs}}}}\mathbf{N}\cdot\left\langle\frac{\mathbf{e}\gamma_{wgs}}{\mathbf{n}_{wgs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgsM},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{P}}}\sum_{i\in\mathcal{I}_{s}}\frac{1}{\theta^{\overline{\overline{\iota}}}}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}_{\text{ext}}\right)\rho_{\iota}\omega_{i\iota}\left(\mu_{i\iota}+\psi_{i\iota}-\mu^{\overline{\overline{i\iota}}}-\psi^{\overline{\overline{i\iota}}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$-\sum_{\iota\in\mathcal{I}_{\mathrm{f}}}\left\langle\frac{\mathbf{e}\cdot\displaystyle\sum_{i\in\mathcal{I}_{s}}\rho_{\iota}\omega_{i\iota}\mathbf{u}_{i\iota}\left(\frac{\mu_{i\iota}+\psi_{i\iota}}{\theta_{\iota}}-\frac{\mu^{\overline{\overline{i\iota}}}+\psi^{\overline{\overline{i\iota}}}}{\theta^{\overline{\overline{\iota}}}}\right)}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}$$

$$+\sum_{\iota\in\mathcal{I}}\left\langle\frac{\left(\frac{1}{\theta^{\overline{\overline{\iota}}}}-\frac{1}{\theta_{\iota}}\right)\mathbf{e}\cdot\left[\mathbf{q}_{\iota}-\left(\mathbf{v}_{\iota}-\mathbf{v}_{\text{ext}}\right)\theta_{\iota}\eta_{\iota}\right]}{\mathbf{n}_{\iota}\cdot\mathbf{e}}\right\rangle_{\Gamma_{\iota M},\Omega}=\Lambda\geq0.$$

B.12. Evolution Equations

Recall Eq. (B.348)

$$(\text{B.361})\quad\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wgs}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega}\approx\chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^{ss}}{\mathrm{D}t}+\epsilon^{ss}\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}+\chi_{ws}^{ss}\epsilon^{ss}\mathbf{G}^{ss}:\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-J_{s}^{ws}\left[\chi_{ws}^{ss}\frac{\mathrm{D}^{\overline{s}}\epsilon^{s}}{\mathrm{D}t}-\chi_{ws}^{ss}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega},$$

Eq. (B.349)

(B.362) $\quad \left\langle \mathbf{n}_{gs} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \chi_{gs}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^{ss}}{\mathrm{D}t} + \epsilon^{ss} \frac{\mathrm{D}^{\overline{s}} \chi_{gs}^{ss}}{\mathrm{D}t} + \chi_{gs}^{ss} \epsilon^{ss} \mathbf{G}^{ss} {:} \mathbf{d}^{\backslash \overline{\overline{s}}}$

$$\quad - J_s^{gs} \left[\chi_{gs}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \chi_{gs}^{ss} \left\langle \mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$$

$$\quad - \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega},$$

Eq. (B.350)

(B.363) $\quad \dfrac{\mathrm{D}^{\overline{s}} \epsilon^{ss}}{\mathrm{D}t} + \epsilon^{ss} \mathbf{G}^{ss} {:} \mathbf{d}^{\backslash \overline{\overline{s}}} - J_s^{ss} \left[\dfrac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$

$$\approx \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} + \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega},$$

and Eq. (B.352)

(B.364) $\quad \left\langle \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \epsilon^{ss} \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t}$

$$\quad - \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} + \chi_{ws}^{ss} \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega}.$$

Eqs. (B.362) and (B.363) can be combined to yield

(B.365) $\quad \left\langle \mathbf{n}_{gs} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} \approx \epsilon^{ss} \frac{\mathrm{D}^{\overline{s}} \chi_{gs}^{ss}}{\mathrm{D}t}$

$$\quad + \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} - \chi_{ws}^{ss} \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega}.$$

Combining Eqs. (B.361) and (B.364) produces the evolution equation

(B.366) $\quad \chi_{ws}^{ss} \dfrac{\mathrm{D}^{\overline{s}} \epsilon^{ss}}{\mathrm{D}t} + \epsilon^{ss} \dfrac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t} + \chi_{ws}^{ss} \epsilon^{ss} \mathbf{G}^{ss} {:} \mathbf{d}^{\backslash \overline{\overline{s}}}$

$$\quad - J_s^{ws} \left[\chi_{ws}^{ss} \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \chi_{ws}^{ss} \left\langle \mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right]$$

$$\quad - \left\langle \frac{\mathbf{e} {\cdot} \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} {\cdot} \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} - \epsilon^{ss} \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t}$$

$$+\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}-\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\approx 0,$$

or

$$(\text{B.367})\quad \frac{\text{D}^{\overline{s}}\epsilon^{ws}}{\text{D}t}+\epsilon^{ws}\mathbf{G}^{ss}\mathbf{:}\mathbf{d}^{\backslash\overline{\overline{s}}}-J_s^{ws}\chi_{ws}^{ss}\left[\frac{\text{D}^{\overline{s}}\epsilon^s}{\text{D}t}-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$-\epsilon^{ss}\frac{\text{D}^{\overline{s}}\chi_{ws}^{ss}}{\text{D}t}-\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}$$

$$-\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\approx 0.$$

Combining Eqs. (B.362) and (B.365) produces the evolution equation

$$(\text{B.368})\quad \chi_{gs}^{ss}\frac{\text{D}^{\overline{s}}\epsilon^{ss}}{\text{D}t}+\epsilon^{ss}\frac{\text{D}^{\overline{s}}\chi_{gs}^{ss}}{\text{D}t}+\chi_{gs}^{ss}\epsilon^{ss}\mathbf{G}^{ss}\mathbf{:}\mathbf{d}^{\backslash\overline{\overline{s}}}$$

$$-J_s^{gs}\left[\chi_{gs}^{ss}\frac{\text{D}^{\overline{s}}\epsilon^s}{\text{D}t}-\chi_{gs}^{ss}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$-\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}-\epsilon^{ss}\frac{\text{D}^{\overline{s}}\chi_{gs}^{ss}}{\text{D}t}$$

$$-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}+\chi_{ws}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\approx 0,$$

or

$$(\text{B.369})\quad \frac{\text{D}^{\overline{s}}\epsilon^{gs}}{\text{D}t}+\epsilon^{gs}\mathbf{G}^{ss}\mathbf{:}\mathbf{d}^{\backslash\overline{\overline{s}}}-J_s^{gs}\chi_{gs}^{ss}\left[\frac{\text{D}^{\overline{s}}\epsilon^s}{\text{D}t}-\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right]$$

$$-\epsilon^{ss}\frac{\text{D}^{\overline{s}}\chi_{gs}^{ss}}{\text{D}t}-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}$$

$$-\chi_{gs}^{ss}\left\langle\frac{\mathbf{e}\cdot\left(\mathbf{v}_{\text{ext}}-\mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}\approx 0.$$

Recalling Eq. (B.339), we can set $\iota=wg$ so that

(B.370) $\dfrac{\mathrm{D}^{\overline{s}}\epsilon^{wg}}{\mathrm{D}t} = -\nabla'\cdot\left[\epsilon^{wg}\left(\mathbf{w}^{\overline{\overline{wg}}} - \mathbf{G}^{wg}\cdot\mathbf{v}^{\overline{s}}\right)\right] - \epsilon^{wg}\mathbf{G}^{wg}\mathbf{:}\mathbf{d}^{\overline{\overline{s}}}$

$\qquad + J_w^{wg}\left\langle\mathbf{n}_w\cdot\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wg},\Omega} + \left\langle\left(\nabla'\cdot\mathbf{n}_w - J_w^{wg}\right)\mathbf{n}_w\cdot\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wg},\Omega}$

$\qquad + \left\langle\mathbf{n}_{wg}\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega} + \left\langle\dfrac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{wg}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgM},\Omega},$

for $\alpha \in \left(\mathfrak{I}_{cwg} \cap \mathfrak{I}_{\mathrm{P}}\right)$. We can make use of the identity given in Eq. (B.298) to express $\mathbf{n}_{wg}$ in terms of $\mathbf{n}_{ws}$ and $\mathbf{n}_s$. In addition we approximate that the contact angle can be decoupled from the velocity of the common curve. With those changes, Eq. (B.370) becomes

(B.371) $\dfrac{\mathrm{D}^{\overline{s}}\epsilon^{wg}}{\mathrm{D}t} \approx -\nabla'\cdot\left[\epsilon^{wg}\left(\mathbf{w}^{\overline{\overline{wg}}} - \mathbf{G}^{wg}\cdot\mathbf{v}^{\overline{s}}\right)\right] - \epsilon^{wg}\mathbf{G}^{wg}\mathbf{:}\mathbf{d}^{\overline{\overline{s}}}$

$\qquad + J_w^{wg}\left\langle\mathbf{n}_w\cdot\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wg},\Omega} + \left\langle\left(\nabla'\cdot\mathbf{n}_w - J_w^{wg}\right)\mathbf{n}_w\cdot\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wg},\Omega}$

$\qquad + \left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega}\cos\varphi^{\overline{\overline{ws,wg}}}$

$\qquad - \left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wgs},\Omega}\sin\varphi^{\overline{\overline{ws,wg}}} + \left\langle\dfrac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{wg}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgM},\Omega}.$

Next we can apply Eq. (B.329), Eq. (B.352), and Eq. (B.354) to Eq. (B.371) to get

(B.372) $\dfrac{\mathrm{D}^{\overline{s}}\epsilon^{wg}}{\mathrm{D}t} \approx -\nabla'\cdot\left[\epsilon^{wg}\left(\mathbf{w}^{\overline{\overline{wg}}} - \mathbf{G}^{wg}\cdot\mathbf{v}^{\overline{s}}\right)\right] - \epsilon^{wg}\mathbf{G}^{wg}\mathbf{:}\mathbf{d}^{\overline{\overline{s}}}$

$\qquad + J_w^{wg}\left(\dfrac{\mathrm{D}^{\overline{s}}\epsilon^w}{\mathrm{D}t} + \chi_{ws}^{ss}\dfrac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} - \left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{wM},\Omega}\right.$

$\qquad\qquad \left. - \chi_{ws}^{ss}\left\langle\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)$

$\qquad + \left\langle\left(\nabla'\cdot\mathbf{n}_w - J_w^{wg}\right)\mathbf{n}_w\cdot\left(\mathbf{v}_{wg} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wg},\Omega}$

$\qquad + \left(\epsilon^{ss}\dfrac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t} - \chi_{gs}^{ss}\left\langle\dfrac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}\right.$

$\qquad\qquad \left. + \chi_{ws}^{ss}\left\langle\dfrac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\right)\cos\varphi^{\overline{\overline{ws,wg}}}$

$$-\frac{\epsilon^{wgs}}{\epsilon^{ss}}\left(\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)\sin\varphi^{\overline{\overline{ws,wg}}}$$

$$+\left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)}{\mathbf{n}_{wg}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wgM},\Omega}.$$

Following [89], we define

$$e^{\overline{\overline{wg}}} = \left\langle \left(\nabla'\cdot\mathbf{n}_w - J_w^{wg}\right)\mathbf{n}_w\cdot\left(\mathbf{v}_{wg} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wg},\Omega}$$

where $e^{\overline{\overline{wg}}}$ represents the processes of coalescence and division of phase resulting from the creation or destruction of interfacial area and is subject to experimentation. We approximate $e^{\overline{\overline{wg}}}$ using a linear relation

$$e^{\overline{\overline{wg}}} \approx -\hat{k}^{wg}\left(\epsilon^{wg} - \epsilon_{\mathrm{eq}}^{wg}\right)$$

where $\epsilon_{\mathrm{eq}}^{wg}$ and $\hat{k}^{wg}$ are as described in Eq. (B.333) and Eq. (B.334). So the evolution of the wg interface is described by

$$\text{(B.373)}\quad \frac{\mathrm{D}^{\bar{s}}\epsilon^{wg}}{\mathrm{D}t} + \nabla'\cdot\left[\epsilon^{wg}\left(\mathbf{w}^{\overline{\overline{wg}}} + \mathbf{G}^{wg}\cdot\mathbf{v}^{\bar{s}}\right)\right] + \epsilon^{wg}\mathbf{G}^{wg}\mathbf{:}\mathbf{d}^{\bar{\bar{s}}}$$

$$-J_w^{wg}\left(\frac{\mathrm{D}^{\bar{s}}\epsilon^w}{\mathrm{D}t} + \chi_{ws}^{ss}\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{wM},\Omega}\right.$$

$$\left. -\chi_{ws}^{ss}\left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)$$

$$+\hat{k}^{wg}\left(\epsilon^{wg} - \epsilon_{\mathrm{eq}}^{wg}\right)$$

$$-\left(\epsilon^{ss}\frac{\mathrm{D}^{\bar{s}}\chi_{ws}^{ss}}{\mathrm{D}t} - \chi_{gs}^{ss}\left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)}{\mathbf{n}_{ws}\cdot\mathbf{e}}\right\rangle_{\Gamma_{wsM},\Omega}\right.$$

$$\left. +\chi_{ws}^{ss}\left\langle \frac{\mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)}{\mathbf{n}_{gs}\cdot\mathbf{e}}\right\rangle_{\Gamma_{gsM},\Omega}\right)\cos\varphi^{\overline{\overline{ws,wg}}}$$

$$+\frac{\epsilon^{wgs}}{\epsilon^{ss}}\left(\frac{\mathrm{D}^{\bar{s}}\epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e}\cdot\left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Gamma_{sM},\Omega}\right)\sin\varphi^{\overline{\overline{ws,wg}}}$$

$$-\left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{wg} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgM},\Omega} \approx 0.$$

For the common curve we use the transport theorem Eq. (3.13) and add to it $\mathbf{v}^{\overline{s}}$ multiplied by the gradient theorem given by Eq. (3.12). Using the definitions for the geometric and normal curvatures we are able to write

$$(\text{B.374}) \quad \frac{D^{\overline{s}} \epsilon^{wgs}}{Dt} + \nabla' \cdot \left[\epsilon^{wgs} \left(\mathbf{w}^{\overline{wgs}} - \mathbf{G}^{wgs} \cdot \mathbf{v}^{\overline{s}} \right) \right] + \epsilon^{wgs} \mathbf{G}^{wgs} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \left\langle \kappa_{Nwgs} \mathbf{n}_s \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega} + \left\langle \kappa_{Gwgs} \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

$$- \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgs},\Omega} \approx 0.$$

Adding in and subtracting out the curvatures and using Eqs. (B.352) and (B.354) we obtain

$$(\text{B.375}) \quad \frac{D^{\overline{s}} \epsilon^{wgs}}{Dt} + \nabla' \cdot \left[\epsilon^{wgs} \left(\mathbf{w}^{\overline{wgs}} - \mathbf{G}^{wgs} \cdot \mathbf{v}^{\overline{s}} \right) \right] + \epsilon^{wgs} \mathbf{G}^{wgs} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \left\langle \left(\kappa_{Nwgs} - \kappa_N^{\overline{wgs}} \right) \mathbf{n}_s \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

$$+ \left\langle \left(\kappa_{Gwgs} - \kappa_G^{\overline{wgs}} \right) \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

$$+ \left(\epsilon^{ss} \frac{D^{\overline{s}} \chi_{ws}^{ss}}{Dt} - \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} \right.$$

$$\left. + \chi_{ws}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega} \right) \kappa_G^{\overline{wgs}}$$

$$+ \frac{\epsilon^{wgs}}{\epsilon^{ss}} \left(\frac{D^{\overline{s}} \epsilon^s}{Dt} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right) \kappa_N^{\overline{wgs}}$$

$$- \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\text{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgs},\Omega} \approx 0.$$

Following the arguments of [89] we define

$$\text{(B.376)} \quad e^{\overline{\overline{wgs}}} = -\left\langle \left(\kappa_{Nwgs} - \kappa_N^{\overline{\overline{wgs}}} \right) \mathbf{n}_s \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

$$- \left\langle \left(\kappa_{Gwgs} - \kappa_G^{\overline{\overline{wgs}}} \right) \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wgs} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wgs},\Omega}$$

and linearly approximate this term by

$$e^{\overline{\overline{wgs}}} \approx -\hat{k}^{wgs} \left(\epsilon^{wg} - \epsilon_{\mathrm{eq}}^{wgs} \right)$$

where $\epsilon_{\mathrm{eq}}^{wgs} = \epsilon_{\mathrm{eq}}^{wgs}(s^w, J_w^{wg})$ is the equilibrium common curve length density and $\hat{k}^{wgs}$ is a common curve generation rate coefficient. Applying these definitions our expression becomes

$$\text{(B.377)} \quad \frac{\mathrm{D}^{\overline{s}} \epsilon^{wgs}}{\mathrm{D}t} + \nabla' \cdot \left[\epsilon^{wgs} \left(\mathbf{w}^{\overline{\overline{wgs}}} - \mathbf{G}^{wgs} \cdot \mathbf{v}^{\overline{s}} \right) \right] + \epsilon^{wgs} \mathbf{G}^{wgs} : \mathbf{d}^{\overline{\overline{s}}}$$

$$+ \left(\epsilon^{ss} \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t} - \chi_{gs}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{ws} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wsM},\Omega} \right.$$

$$\left. + \chi_{ws}^{ss} \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{gs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{gsM},\Omega} \right) \kappa_G^{\overline{\overline{wgs}}}$$

$$+ \frac{\epsilon^{wgs}}{\epsilon^{ss}} \left(\frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} - \left\langle \mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Gamma_{sM},\Omega} \right) \kappa_N^{\overline{\overline{wgs}}}$$

$$- \left\langle \frac{\mathbf{e} \cdot \left(\mathbf{v}_{\mathrm{ext}} - \mathbf{v}^{\overline{s}} \right)}{\mathbf{n}_{wgs} \cdot \mathbf{e}} \right\rangle_{\Gamma_{wgs},\Omega} + \hat{k}^{wgs} \left(\epsilon^{wg} - \epsilon_{\mathrm{eq}}^{wgs} \right) \approx 0.$$

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