ASSESSING THE MINIMUM ENTROPY PRODUCTION RATE PRINCIPLE FOR MULTIPHASE FLOW USING THE THERMODYNAMICALLY CONSTRAINED AVERAGING THEORY APPROACH

Sydney J. Bronson

A thesis submitted to the faculty at the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Department of Environmental Sciences and Engineering.

Chapel Hill
2014

Approved by:

William G. Gray

Cass T. Miller

Stephen C. Whalen

ABSTRACT

SYDNEY J. BRONSON: ASSESSING THE MINIMUM ENTROPY PRODUCTION RATE PRINCIPLE FOR MULTIPHASE FLOW USING THE THERMODYNAMICALLY CONSTRAINED AVERAGING THEORY APPROACH
(Under the direction of William G. Gray)

The thermodynamically constrained averaging theory (TCAT) approach was used to derive a general model for multiphase flow in porous media. Additionally, an entropy inequality was derived which provides an expression for the entropy production rate of the system. Non-equilibrium thermodynamic theory aims to characterize systems away from equilibrium where irreversible processes produce entropy, while classical thermodynamics characterizes equilibrium states. The maximum entropy principle of classical thermodynamics allows equilibrium states to be described using entropy, and the minimum entropy production rate principle (MEPRP) attempts to serve the same role for non-equilibrium systems at steady-state. The MEPRP is highly debated and has not been investigated for hydrologic systems, so to serve this purpose, simplifying assumptions were applied to the multiphase flow model to arrive at a standard model for unsaturated flow: Richards' equation. Then, using two common pressure-saturation-permeability models, Richards' equation was numerically simulated and found to satisfy the MEPRP under infiltration conditions.

ACKNOWLEDGMENTS

I would like to thank Bill Gray, and Casey Miller for their time and support; they have been dedicated mentors, and examples of outstanding researchers. Among other things, Bill taught me the importance of communication and collaboration, while Casey helped me realize the importance of deadlines (even the arbitrary ones). While the long hours spent struggling through the multiphase class were painful, I will surely remain grateful for the skills I gained while up against the Bill and Casey firing squad.

I thank my classmates and friends, Amanda Dye and Tim Weigand, for providing intellectual and emotional support through the research process; struggling through the TCAT learning curve was bearable, and even enjoyable, with their company. Additionally, I'd like to thank my parents, Sharon and Bill, along with my sister Dana, for keeping me grounded through my first foray into the graduate school experience and updated on their Pacific Northwest adventures.

Finally, I acknowledge my funding sources: National Science Foundation grant, ATM-0941235, and Department of Energy grant, DE-SC0002163.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

$^{-}$	above a superscript refers to a density weighted macroscale average
$^{=}$	above a superscript refers to a uniquely defined macroscale average
$'$	vector tangent to a surface
$''$	vector tangent to a common curve
$\mathcal{E}$	associated with the total energy conservation equation
$\mathbb{E}^*$	equation of state based on internal energy variables
eq	equilibrium
g	gas-phase qualifier
i	chemical species qualifier
$\mathcal{M}$	associated with the mass conservation equation
n	non-wetting-phase qualifier
ns	qualifier for interface between n and s phases
$\mathcal{P}$	associated with the momentum conservation equation
s	solid-phase qualifier
T	transpose
$\mathcal{T}$	associated with the thermodynamic equation
V	volume
w	wetting-phase qualifier
wn	qualifier for interface between w and n phases
wns	qualifier for common curve

ws	qualifier for interface between w and s phases
$\overline{\alpha}$	mass average over entity α
α	entity index
β	entity index
$\hat{\beta}$	isothermal compressibility
$\hat{\beta}_w$	w phase compressibility
Γ	boundary of a domain
γ	interfacial or surface tension; common curve lineal tension
γ	entity index
ϵ	porosity
$\epsilon^{\overline{\overline{\alpha}}}$	specific entity measure
η	entropy density
$\overline{\eta}$	partial mass entropy
$\eta^{\overline{\overline{\alpha}}}$	macroscale entropy of entity α per volume
$\eta_M^{\overline{\overline{\alpha}}}$	macroscale entropy averaged over Γ_M
$\overline{\eta}^{\overline{\overline{\alpha,\beta}}}$	macroscale sum of weighted partial mass entropy
θ	temperature
$\theta^{\overline{\overline{\alpha}}}$	entropy weighted macroscale temperature of entity α
$\theta_\alpha^{\overline{\overline{\alpha\beta}}}$	entropy-weighted average of microscale temperature
θ^w	volumetric water content
θ_r^w	residual volumetric water content
θ_s^w	saturated volumetric water content

κ	entity index
κ_{Gwns}	microscale geodesic curvature
κ_{Nwns}	microscale normal curvature
Λ	entropy production rate
$\Lambda^{\overline{\overline{\alpha}}}$	macroscale entropy production rate associated with entity α
λ	Lagrange multiplier
$\lambda^{\alpha}_{\mathcal{E}}$	Lagrange multiplier for energy conservation equation
$\lambda^{\alpha}_{\mathcal{G}}$	Lagrange multiplier for potential energy balance
$\lambda^{\alpha}_{\mathcal{M}}$	Lagrange multiplier for mass conservation equation
$\lambda^{\alpha}_{\mathcal{T}}$	Lagrange multiplier for thermodynamic equation
$\lambda^{\alpha}_{\mathcal{TG}}$	Lagrange multiplier for derivative of potential energy
$\boldsymbol{\lambda}$	vector Lagrange multiplier
$\boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}$	Lagrange multiplier for momentum conservation equation
μ	chemical potential
$\hat{\mu}$	dynamic viscosity
ρ	mass density
$\overset{\beta\to\alpha}{\Phi}$	general macroscale transfer of entropy
$\overset{\beta\to\alpha}{\Phi}_M$	general macroscale transfer of entropy averaged over Γ_M
$\varphi_{ws,wn}$	microscale contact angle between ws and wn interfaces
$\varphi^{\overline{\overline{ws,wn}}}$	macroscale measure of contact angle
$\boldsymbol{\varphi}$	non-advective entropy flux
$\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}$	macroscale non-advective entropy flux associated with entity α

$\chi_{\alpha}^{\overline{\overline{\kappa}}}$	fraction of boundary of entity α in contact with entity κ
ψ	body force potential per unit mass
$\psi^{\overline{\overline{\alpha,\beta}}}$	macroscale average of body force potential density
$\psi_{M}^{\overline{\overline{\alpha,\beta}}}$	macroscale average of body force potential densit averaged over Γ_M
Ω	domain
Ω_C	curve within global domain of interest
Ω_{PT}	set of points within global domain of interest
Ω_S	surface within global domain of interest
Ω_V	a three-dimensional domain subset of the global domain
$\bar{\Omega}$	domain including its boundary
ω	mass fraction
A	cross-sectional area of the REV
b	entropy body source density
$\hat{c}^{\alpha}$	closure coefficient for $\alpha \in \mathcal{I}_{\mathrm{I}}$, and $\mathcal{I}_{\mathrm{C}}$
$\mathbf{d}^{\overline{\overline{\alpha}}}$	macroscale rate of strain tensor
E	internal energy density
$E^{\overline{\overline{\alpha}}}$	macroscale energy of entity α per total volume,
$E_{M}^{\overline{\overline{\alpha}}}$	macroscale energy per total volume, averaged over Γ_M
$\overline{E}$	partial mass internal energy
$\mathbb{E}$	internal energy
$\mathcal{E}$	partial derivative form of a energy conservation equation
$\mathcal{E}^{\overline{\overline{\alpha}}}$	partial derivative form of a energy conservation equation

$\mathcal{E}_*^{\overline{\overline{\alpha}}}$	material derivative form of a energy conservation equation
$e^{\overline{\overline{wn}}}$	interface curvature deviation term
$e_J^{\overline{\overline{wn}}}$	deviation term involving curvature
$e_P^{\overline{\overline{wn}}}$	deviation term involving pressure
$e_\gamma^{\overline{\overline{wn}}}$	deviation term involving surface tension
$\mathbf{G}_{\alpha\beta}$	microscale orientation tensor for $\alpha\beta$ interface
$\mathbf{G}_{wns}$	microscale orientation tensor for wns common curve
$\mathbf{g}$	body force per unit mass, acceleration
h	energy source density
$h^{\overline{\overline{\alpha}}}$	macroscale energy source density for entity α
$\mathbf{I}$	unit tensor
$\mathbf{I}'$	unit tensor in a surface
$\mathbf{I}''$	unit tensor in a common curve
$\mathbf{I}_\alpha^{(n)}$	unit tensor associated with $3-n$-dimensional entity, α
$\mathcal{I}$	set of entity indices
$\mathcal{I}_{\mathrm{C}}$	set of common curve indices
$\mathcal{I}_{\mathrm{c}\alpha}$	connected set of indices for entity α, $= \mathcal{I}_{\mathrm{c}\alpha}^+ \cup \mathcal{I}_{\mathrm{c}\alpha}^-$
$\mathcal{I}_{\mathrm{c}\alpha}^+$	connected set of indices of one dimension higher than entity α
$\mathcal{I}_{\mathrm{c}\alpha}^-$	connected set of indices of one dimension lower than entity α
$\mathcal{I}_{\mathrm{f}}$	set of fluid-phase indices
$\mathcal{I}_{\mathrm{I}}$	set of interface indices
$\mathcal{I}_{\mathrm{P}}$	set of phase indices

J	first curvature equal to twice the mean curvature
J	scalar thermodynamic flux
$J_{\alpha}^{\alpha\beta}$	macroscale average of first curvature, $\nabla' \cdot \mathbf{n}_{\alpha}$, over $\alpha\beta$ interface
J_i	particular thermodynamic flux
$K_{E\alpha}$	deviation kinetic energy per mass of entity α
$K_E^{\overline{\overline{\alpha}}}$	entity-based macroscale deviation kinetic energy
$K_E^{\overline{\overline{\alpha,\beta}}}$	average of a deviation kinetic energy over the boundary of an entity
$K_{EM}^{\overline{\overline{\alpha,\beta}}}$	deviation kinetic energy averaged over Γ_M
$\hat{K}_{\alpha}$	closure coefficient for entity α
$\hat{k}^{wn}$	parameter for rate of relaxation of interfacial area
$\hat{k}_1^{wn}$	parameter for rate of relaxation of interfacial area
$\hat{k}^{wns}$	parameter for rate of relaxation of common curve length
$\mathbb{L}$	general extensive length
ℓ	length scale
ℓ_{mo}	molecular length scale
ℓ_{mi}	microscale length scale
$\ell_{\mathrm{r}}^{\mathrm{r}}$	resolution length scale
ℓ^{ma}	macroscale length scale
ℓ^{me}	megascale length scale
M	subscript denoting a megascale quantity or average
$\mathbb{M}$	mass
$\overset{\beta\to\alpha}{M}$	macroscale transfer rate of mass per entity extent

$\overset{\beta\to\alpha}{M}_M$	macroscale transfer rate of mass averaged over Γ_M
$\mathcal{M}$	particular partial derivative form of a mass conservation equation
$\mathcal{M}^{\overline{\overline{\alpha}}}$	partial derivative form of a mass conservation equation
$\mathcal{M}_*^{\overline{\overline{\alpha}}}$	material derivative form of a mass conservation equation
$\mathbf{n}$	unit normal vector
ns	interface between n and s phases
P_{wn}	microscale term grouping
$\boldsymbol{\mathcal{P}}$	partial derivative form of a momentum conservation equation
$\boldsymbol{\mathcal{P}}^{\overline{\overline{\alpha}}}$	partial derivative form of a momentum conservation equation
$\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$	material derivative form of a momentum conservation equation
p	pressure
p_{wn}^c	microscale capillary pressure at wn interface
$\overset{\beta\to\alpha}{Q}$	general macroscale transfer of energy
$\overset{\beta\to\alpha}{Q}_M$	general macroscale transfer of energy, averaged over Γ_M
$\mathbf{q}$	non-advective energy flux
$\mathbf{q}^{\overline{\overline{\alpha}}}$	macroscale non-advective energy flux
$\hat{R}$	closure scalar
$\hat{\mathbf{R}}^{\alpha}$	closure tensor
$\hat{\mathbf{R}}_{\beta}^{\alpha}$	closure tensor involving α and β entities
$\mathbb{R}$	real space
$\mathbf{S}_{\Gamma}$	non-advective boundary source
S_{Ω}	body source independent of fluxes from adjacent entities

$S_{\Omega T}$	total body source
$\mathbb{S}$	entropy
$\mathcal{S}$	partial derivative form of an entropy balance equation
$\mathcal{S}^{\overline{\overline{\alpha}}}$	partial derivative form of a macroscale entropy balance
$\mathcal{S}_*^{\overline{\overline{\alpha}}}$	material derivative form of a macroscale entropy balance
$s^{\overline{\overline{\alpha}}}$	saturation of fluid phase α
$\overset{\beta\to\alpha}{\mathbf{T}}$	general macroscale transfer of momentum
$\overset{\beta\to\alpha}{\mathbf{T}}_M$	general macroscale transfer of momentum averaged over Γ_M
$\mathcal{T}^{\overline{\overline{\alpha}}}$	partial derivative form of a macroscale Euler equation
$\mathcal{T}_*^{\overline{\overline{\alpha}}}$	material derivative form of a macroscale Euler equation
t	time
$\mathbf{t}$	stress tensor
$\mathbf{t}^{\overline{\overline{s}}}$	macroscale solid-phase stress tensor
$\mathbf{t}^{\overline{\overline{\alpha}}}$	macroscale stress tensor
$\overline{V}$	partial mass volume
$\mathcal{V}$	set of variables
$\mathbb{V}$	extensive volume
$\mathbf{v}$	velocity
$\mathbf{v}^{\overline{\overline{\alpha,\beta}}}$	velocity of flow averaged over the boundary of the entity
$\mathbf{v}_M^{\overline{\overline{\alpha,\beta}}}$	particular macroscale velocity of flow
W	weighting function for averaging
w	wetting phase

wn	interface between w and n phases
wns	common curve at boundary of wn, ws, and ns interfaces
ws	interface between w and s phases
$\mathbf{w}$	velocity of a domain boundary
X	group of exchange terms encountered in CEI derivation
$\mathbf{x}$	position vector
X_i	particular thermodynamic force
AEI	augmented entropy inequality
BC	Brooks-Corey Model
BCB	Brooks-Corey Burdine model
CEI	constrained entropy inequality
CIT	classical irreversible thermodynamics
EI	entropy inequality
EOS	equations of state
EPR	entropy production rate
MEPRP	minimum entropy production rate principle
p-S	pressure-saturation relation
p-S-k	pressure-saturation-permeability relations
RE	Richards' Equation
REV	representative elementary volume
SEI	simplified entropy inequality
S-k	saturation-permeability relation

TCAT	thermodynamically constrained averaging theory
UNC	University of North Carolina
VG	van Genuchten model
VGM	van Genuchten Mualem model

CHAPTER 1

INTRODUCTION

1.1 Entropy and the Minimum Entropy Production Rate Principle

1.1.1 Entropy Overview

Referred to by some as the most abused word in science [32, 37], entropy as a homonym, and a thermodynamic concept requires a brief introduction. The thermodynamic entropy shares its name with Shannon's entropy, sometimes called information entropy, which was introduced by Claude E. Shannon in 1948 for use in information theory; information entropy is a measure of the uncertainty in a random variable [29]. Even within thermodynamic theory, entropy has been used with multiple meanings, most notably by Clausius, Gibbs, and Boltzmann; the interrelations between these entropies has been discussed at length by Jaynes [29–31].

While defining and interpreting entropy has been an existential pursuit for many, Lambert informally describes the entropy as a measure of energy's diffusion at a given temperature [37]; this definition aims to provide some physical intuition to a classic statement of the second law of thermodynamics. Another useful interpretation is entropy as a measure of the extent to which a system's energy is

distributed over the range of possible states [23]; as with the previous example, this definition makes use of the second law when referencing the possible states of a system.

Following the Gibbsian approach to thermodynamics, the entropy function is assumed to be known, and can therefore be directly postulated along with the internal energy function, as was done by Callen [9, 33]. This approach allows entropy to be interpreted mathematically, rather than observationally as in the early development of thermodynamics by Clausius and Kelvin [23]. Classical thermodynamic theory seeks to describe systems at equilibrium; therefore, characterizing equilibrium states is a fundamental task. Adopting the postulational framework, we will say that equilibrium states exist that are completely characterized by the extensive variables of the phase $\mathbb{E}, \mathbb{V}$, and $\mathbb{M}_i$; these are the internal energy, volume, and mass of each of the chemical species i in the phase respectively [28].

Additionally, we will postulate that there exists a function $\mathbb{S}$ called entropy which has can be written as

$$\mathbb{S} = \mathbb{S}^* \left(\mathbb{E}, \mathbb{V}, \mathbb{M}_1, \cdots, \mathbb{M}_N \right) \tag{1.1}$$

Eq. (1.1) is often called the fundamental relation. It is postulated that the dependent variables assume values which maximize $\mathbb{S}$ in the absence of constraints [9]; this is a statement of the entropy maximum principle. It's important to note that Eq. (1.1) applies to fluid-phase equilibrium thermodynamics; thermodynamic

statements for solid phases, and away from equilibrium require further analysis which will not be considered here, but exists elsewhere [23, 28].

The third postulate is that entropy is a homogeneous first-order function of the extensive variables for a simple system, which is continuous, differentiable, and a monotonically increasing function of the internal energy [9]. This postulate implies that the entropy function can be inverted, revealing the other form of the fundamental relation

$$\mathbb{E} = \mathbb{E}^* \left(\mathbb{S}, \mathbb{V}, \mathbb{M}_1, \cdots, \mathbb{M}_N \right) \tag{1.2}$$

Eq. (1.2) obeys a minimum energy principle which states that the variables assume values which will minimize $\mathbb{E}$ in the absence of constraints. Systems at equilibrium can be characterized using the entropy maximum and energy minimum principles; however, classical thermodynamic theory doesn't describe the entropy producing irreversible processes that govern systems away from equilibrium. Many real-world systems approach equilibrium very slowly, or alternatively, are kept from achieving equilibrium due to external boundary conditions; these systems have gradients in quantities such as temperature and composition which drive heat flow and diffusion, i.e. dynamic irreversible processes.

Traditional thermodynamics, or perhaps more accurately thermostatics, does not provide us with any knowledge of non-equilibrium processes, so tackling interesting real-world problems requires extending classical theory [53]. The second

law, which can be stated as

$$\frac{\mathrm{d}\mathbb{S}}{\mathrm{d}t} \geq 0 \tag{1.3}$$

provides a natural bridge between equilibrium and non-equilibrium thermodynamic theory because it provides information about the entropy production rate of all systems.

Eq. (1.3) is an equality at equilibrium where $\mathbb{S}$ achieves a maximum, while away from equilibrium we simply know that the entropy production rate must be greater than zero; this suggests that extending classical thermodynamics to non-equilibrium, irreversible processes requires forming an explicit expression for the entropy production rate [52]. A foundational concept in non-equilibrium thermodynamics is that of local equilibrium which asserts that for systems away from equilibrium, thermodynamic quantities remain well-defined locally, or in some neighborhood of equilibrium. One can picture a system divided up into smaller elemental volumes as in Figure 1.1, within which the system can be characterized via intensive thermodynamic quantities like temperature, pressure, and concentration even if these variables are not well-defined globally [36].

The local equilibrium assumption is not universally applicable, as systems with large spatial and/or temporal gradients in intensive variables will not be in equilibrium locally, or globally. However, for systems for which it is appropriate the local equilibrium assumption asserts that entropy remains dependent on the same variables as at equilibrium [53]. Extensive thermodynamic variables expressed locally correspond to density quantities such as entropy and internal energy per

volume; these local quantities, along with the idea of thermodynamic forces and fluxes which describe irreversible processes, can be used to extend Eq. (1.3) to non-equilibrium systems [36].

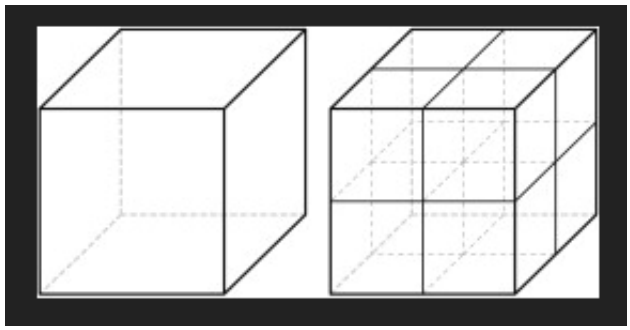

Figure 1.1: Visualization of the local equilibrium assumption [8].

The idea is that thermodynamic fluxes (or flows), such as heat flow or diffusive flux, occur because of a corresponding thermodynamic force or gradient such as a temperature or concentration gradient. This means that the total entropy production rate is the sum of these force-flux pairs, or irreversible processes, such that we have

$$\Lambda = \frac{\mathrm{d}\mathbb{S}}{\mathrm{d}t} = \sum_{i=1}^{n} J_i X_i \geq 0 \tag{1.4}$$

where n is the number of force-flux pairs, J_i terms correspond to the i thermodynamic fluxes, X_i are their corresponding forces, and Λ is the entropy production rate [36]. Of course at equilibrium, just as in Eq. (1.3), we have $J_i = 0$ and $X_i = 0$ for all i. Thermodynamic forces and fluxes are assumed to be related linearly, and homogeneously such that

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \tag{1.5}$$

where

$$L_{ij} = L_{ji} \tag{1.6}$$

L_{ij} are phenomenological coefficients, and Eq. (1.6) is a statement of Onsager's reciprocity relations between corresponding forces and fluxes [49]. For example, eqn (1.5) can be written for a system with n force-flux pairs as

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + \cdots + L_{1n}X_n \\ J_2 &= L_{21}X_1 + L_{22}X_2 + \cdots + L_{2n}X_n \\ \vdots \quad & \quad \vdots \quad \quad \vdots \quad \quad \vdots \\ J_n &= L_{n1}X_1 + L_{n2}X_2 + \cdots + L_{nn}X_n \end{aligned} \tag{1.7}$$

and eqn (1.6) states that the cross-coefficients are equal such that

$$L_{12} = L_{21}, \cdots, L_{1n} = L_{n1}, \text{ and } L_{2n} = L_{n2} \tag{1.8}$$

Empirically derived laws such as Fourier's law of heat conduction, written as

$$J_i = -k\nabla\theta \tag{1.9}$$

are consistent with the assumption of linear relations implied by eqn (1.5) [53].

In eqn (1.9) J_i is the heat flux, which is linearly related to the gradient in temperature $\nabla\theta$ (the force), and k is the phenomenological coefficient called the

thermal conductivity. The concept of linear relations between thermodynamic forces and fluxes as expressed in Eq. (1.5) is important for understanding the minimum entropy production rate principle.

1.1.2 Minimum Entropy Production Rate Principle

In an effort to characterize non-equilibrium systems beyond the description provided in Eqs. (1.5) and (1.6), the minimum entropy production rate principle was derived. Many systems are constrained by boundary conditions which prevent a global equilibrium state from being reached, where the entropy production rate would be zero via the second law [36]. The minimum entropy production rate principle (MEPRP) attempts to describe such systems. It asserts that in lieu of an equilibrium state, a state of least dissipation, or a steady-state (as opposed to a time-dependent state) will be achieved which can be described as a state at which the entropy production rate is a minimum [14, 53].

More formally, the MEPRP states that the steady state of an irreversible process is characterized by a minimum value of the entropy production rate with respect to other possible states with the same boundary conditions [4, 34]. This principle is naturally intuitive in that we know the entropy production rate is zero at equilibrium, so if a constraint such as an externally maintained temperature gradient prevents the system from attaining equilibrium the next closest state is a steady-state where the entropy production is a minimum [34]. However, the MEPRP requires restrictions beyond the linear relations that were assumed in

Eq. (1.5) in that it applies in a small neighborhood around equilibrium such that the phenomenological coefficients are constants [53]. This restriction makes the MEPRP a highly debated variational principle in that it requires thermodynamic gradients within the system to be sufficiently small without formally establishing how small they should be, or in other words, how close to equilibrium the system needs to be [4].

The principle has had some success in identifying the steady-state for irreversible-processes. For instance, it has been shown that for simple systems involving stationary heat conduction, the MEPRP accurately predicted the steady-state as the state that minimizes the entropy production [12, 14, 34, 35]. Although, some of these results, particularly those of Ferchmin [12], have been called into question [4, 26]. It has been shown that with a small jump in complexity from stationary heat conduction, a system with steady state shear flow with heat conduction is not properly described using the MEPRP [4].

In fact, the MEPRP fails to adequately characterize steady-states for a few notable systems. Landauer asserts that the MEPRP is only a "frequently useful approximation;" he showed that even for a very simple system of linear circuits the MEPRP does not correctly predict the steady-state [38]. This has led many to conclude that without establishing a domain over which the MEPRP applies, it should not be considered a universal principle [4, 39]. It has also been established that the MEPRP is not suited for Benard problems which have applications in hydrodynamic stability [14]. These investigations highlight the mixed success

of MEPRP to properly describe a steady-state for numerous flow and transport systems, and serve to explain the theory's mixed reception in the scientific community.

1.2 Multiphase Flow Modeling in Porous Media

Porous media systems are characterized by a division of the volume into a continuous solid matrix and a connected pore space which can be filled with one or more fluid phases [3]. Multiphase systems include a solid phase and multiple fluid phases; typical two-fluid-phase models are composed of a solid s-phase, a wetting w-phase, and a non-wetting n-phase where the wetting phase is that which preferentially wets the solid [45]. Subsurface systems like groundwater aquifers are a common example of a multiphase system that involves flow through porous media. Modeling the subsurface is used to assess groundwater supply and quality, develop resource management strategies, and assist remediation efforts of contaminated groundwater sources [44].

The modeling approach ideally combines a mature theoretical understanding of the system physics with developed numerical methods; together these form a mathematical description of the system that can be supplemented via experimental approaches. The mathematical model can then be simulated to provide predictions of real-world system behavior in lieu of constructing costly field-scale experiments [42]. The type and level of sophistication of the model depends on the phenomena of interest. For example, porous media models can describe single-

phase or multiphase fluid flow; alternatively, they can describe single or multiphase flow and species transport [27]. For instance, flow and transport models are often needed when characterizing contaminated sites in order to capture the fate and transport of the pollutants, whereas a simpler flow model is more appropriate for homogeneous systems (systems in which compositional effects are unimportant). Single and multiphase flow and transport models can also incorporate heat transfer effects by utilizing a conservation of energy equation.

Identifying the scale of interest is also a key aspect of model development as the length and time scales over which processes occur must be identified and incorporated into a model for it to be useful [41]. Resolving system phenomena down to the smallest spatial and temporal scales may be necessary when describing small-scale laboratory experiments but may prove to be unnecessary and computationally burdensome, if not impossible, when modeling field-scale systems like county and citywide groundwater networks. For this reason, a brief discussion of the hierarchy of length scales used in porous media applications is warranted.

The scales, from smallest to largest may be represented as

$$\ell_{\mathrm{mo}} \ll \ell_{\mathrm{mi}} \ll \ell_{\mathrm{r}}^{\mathrm{r}} \ll \ell^{\mathrm{ma}} \ll \ell^{\mathrm{me}} \tag{1.10}$$

where

- ℓ_{mo} is the molecular scale which is identified as the average distance a molecule travels between collisions with other molecules, or the mean free

path [23]; this scale is too small to incorporate into porous media models.

- ℓ_{mi} is the microscale, which is also referred to as the pore scale [45]. The microscale is much larger than the molecular scale, and as such, each microscale point incorporates an ensemble of molecules. Pore morphology and topology is completely resolved at this scale, and fluids are considered continuous [2]; this is the smallest length scale at which a continuum model can be applied [41].

- $\ell_{\mathrm{r}}^{\mathrm{r}}$ is the resolution scale. This scale is system specific, in that it relates to the natural length scale of the system; for a porous media system this could be the average grain size [23]. At this scale the features of interest of a given flow are resolved; these features depend on system phenomena [41].

- ℓ^{ma} is the macroscale, or the Darcy scale for porous medium systems. Each macroscale point represents a continuum of microscale entities; the distribution of individual phases is no longer resolved, and is instead represented on average [17]. The concept of a representative elementary volume (REV) applies here in that average characteristics of the porous media, such as the porosity ϵ which can be measured experimentally, arise at this scale [16].

- ℓ^{me} is the megascale, or the system scale. As the name suggests, this scale is the length scale of the domain of the system of interest which can vary in different directions [17].

In other words, a broad range of multi-scale problems are relevant in subsurface

porous media modeling. Incorporating length and time scale considerations into mathematical models based on the system of interest and computational resources is an important part of the modeling process. Macroscale multiphase models will be covered in this work, first by presenting the traditional macroscale models and their merits, and then by exploring the thermodynamically constrained averaging theory (TCAT) approach which provides a general framework for developing closed mathematical models based on conservation and thermodynamic principles.

1.2.1 Traditional Approaches

Standard macroscale multiphase flow models involve writing conservation of mass equations for each phase, using a multiphase form of Darcy's law as an approximate conservation of momentum equation, and specifying constitutive pressure-saturation-permeability (p-S-k) relations and equations of state (EOS) for a simplified system [27, 42].

For typical two-phase-flow systems with w, n, and s-phases, common simplifications include assuming that compositional effects are unimportant such that the conservation equations can be written on a phase basis; assuming the solid is immobile and inert, meaning conservation equations only need to be written for the w and n-phases; and assuming the system is isothermal such that conservation of energy equations aren't formulated. These assumptions reduce traditional models to the following equations:

- <u>Conservation of Mass</u>:

$$\frac{\partial\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\right)}{\partial t} + \nabla\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\right) = 0 \quad \text{for } \alpha = \{w, n\} \tag{1.11}$$

where ρ^{α} is the density, $\epsilon^{\overline{\overline{\alpha}}}$ is the volume fraction (the fraction of the pore space filled by the α-phase), and $\mathbf{v}^{\overline{\alpha}}$ is the velocity. The assumption that the fluid phases do not exchange mass was also utilized in writing Eq. (1.11).

- <u>Approximate Conservation of Momentum, Darcy's Law</u>:

$$\epsilon^{\overline{\overline{\alpha}}}\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) = -\hat{K}^{\alpha}\left(\nabla p^{\alpha} - \rho^{\alpha}\mathbf{g}\right) \quad \text{for } \alpha = \{w, n\} \tag{1.12}$$

where p^{α} is the pressure, $\hat{K}^{\alpha}$ is the scalar hydraulic conductivity which is written assuming the media is isotropic, and $\mathbf{g}$ is the gravitational acceleration. Eq. (1.12) can also be written as

$$\epsilon^{\overline{\overline{\alpha}}}\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) = -\frac{\hat{k}^{s}\hat{k}^{\alpha}_{rel}}{\mu^{\alpha}}\left(\nabla p^{\alpha} - \rho^{\alpha}\mathbf{g}\right) \quad \text{for } \alpha = \{w, n\} \tag{1.13}$$

where $\hat{k}^{s}$ is the intrinsic permeability, $\hat{k}^{\alpha}_{rel}$ is the relative permeability, and μ^{α} is the dynamic viscosity. The intrinsic permeability is a material property of the solid phase and is related to the hydraulic conductivity via the relation

$$\hat{K}^{\alpha} = \frac{\hat{k}^{s}\rho^{\alpha}g}{\mu^{\alpha}} \quad \text{for } \alpha = \{w, n\} \tag{1.14}$$

The relative permeability is a function of $s^{\overline{\overline{w}}}$ and is a dimensionless quantity

which assumes values from 0 to 1; it accounts for the reduction of the intrinsic permeability due to the incomplete saturation of fluid phase α [27]. The relative permeability it is related to the intrinsic permeability via the relation

$$\hat{k}^{w}_{rel} = \frac{\hat{k}^{\alpha s}}{\hat{k}^{s}} \quad \text{for } \alpha = \{w, n\} \tag{1.15}$$

where $\hat{k}^{\alpha s}$ is the apparent intrinsic permeability which is dependent on the material properties of the solid and the presense of the other fluids in the multiphase system [51]. When the system if fully saturated the apparent permeability is equal to the intrinsic permeability. Eq. (1.13), which incorporates the permeability terms rather than the hydraulic conductivity, is useful when introducing the pressure-saturation-permeability relations.

- Equations of State:

Equations of state are constitutive relations which describe the relationship between intensive state variables like temperature, pressure, and chemical potential [13]. More specifically, the intensive variables are functions of the independent extensive variables ($\mathbb{S}, \mathbb{V}$, and $\mathbb{M}_i$), and the functional relationships which express the intensive variables in terms of extensive variables are called equations of state [9]. One classic example of an EOS is the ideal gas law which relates the pressure, volume, temperature, and the number of moles of an ideal gas. For porous medium systems it is common for the chemical composition to be constant and the system to be isothermal. With

these facts in mind the remaining EOS is

$$\rho^{\alpha} = \rho^{\alpha}\left(p^{\alpha}\right) \quad \text{for } \alpha = \{w, n\} \tag{1.16}$$

which relates the pressure and density at the macroscale. Eq. (1.16) is a functional form that is typical at the microscale, and is derived from the microscale energy's dependence on independent variables. Using the TCAT approach it can be shown that microscale functional forms may not be appropriate at the macroscale. Microscale and macroscale thermodynamic forms will be discussed later, but this subtlety is not incorporated into standard models.

- <u>Pressure-saturation-permeability (p-S-k) relations</u>:

  The functional relationships between the capillary pressure, saturation, and permeability need to be specified in order to form a closed model. These functions are

$$p^{n} - p^{w} = p^{c}_{wn}\left(s^{\overline{\overline{\alpha}}}\right) \quad \text{for } \alpha = \{w, n\} \tag{1.17}$$

  where the saturation of each phase $s^{\overline{\overline{\alpha}}}$ follows

$$s^{\overline{\overline{n}}} + s^{\overline{\overline{w}}} = 1 \tag{1.18}$$

  and

$$\hat{k}^{\alpha}_{rel} = \hat{k}^{\alpha}_{rel}\left(s^{\overline{\overline{\alpha}}}\right) \quad \text{for } \alpha = \{w, n\} \tag{1.19}$$

where $\hat{k}_{rel}^{\alpha}$ is the relative permeability which was introduced in the multiphase form of Darcy's law (Eq. (1.13)). Eq. (1.19) must be specified because constitutive saturation-permeability relations are typically expressed in terms of the relative permeability. The capillary pressure and relative permeability are most commonly assumed to be functions of the saturation alone (as is presented here), but these variables may also depend on quantities such as interfacial area which are used in full TCAT formulations [41]. Eq. (1.17) originates from microscale equilibrium conditions which relate the capillary pressure, defined as

$$p_{wn}^{c} = -\left(\nabla' \cdot \mathbf{n}_{w}\right) \gamma_{wn} \tag{1.20}$$

to the difference in phase pressures evaluated at the fluid-fluid interface.

As with the equation of state posited at the macroscale, Eq. (1.17) is based on a microscale equilibrium form and therefore ignores dependences that arise at the macroscale. Eqs. (1.17) and (1.19) are specified via constitutive relationships which are often empirically based and hysteretic in nature [42]; the hysteresis highlights that the functional dependence of capillary pressure at the macroscale shown in Eq. (1.17) is incomplete.

Eqs. (1.11)–(1.12) can be combined to form Richards' equation under some simplifying conditions, including the assumption that the w-phase is incompressible. Richards' equation is a standard model for flow in the unsaturated zone, and

can be written as

$$\epsilon \frac{\partial s^{\overline{\overline{w}}}}{\partial t} = \nabla \cdot \left[\hat{K}^w \left(\nabla p^w - \rho^w \mathbf{g} \right) \right] \tag{1.21}$$

where $s^{\overline{\overline{w}}}$ is the saturation of the w-phase, and ϵ is the porosity such that

$$\epsilon^{\overline{\overline{w}}} = \epsilon s^{\overline{\overline{w}}} \tag{1.22}$$

More generally, utilizing mass conservation equations and Darcy's law, or a multiphase form or Darcy's law, is a standard approach taken by researchers in academia [42–44] for single and multiphase problems. Consultants in practice almost exclusively take a similar, although more simplified approach when using the popular groundwater code MODFLOW which was developed by the USGS [24]. Some issues with using this approach to develop multiphase models include the foundational assumptions that underlie Darcy's law.

Originally, Darcy's law was formulated at the megascale where spatial variability wasn't considered, but instead average conditions of the entire system and its boundaries were observed [19, 21]. However, Eq. (1.12) is written at the macroscale where spatial variability is important. In other words, using Darcy's law in place of a macroscale conservation of momentum equation means that the connection between microscale variables, which are well defined and understood, and macroscale variables is lost. There are implicit approximations in a multiphase model using Darcy's law, but these approximations are difficult to identify and refine if model behavior is considered unsatisfactory [17, 44]. Additionally, the

use of Darcy's Law has become such a standard approach that it is often used in an ad-hoc fashion.

Another potential concern regarding the use of Darcy's law for multiphase systems is that it was developed empirically based on experiments involving single-phase flow in low Reynolds number conditions [44]. Most flow in aquifers operates under this regime, so Darcy's law has proved effective for single-phase flow models of this type; however, its multiphase extension (Eq. (1.12)) was not formulated on strong theoretical ground [41]. The form of Darcy's law shown in Eq. (1.12) is an extension of Darcy's original law to multiphase flow which assumes the pressure gradients of individual phases are driving forces for those phases alone [48]. The limitations of this approach have been acknowledged [42, 46], and work to move beyond this formulation exists [20, 28], although so far, little progress has been made in changing the equations used in practice.

Beyond problems with Darcy's law, formulating and solving equations like Richards' eqn (1.21) requires constitutive p-S-k relations and EOS which are unknown and often posited in an crude manner; this also contributes to the lost connection between microscale and macroscale variables [44]. The fact that the most popular p-S-k relations exhibit hysteretic behavior suggests that the existing approximations for these functional relationships is incomplete at best [5, 6, 22]. The issues with classical models discussed here point to problems with incomplete physical descriptions of the systems of interest, and empirically based closure relations which include variables that aren't connected to their microscale precursors

[17]. These shortcomings indicate that a more systematic approach to mutli-scale model development which is based on known microscale theory and experimentation is needed to improve upon the existing multiphase models.

1.2.2 TCAT Approach

The thermodynamically constrained averaging theory (TCAT) provides a framework which allows for a flexible and systematic approach for developing a vast array of multiscale and multiphase flow and transport models. The TCAT approach involves formulating microscale conservation principles and thermodynamics along with an entropy inequality, which ensures the second law of thermodynamics is satisfied, for each entity in the system (phases, interfaces, common curves, and common points). Then, the microscale equations are systematically averaged to the desired scale(s) using averaging theorems [27], thus generating equations which are precisely connected to their microscale counterparts.

Developing a TCAT model first requires identifying the entities within the given system; next, the TCAT approach can be carried out using the following general steps:

- Formulate microscale equations for the identified entities within the system of interest:
    1. Conservation of mass
    2. Conservation of momentum

3. Conservation of energy
4. Balance of entropy
5. Thermodynamic forms based on chosen microscale thermodynamic theory

- Form the entropy inequality (EI) by adding together the entropy balance equations
- Average the microscale conservation and thermodynamic equations to a larger scale using averaging theorems [16]
- Form the augmented entropy inequality (AEI) using Lagrange multipliers multiplied by the macroscale conservation and thermodynamic equations
- Form the constrained entropy inequality (CEI) by solving for Lagrange multipliers such that time derivatives are eliminated from the AEI
- Form the simplified entropy inequality (SEI) by using evolution equations, derived from geometric identities and approximations, to eliminate remaining time derivatives from the CEI
- Posit closure relations based on the SEI and available microscale and macroscale theory, simulation, and/or experimentation

A flowchart of this process is visible in Figure 1.2. The TCAT method provides an alternative to the classical approach by retaining the connection between scales

through rigorous averaging; using the averaging process macroscale variables are precisely defined in terms of averages of microscale precursors. Additionally, the framework is flexible in that the CEI, which is the final exact expression in the TCAT approach, serves as a point of return to examine and refine applied assumptions and approximations that were used to yield a closed model.

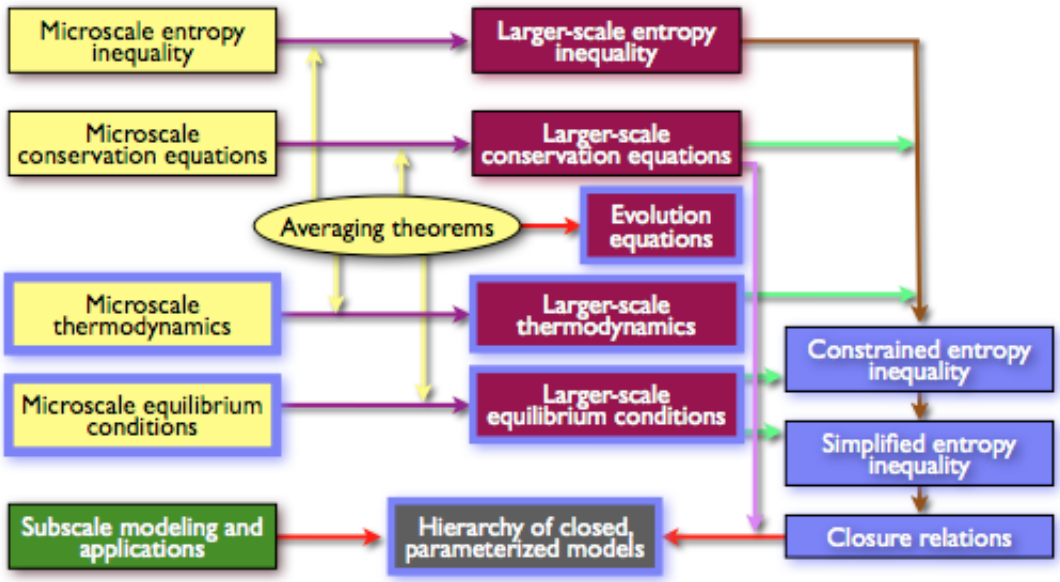

Figure 1.2: Flow chart for the TCAT modeling approach [23].

1.3 Research Objectives

Elements of traditional modeling approaches can be expanded upon and verified using the TCAT framework. For instance, work has been done to compare the standard megascale formulation of Darcy's law with a similar macroscale formulation derived using TCAT [21]. The goal of this work is interact with the TCAT method, while also incorporating elements of the standard modeling approach

to evaluate Richards' equation in light of the minimum entropy production rate principle.

The specific research objectives of this work are:

1. Using the TCAT framework, derive a hierarchy of macroscale models for two-fluid-phase flow in a porous medium system using averaging theorems which transform equations with variability in three microscale dimensions, to those with one dimension of macroscale variability while the remaining dimensions are averaged over the system at the megascale.

2. Working from the CEI, formulate a closed simplified model for flow through unsaturated media, applying traditionally used approximations to yield Richards' equation (RE) and an SEI.

3. Simulate RE numerically and calculate the global entropy production of the system using the SEI for different formulations of commonly used p-S-k relations.

4. Evaluate whether Richards' equation satisfies the MEPRP for the chosen constitutive relations and simulation conditions.

CHAPTER 2

SYSTEM DESCRIPTION AND MODEL DERIVATION

2.1 Primary Restrictions

Within the TCAT approach, primary restrictions are used to specify the system to be modeled; the entities within the system and the scale at which they are to be modeled, the phenomena to be modeled, and the thermodynamic theory to be used are all explicitly specified under this category of restrictions [23].

In this work, the following primary restrictions will be used:

1. The entities of interest are two fluid phases w, and n, a relatively immobile solid phase s, three interfaces wn, ws, and ns, and a common curve wns. Additionally, modeling will take place at the macroscale.

2. The transport of mass, momentum, and energy will be modeled on an entity basis.

3. The non-equilibrium thermodynamic theory to be used is classical irreversible thermodynamics (CIT).

2.2 Averaging Theorems

Averaging theorems are used to transform equations from one spatial scale to another scale, or combination of other scales, and are an important tool used in TCAT analysis to facilitate the development of macroscale conservation, balance, and thermodynamic equations from their microscale precursors [23]. The most common of these theorems are the transport and divergence theorems which transform three-dimensional microscopic equations into three-dimensional macroscale equations; these theorems appear often in the study of fluid mechanics, among other fields [16]. These theorems become necessary when averaging microscale equations to larger scales because averages of spatial and temporal derivatives are often impossible to evaluate. Usable models can be derived by exchanging the order of averaging (integration) and differentiation via the averaging theorems; this process yields equations which include derivatives of averaged microscale quantities and boundary terms [23].

Modeling porous media systems at the macroscale or the megascale is not only computationally necessary, it is also more useful when describing real world systems such as groundwater aquifers which are often modeled on a city-wide scale or larger [41]. On a city-wide scale, information about the location of each phase, including details of flow within individual pores, is not only inaccessible, but largely irrelevant. With TCAT the goal is to comply with microscale physical principles while scaling-up to the system of interest, thereby retaining enough information to yield an accurate model. Even if microscale information were

available for a system at the field scale, the computational effort to model such a system would be impossibly large, thus further necessitating an averaging process. Before introducing the averaging theorems, a general averaging operator can be defined as

$$\langle \mathcal{P}_\alpha \rangle_{\Omega_\beta,\Omega_\gamma,W} = \frac{\int\limits_{\Omega_\beta} W \mathcal{P}_\alpha \, \mathrm{d}r}{\int\limits_{\Omega_\gamma} W \, \mathrm{d}r} \text{ for } \dim \Omega_\beta > 0, \dim \Omega_\gamma > 0 \tag{2.1}$$

where $\langle\rangle_{\Omega_\beta,\Omega_\gamma,W}$ is the averaging operator, and $\mathcal{P}_\alpha$ is the microscale property being averaged, W is a weighting function, and Ω is a domain of integration. As seen on the right side of Eq. (2.1), the subscripts on the averaging operator designate the domain of integration of the microscale property Ω_β, the domain over which the quantity will be normalized by (for example, the REV) Ω_γ, and the weighting function W respectively. If no third subscript is provided, then W is equal to one.

The subscripts α, β and γ are entity qualifiers which correspond to phases, interfaces, common curves, and common points. Phase entities are three-dimensional at the microscale, while interfaces (which are formed when two phases meet, i.e. they exist at the boundary between two phases) are two-dimensional. Common curves are formed when three phases meet, and are one-dimensional, and finally common points are zero-dimensional entities formed when four or more phases meet. When dealing with common points the definition of the averaging operator includes a summation over the set of points rather than integration over some

domain Ω, but common points don't exist for the three phase system described in this work, so Eq. (2.1) is sufficient.

For convenience, microscale properties and macroscale properties are given subscripts and superscripts to quickly distinguish between them. Furthermore, more than one notation is used for the macroscale superscripts to concisely differentiate between the different types of averages that exist. The two most common types have specific definitions; these include

$$\text{Intrinsic Averages}: \begin{cases} f_\alpha^\beta = \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta} & \text{for } \alpha \neq \beta \\ f^\alpha = \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta} & \text{for } \alpha = \beta \end{cases} \tag{2.2}$$

and

$$\text{Mass Averages}: \begin{cases} f_\alpha^{\overline{\beta}} = \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta, \rho_\alpha} & \text{for } \alpha \neq \beta \\ f^{\overline{\alpha}} = \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta, \rho_\alpha} & \text{for } \alpha = \beta \end{cases} \tag{2.3}$$

Unique averages also exist, and are indicated by a double overbar, $f^{\overline{\overline{\alpha}}}$; the definitions for these averaged quantities will be presented as they appear. Now that the notation for microscale and macroscale quantities has been introduced, and a general averaging operator has been defined, the averaging theorems used in this work can be introduced.

The naming convention of the theorems follows [16, 23], and is of the form $< letter > [i, (j, k), l]$. In this work the theorems of the family $[i, (1, 0), 2]$ will be used, which means i microscale dimensions will be converted into equations that

have one macroscale dimension, and two megascale dimensions. The letter will be a G, D, or T corresponding to gradient, divergence, or transport theorems. The sum of the indices $j+k$ corresponds to the number of resulting macroscale dimensions, but in this case $k = 0$. Many more theorems and information for deriving them using generalized functions exists in [16]; the results will be presented here.

A convenient averaging volume for this set of theorems which converts equations with i microscale dimensions into those with one macroscopic, and two megascopic dimensions, is a slab with thickness D, as shown in Figure 2.1. The macroscopic dimension aligns with the unit vector $\mathbf{N}$ which is normal to the face of the representative averaging volume (RAV), while the megascopic dimensions are tangent to the face of the RAV. The edge boundaries of the RAV, designated with the notation $\Gamma_{\alpha M}$, allow for flux terms across the edge of the slab in the megascopic directions.

Starting from the averaging theorem notation provided in [16], updated notation which is consistent with the averaging notation used in TCAT theory is provided. The required theorems are spatial operator theorems in the $[3,(1,0),2]$ family.

<u>Spatial Operator Theorems:</u>

G[3,(1,0),2]:

$$\langle \nabla f_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla^{\backslash\backslash} \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} + \sum_{\beta \in \mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha f_\alpha \rangle_{\Omega_\beta,\Omega} + \langle \mathbf{e} f_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}} \tag{2.4}$$

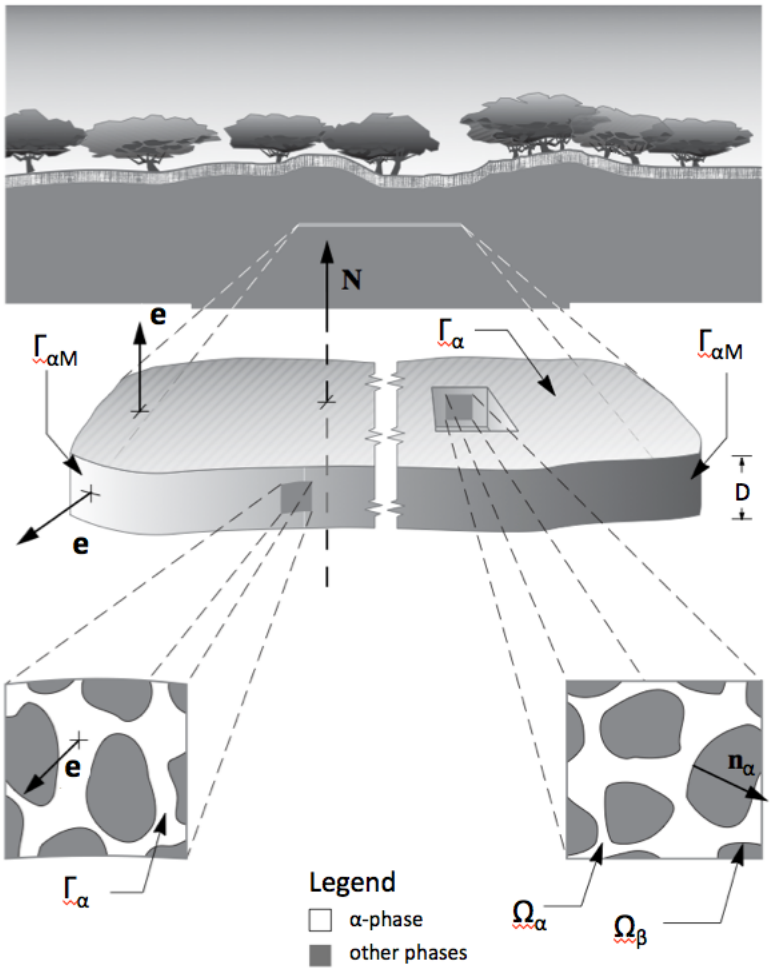

Figure 2.1: RAV for $[i,(1,0),2]$ theorems; adapted from [16].

D[3,(1,0),2]:

$$\langle \nabla \cdot \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla^{\backslash\backslash} \cdot \langle \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} + \sum_{\beta \in \mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{f}_\alpha \rangle_{\Omega_\beta,\Omega} + \langle \mathbf{e} \cdot \mathbf{f}_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}} \tag{2.5}$$

T[3,(1,0),2]:

$$\left\langle \frac{\partial f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \frac{\partial^{\backslash\backslash}}{\partial t} \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} - \sum_{\beta \in \mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta f_\alpha \rangle_{\Omega_\beta,\Omega} - \langle \mathbf{e} \cdot \mathbf{w} f_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}} \tag{2.6}$$

where the $\wedge\!\!\!\wedge$ symbol indicates a macroscale spatial operator, Γ designates the boundary of a domain in TCAT, and $\Gamma_{\alpha M}$ specifically designates the portion of the RAV at the edge boundaries that is occupied by the α-phase; the M signifies that these edge boundaries align with the megascale dimensions. The quantity f_α or $\mathbf{f}_\alpha$ represents a general scalar or vector function respectively, which is defined in the α-phase, $\mathbf{n}_\alpha$ is the unit vector that is outward normal to the α phase, $\mathbf{e}$ is the unit vector that is outward normal to the external boundary of the RAV, and $\mathbf{w}$ is the velocity of the boundary. When moving from the microscale to the macroscale these boundary terms appear which represent the transfer of f_α out of the domain. Additionally, inter-entity transfer terms appear which describe the transfer of f_α between entities; these are the terms with summations in Eqs. (2.4)–(2.6). To understand the summations in Eqs. (2.4)–(2.6) a brief overview of TCAT set notation is required.

The symbol $\mathcal{I}$ represents the set of entity indices which could include phase, interface, common curve, and common point indices; for this three phase system, $\mathcal{I} = \{w, n, s, wn, ws, ns, wns\}$. More specific notation refers to just the set of phase, interface, and common curve indices as the sets $\mathcal{I}_{\mathrm{P}}$, $\mathcal{I}_{\mathrm{I}}$, and $\mathcal{I}_{\mathrm{C}}$ respectively; for instance, $\mathcal{I}_{\mathrm{C}} = \{wns\}$ because one common curve is present. There are also connected sets $\mathcal{I}_{\mathrm{c}\alpha}$ which refer to the set of entities which are bounding, or connected to entity α, thus $\mathcal{I}_{wn} = \{w, n, wns\}$. It is often necessary to refer to the set of higher or lower dimensional entities in the connected set, and $\mathcal{I}^{+}_{\mathrm{c}\alpha}$ and $\mathcal{I}^{-}_{\mathrm{c}\alpha}$ are used for this purpose. For example, if $\alpha = wn$, then $\mathcal{I}^{-}_{\mathrm{cwn}} = \{wns\}$

and $\mathcal{I}^{+}_{\mathrm{cwn}} = \{w, n\}$, which also means that $\mathcal{I}^{+}_{\mathrm{c}\alpha} \cup \mathcal{I}^{-}_{\mathrm{c}\alpha} = \mathcal{I}_{\mathrm{c}\alpha}$. Using this logic, the notation $\beta \in \mathcal{I}_{\mathrm{c}\alpha}$ in Eqs. (2.4)–(2.6) means that the summation is occurring over the members β in the connected set of α.

The spatial and curvilinear theorems won't be explicitly needed because at the macroscale the form of the conservation and balance equations is the same for phases, interfaces, and common curves. This is because the entity type is not observable at the macroscale, in that the location and distribution of individual entities isn't known; that information is lost when moving from the microscale to the macroscale. At the macroscale we have information at the scale of the REV, meaning quantities such as ρ^{α} exist which could be a mass per volume, area, or length depending on which set entity α belongs to. For this reason, it is important to remember that although the forms of the macroscale equations for each entity type are the same, the variable definitions will not be identical.

2.3 Conservation, Balance, and Thermodynamic Equations

The set of conservation, balance, and thermodynamic equations needed to carry out a full TCAT analysis will be presented below, starting with the microscale forms, and averaging up to the macroscale using the [i,(1,0),2] family of averaging theorems. These macroscale equations will then be used to form an entropy inequality for the system that will be used to guide closure of the equations.

2.3.1 Mass Conservation Equation

The microscale mass conservation equation for a phase can be written as

$$\mathcal{M}_\alpha = \frac{\partial \rho_\alpha}{\partial t} + \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha) = 0 \quad \text{for } \alpha \in \mathcal{J}_\mathrm{P} \tag{2.7}$$

Applying an averaging operator to all terms yields

$$\left\langle \frac{\partial \rho_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \langle \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha)\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_\mathrm{P} \tag{2.8}$$

By utilizing the transport and divergence theorems from the [3,(1,0),2] family we can obtain a conservation equation which includes macroscale quantities averaged from the microscale. Applying eqns (2.5) and (2.6) yields

$$\begin{aligned} \frac{\partial^{\backslash\!\backslash}}{\partial t}\langle \rho_\alpha \rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta \rho_\alpha \right\rangle_{\Omega_\beta,\Omega} - \langle \mathbf{e}\cdot\mathbf{w}\rho_\alpha \rangle_{\Gamma_{\alpha M},\Omega} + \nabla^{\backslash\!\backslash}\cdot\langle \rho_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} \\ + \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot (\rho_\alpha \mathbf{v}_\alpha)\rangle_{\Omega_\beta,\Omega} + \langle \mathbf{e}\cdot(\rho_\alpha \mathbf{v}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_\mathrm{P} \end{aligned} \tag{2.9}$$

This equation simplifies to

$$\frac{\partial^{\backslash\backslash}}{\partial t}\langle\rho_\alpha\rangle_{\Omega_\alpha,\Omega} + \nabla^{\backslash\backslash}\cdot\langle\rho_\alpha\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle\rho_\alpha(\mathbf{v}_\beta - \mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}$$

$$- \langle\rho_\alpha(\mathbf{w} - \mathbf{v}_\alpha)\cdot\mathbf{e}\rangle_{\Gamma_{\alpha M},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}} \tag{2.10}$$

If A is the cross sectional area being considered, Eq. (2.10) can be written

$$A\mathcal{M}^{\overline{\overline{\alpha}}} = \frac{\partial(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A)}{\partial t} + \nabla^{\backslash\backslash}\cdot(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\mathbf{v}^{\overline{\alpha}}A) - \sum_{\beta\in\mathcal{J}_{c\alpha}^{-}} A\overset{\beta\to\alpha}{M} + A\overset{\alpha\to}{M}_M = 0 \quad \text{for } \alpha \in \mathcal{J} \tag{2.11}$$

Alternatively, using the product rule, Eq. (2.11) can be written in material derivative form as

$$A\mathcal{M}_*^{\overline{\overline{\alpha}}} = \frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A)}{\mathrm{D}t} + (\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A)\mathbf{l}^{\backslash\backslash}\mathbf{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \sum_{\beta\in\mathcal{J}_{c\alpha}^{-}} A\overset{\beta\to\alpha}{M} + A\overset{\alpha\to}{M}_M = 0 \quad \text{for } \alpha \in \mathcal{J} \tag{2.12}$$

where

$$\epsilon^{\overline{\overline{\alpha}}} = \langle 1\rangle_{\Omega_\alpha,\Omega} \tag{2.13}$$

$$\overset{\beta\to\alpha}{M}A = \left\langle\rho_\alpha\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \tag{2.14}$$

and

$$\overset{\alpha\to}{M}_M A = \langle\rho_\alpha(\mathbf{v}_\alpha - \mathbf{w})\cdot\mathbf{e}\rangle_{\Gamma_{\alpha M},\Omega} \tag{2.15}$$

The macroscale material derivative and rate of strain tensor are defined as

$$\mathbf{d}^{\overline{\overline{\alpha}}} = \frac{1}{2}\left[\nabla^{\backprime}\mathbf{v}^{\overline{\alpha}} + \left(\nabla^{\backprime}\mathbf{v}^{\overline{\alpha}}\right)^{\mathrm{T}}\right] \tag{2.16}$$

and

$$\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} = \frac{\partial^{\backprime}}{\partial t} + \mathbf{v}^{\overline{\alpha}}\cdot\nabla^{\backprime} \tag{2.17}$$

Eqs. (2.11) and (2.12) are written for the set of all entities because each entity equation takes the same form at the macroscale, as previously mentioned.

2.3.2 Momentum Conservation Equation

The microscale conservation of momentum equation for a phase can be written as

$$\mathcal{P}_\alpha = \frac{\partial(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha - \nabla\cdot\mathbf{t}_\alpha = 0 \tag{2.18}$$

Applying an averaging operator to all terms yields

$$\left\langle \frac{\partial \rho_\alpha \mathbf{v}_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \langle \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha)\rangle_{\Omega_\alpha,\Omega} - \langle \nabla\cdot\mathbf{t}_\alpha\rangle_{\Omega_\alpha,\Omega} - \langle \rho_\alpha \mathbf{g}_\alpha\rangle_{\Omega_\alpha,\Omega} = 0 \tag{2.19}$$

Then, applying the transport and divergence theoremseqns (2.5) and (2.6) yields

$$\frac{\partial^{\backprime}}{\partial t}\langle \rho_\alpha \mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta(\rho_\alpha \mathbf{v}_\alpha)\right\rangle_{\Omega_\beta,\Omega} - \langle \mathbf{e}\cdot\mathbf{w}(\rho_\alpha \mathbf{v}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}$$
$$+ \nabla^{\backprime}\cdot\langle \rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} + \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot (\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha)\rangle_{\Omega_\beta,\Omega} + \langle \mathbf{e}\cdot(\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}$$

$$
\begin{aligned}
&- \langle \rho_\alpha \mathbf{g}_\alpha \rangle_{\Omega_\alpha,\Omega} - \nabla^{\backprime}\cdot\langle \mathbf{t}_\alpha \rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{t}_\alpha \rangle_{\Omega_\beta,\Omega} - \langle \mathbf{e}\cdot\mathbf{t}_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \\
&= 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned} \tag{2.20}
$$

This equation simplifies to

$$
\begin{aligned}
\frac{\partial^{\backprime}}{\partial t}\langle \rho_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} &+ \nabla^{\backprime}\cdot\langle \rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} - \nabla^{\backprime}\cdot\langle \mathbf{t}_\alpha \rangle_{\Omega_\alpha,\Omega} - \langle \rho_\alpha \mathbf{g}_\alpha \rangle_{\Omega_\alpha,\Omega} \\
&- \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\beta - \mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha \right\rangle_{\Omega_\beta,\Omega} - \langle \rho_\alpha \mathbf{v}_\alpha (\mathbf{w} - \mathbf{v}_\alpha)\cdot\mathbf{e} \rangle_{\Gamma_{\alpha M},\Omega} \\
&- \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{t}_\alpha \rangle_{\Omega_\beta,\Omega} - \langle \mathbf{e}\cdot\mathbf{t}_\alpha \rangle_{\Gamma_{\alpha M},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned} \tag{2.21}
$$

Here we consider Ω to be the macroscale length in the direction of flow. Thus, evaluation of the averaging operators yields

$$
\begin{aligned}
A\mathcal{P}^{\overline{\overline{\alpha}}} = \frac{\partial^{\backprime}}{\partial t}(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{v}^{\overline{\alpha}} A) &+ \nabla^{\backprime}\cdot(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{v}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}} A) - \nabla^{\backprime}\cdot(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}} A) - \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{g}^{\overline{\alpha}} A \\
&- \sum_{\beta\in\mathcal{J}_{c\alpha}} \mathbf{v}_\alpha^{\overline{\beta}} \overset{\beta\to\alpha}{M} A - \sum_{\beta\in\mathcal{J}_{c\alpha}} \overset{\beta\to\alpha}{\mathbf{T}} A \\
&+ \mathbf{v}_M^{\overline{\alpha}} \overset{\alpha\to}{M}_M A + \overset{\alpha\to}{\mathbf{T}}_M A = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned} \tag{2.22}
$$

or, rewriting Eq. (2.22) in material derivative form and changing the velocity $\mathbf{v}_\alpha^{\overline{\beta}}$ to its generic form which applies for all entities leaves the final form

$$
\begin{aligned}
A\mathcal{P}_*^{\overline{\overline{\alpha}}} = \frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{v}^{\overline{\alpha}} A)}{\mathrm{D}t} &+ \left(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{v}^{\overline{\alpha}} A\right) \mathbf{I}^{\backprime}\!:\!\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backprime}\cdot(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}} A) - \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{g}^{\overline{\alpha}} A \\
&- \sum_{\beta\in\mathcal{J}_{c\alpha}} \mathbf{v}^{\overline{\overline{\alpha,\beta}}} \overset{\beta\to\alpha}{M} A - \sum_{\beta\in\mathcal{J}_{c\alpha}} \overset{\beta\to\alpha}{\mathbf{T}} A
\end{aligned}
$$

$$+ \mathbf{v}_M^{\overline{\alpha}} \overset{\alpha\rightarrow}{M}_M A + \overset{\alpha\rightarrow}{\mathbf{T}}_M A = 0 \quad \text{for } \alpha \in \mathcal{I} \tag{2.23}$$

where

$$\mathbf{v}^{\overline{\overline{\alpha,\beta}}} = \begin{cases} \mathbf{v}_\alpha^{\overline{\beta}} & \text{if} \quad \beta \in \mathcal{I}_{c\alpha}^- \\ \\ \mathbf{v}_\beta^{\overline{\alpha}} & \text{if} \quad \beta \in \mathcal{I}_{c\alpha}^+ \end{cases} \tag{2.24}$$

$$\mathbf{v}_M^{\overline{\alpha}} = \langle \mathbf{v}_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \tag{2.25}$$

$$\epsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} A = \left\langle \mathbf{t}_\alpha - \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha,\Omega} \tag{2.26}$$

$$\overset{\beta\rightarrow\alpha}{\mathbf{T}} A = \left\langle \left[\mathbf{t}_\alpha + \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\overline{\alpha,\beta}}} \right) \left(\mathbf{v}_\beta - \mathbf{v}_\alpha \right) \right] \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_\beta,\Omega} \tag{2.27}$$

$$\overset{\alpha\rightarrow}{\mathbf{T}}_M A = -\left\langle \left[\mathbf{t}_\alpha - \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}_M^{\overline{\alpha}} \right) \left(\mathbf{v}_\alpha - \mathbf{v}_{\text{ext}} \right) \right] \cdot \mathbf{e} \right\rangle_{\Gamma_{\alpha M},\Omega} \tag{2.28}$$

2.3.3 Energy Conservation Equation

The microscale energy conservation equation for a phase can be written as

$$\begin{aligned} \mathcal{E}_\alpha = & \frac{\partial \left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha \right)}{\partial t} + \nabla \cdot \left[\left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha \right) \mathbf{v}_\alpha \right] \\ & - \nabla \cdot \left(\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha \right) - h_\alpha - \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} = 0 \end{aligned} \tag{2.29}$$

Applying an averaging operator to all terms yields

$$\begin{aligned} & \left\langle \frac{\partial \left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha \right)}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} \\ & + \left\langle \nabla \cdot \left[\left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha \right) \mathbf{v}_\alpha \right] \right\rangle_{\Omega_\alpha,\Omega} \end{aligned}$$

$$- \langle \nabla \cdot (\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha) \rangle_{\Omega_\alpha,\Omega} - \langle h_\alpha \rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = 0 \tag{2.30}$$

The full derivation of the macroscale energy equation proceeds like that of the mass and momentum equation, but requires many more manipulations. For this reason, the full derivation is provided in the appendix. The macroscale energy equation can be written as

$$\begin{aligned}
A\mathcal{E}^{\overline{\overline{\alpha}}} = & \frac{\partial^{\backprime}}{\partial t} \left(E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \left[\frac{1}{2} \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right] \right) \\
& + \nabla^{\backprime} \cdot \left[\left(E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \left[\frac{1}{2} \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right] \right) \mathbf{v}^{\overline{\alpha}} - A\epsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} - A\epsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} \cdot \mathbf{v}^{\overline{\alpha}} \right] \\
& - \sum_{\beta \in \mathcal{J}_{c\alpha}} \left(\left[\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2} \mathbf{v}_\alpha^{\overline{\beta}} \cdot \mathbf{v}_\alpha^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_\alpha^{\overline{\beta}} \right] A \overset{\beta \to \alpha}{M} + A \overset{\beta \to \alpha}{\mathbf{T}} \cdot \mathbf{v}_\alpha^{\overline{\beta}} + A \overset{\beta \to \alpha}{Q} \right) \\
& - \left(\left[\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2} \mathbf{v}_M^{\overline{\alpha}} \cdot \mathbf{v}_M^{\overline{\alpha}} + K_{E_M}^{\overline{\overline{\alpha}}} + \psi_M^{\overline{\alpha}} \right] A \overset{\alpha \to}{M}_M + A \overset{\alpha \to}{\mathbf{T}}_M \cdot \mathbf{v}_M^{\overline{\alpha}} + A \overset{\alpha \to}{Q}_M \right) \\
& - \epsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{\alpha}}} A - \left\langle \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned} \tag{2.31}$$

In order to write Eq. (2.31) in a generic form that applies to all entities, the following identity is employed

$$\left\langle \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \left\langle \rho_\alpha \frac{\partial^{(n)} \psi_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \mathbf{v}_\alpha \cdot \left(\mathbf{I} - \mathbf{I}_\alpha^{(n)} \right) \cdot \mathbf{g}_\alpha \right\rangle_{\Omega_\alpha,\Omega} \tag{2.32}$$

Eq. (2.32) describes the relationship between the partial time derivative and that which is fixed to a surface ($n = 1$) or a curve ($n = 2$) where n corresponds to the number of primes. From Eq. (2.32) it's apparent that when $n = 0$ as for a

volume, the second term on the right vanishes, which is why it does not appear in Eq. (2.31).

Applying Eq. (2.32), using the definition of the material derivative, and rewriting terms in Eq. (2.31) of the form $f_\alpha^{\overline{\beta}}$ into generic form (as was done when forming the momentum equation) yields the macroscale total energy equation

$$
\begin{aligned}
A\mathcal{E}_*^{\overline{\overline{\alpha}}} &= \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right) \\
&+ \left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right)\mathbf{I}^{\backslash\backslash}\!:\!\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backslash\backslash}\cdot\left(A\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}} + A\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right) \\
&- \sum_{\beta\in\mathcal{I}_{c\alpha}}\left(\left[\overline{E}^{\overline{\overline{\alpha,\beta}}} + \frac{1}{2}\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\beta}}} + K_E^{\overline{\overline{\alpha,\beta}}} + \psi^{\overline{\overline{\alpha,\beta}}}\right]A\overset{\beta\to\alpha}{M} + A\overset{\beta\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\beta}}} + A\overset{\beta\to\alpha}{Q}\right) \\
&- \left(\left(\overline{E}_M^{\overline{\overline{\alpha}}} + \frac{1}{2}\mathbf{v}_M^{\overline{\overline{\alpha}}}\cdot\mathbf{v}_M^{\overline{\overline{\alpha}}} + K_{EM}^{\overline{\overline{\alpha}}} + \psi_M^{\overline{\alpha}}\right)A\overset{\alpha\to}{M}_M + A\overset{\alpha\to}{\mathbf{T}}_M\cdot\mathbf{v}_M^{\overline{\alpha}} + A\overset{\alpha\to}{Q}_M\right) \\
&- \epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A - \left\langle\rho_\alpha\frac{\partial^{(n)}\psi_\alpha}{\partial t}\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\mathbf{v}_\alpha\cdot\left(\mathbf{I} - \mathbf{I}_\alpha^{(n)}\right)\cdot\mathbf{g}_\alpha\right\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha\in\mathcal{I}
\end{aligned}
\tag{2.33}
$$

where

$$
K_E^{\overline{\overline{\alpha,\beta}}} = \begin{cases} K_{E\alpha}^{\overline{\beta}} & \text{if} \quad \beta\in\mathcal{I}_{c\alpha}^- \\ K_{E\beta}^{\overline{\alpha}} & \text{if} \quad \beta\in\mathcal{I}_{c\alpha}^+ \end{cases}
\tag{2.34}
$$

$$
\psi^{\overline{\overline{\alpha,\beta}}} = \begin{cases} \psi_\alpha^{\overline{\beta}} & \text{if} \quad \beta\in\mathcal{I}_{c\alpha}^- \\ \psi_\beta^{\overline{\alpha}} & \text{if} \quad \beta\in\mathcal{I}_{c\alpha}^+ \end{cases}
\tag{2.35}
$$

$$\overline{E}^{\overline{\overline{\alpha,\beta}}} = \begin{cases} \frac{E_{\alpha}^{\overline{\beta}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}} & \text{if} \quad \beta \in \mathcal{J}_{c\alpha}^{-} \\ \frac{E_{\beta}^{\overline{\alpha}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}} & \text{if} \quad \beta \in \mathcal{J}_{c\alpha}^{+} \end{cases} \tag{2.36}$$

and

$$\overline{E}_{M}^{\overline{\overline{\alpha}}} = \frac{E_{M}^{\overline{\alpha}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}} \tag{2.37}$$

2.3.4 Entropy Balance Equation

The microscale entropy balance equation can be written as

$$\mathcal{S}_{\alpha} = \frac{\partial \eta_{\alpha}}{\partial t} + \nabla\cdot\left(\eta_{\alpha}\mathbf{v}_{\alpha}\right) - \nabla\cdot\boldsymbol{\varphi}_{\alpha} - b_{\alpha} = \Lambda_{\alpha} \geq 0 \tag{2.38}$$

Applying an averaging operator to all terms yields

$$\left\langle \frac{\partial \eta_{\alpha}}{\partial t} \right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \nabla\cdot\left(\eta_{\alpha}\mathbf{v}_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega} - \left\langle \nabla\cdot\boldsymbol{\varphi}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} - \left\langle b_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} = \left\langle \Lambda_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} \geq 0 \tag{2.39}$$

Then, applying the transport and divergence theorems eqns (2.5) and (2.6) yields

$$\begin{aligned} &\frac{\partial^{\backprime}}{\partial t}\left\langle \eta_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_{\alpha}\cdot\mathbf{v}_{\beta}\eta_{\alpha}\right\rangle_{\Omega_{\beta},\Omega} - \left\langle \mathbf{e}_{\alpha}\cdot\mathbf{w}\eta_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega} + \nabla^{\backprime}\cdot\left\langle \eta_{\alpha}\mathbf{v}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} \\ &\quad + \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_{\alpha}\cdot\mathbf{v}_{\alpha}\eta_{\alpha}\right\rangle_{\Omega_{\beta},\Omega} + \left\langle \mathbf{e}_{\alpha}\cdot\mathbf{v}_{\alpha}\eta_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega} - \nabla^{\backprime}\cdot\left\langle \boldsymbol{\varphi}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} \\ &\quad - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_{\alpha}\cdot\boldsymbol{\varphi}_{\alpha}\right\rangle_{\Omega_{\beta},\Omega} - \left\langle \mathbf{e}_{\alpha}\cdot\boldsymbol{\varphi}_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega} - \left\langle b_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} \\ &\quad = \left\langle \Lambda_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} \end{aligned} \tag{2.40}$$

Now we can average this equation; evaluating the operators term by term yields

$$\frac{\partial^{\backprime}}{\partial t}\langle \eta_\alpha \rangle_{\Omega_\alpha,\Omega} = \frac{\partial^{\backprime}}{\partial t}\left(\eta^{\overline{\overline{\alpha}}} A\right) \tag{2.41}$$

$$\langle b_\alpha \rangle_{\Omega_\alpha,\Omega} = \epsilon^{\overline{\overline{\alpha}}} b^\alpha A \tag{2.42}$$

$$\langle \Lambda_\alpha \rangle_{\Omega_\alpha,\Omega} = \Lambda^{\overline{\overline{\alpha}}} A \tag{2.43}$$

The divergence terms require some manipulation. Starting with the entropy term and expanding the velocity gives

$$\begin{aligned}\nabla^{\backprime}\cdot\langle \eta_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} &= \nabla^{\backprime}\cdot\left\langle \eta_\alpha \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right]\right\rangle_{\Omega_\alpha,\Omega} \\ &= \nabla^{\backprime}\cdot\left\langle \eta_\alpha \mathbf{v}^{\overline{\alpha}}\right\rangle_{\Omega_\alpha,\Omega} + \nabla^{\backprime}\cdot\left\langle \eta_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}\end{aligned} \tag{2.44}$$

The first term in eqn (2.44) evaluates to

$$\nabla^{\backprime}\cdot\left\langle \eta_\alpha \mathbf{v}^{\overline{\alpha}}\right\rangle_{\Omega_\alpha,\Omega} = \nabla^{\backprime}\cdot\left(\eta^{\overline{\overline{\alpha}}} \mathbf{v}^{\overline{\alpha}} A\right) \tag{2.45}$$

Continuing with the divergence terms, we can combine the entropy flux vector term with the last term in eqn (2.44) which leaves

$$\nabla^{\backprime}\cdot\left\langle \boldsymbol{\varphi}_\alpha - \eta_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} = \nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} A\right) \tag{2.46}$$

Moving on to the unit normal vector terms, we have

$$
\begin{aligned}
&-\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta \eta_\alpha \rangle_{\Omega_\beta,\Omega} + \sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\alpha \eta_\alpha \rangle_{\Omega_\beta,\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \boldsymbol{\varphi}_\alpha \rangle_{\Omega_\beta,\Omega} \\
&= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle [\boldsymbol{\varphi}_\alpha + \eta_\alpha (\mathbf{v}_\beta - \mathbf{v}_\alpha)] \cdot \mathbf{n}_\alpha \rangle_{\Omega_\beta,\Omega} \\
&= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left[\boldsymbol{\varphi}_\alpha + \left[\frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} + \frac{\eta_\alpha}{\rho_\alpha} - \frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \right] \rho_\alpha (\mathbf{v}_\beta - \mathbf{v}_\alpha) \right] \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_\beta,\Omega} \\
&= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \overset{\beta\to\alpha}{M} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left[\boldsymbol{\varphi}_\alpha + \left[\frac{\eta_\alpha}{\rho_\alpha} - \frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \right] \rho_\alpha (\mathbf{v}_\beta - \mathbf{v}_\alpha) \right] \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_\beta,\Omega}
\end{aligned}
\tag{2.47}
$$

We can define the last quantity in eqn (2.47) as

$$
\overset{\beta\to\alpha}{A\ \Phi} = \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left[\boldsymbol{\varphi}_\alpha + \left[\frac{\eta_\alpha}{\rho_\alpha} - \frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \right] \rho_\alpha (\mathbf{v}_\beta - \mathbf{v}_\alpha) \right] \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_\beta,\Omega} \tag{2.48}
$$

which reduces eqn (2.47) to

$$
\begin{aligned}
&-\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta \eta_\alpha \rangle_{\Omega_\beta,\Omega} + \sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\alpha \eta_\alpha \rangle_{\Omega_\beta,\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \boldsymbol{\varphi}_\alpha \rangle_{\Omega_\beta,\Omega} \\
&\quad = -\sum_{\beta\in\mathcal{I}_{c\alpha}} \left(\frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \overset{\beta\to\alpha}{M} + \overset{\beta\to\alpha}{A\ \Phi} \right)
\end{aligned}
\tag{2.49}
$$

That leaves the unit tangent vector terms from eqn (2.40)

$$
\begin{aligned}
&-\langle \mathbf{e}_\alpha \cdot \mathbf{w} \eta_\alpha \rangle_{\Gamma_{\alpha M},\Omega} + \langle \mathbf{e}_\alpha \cdot \mathbf{v}_\alpha \eta_\alpha \rangle_{\Gamma_{\alpha M},\Omega} - \langle \mathbf{e}_\alpha \cdot \boldsymbol{\varphi}_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \\
&\quad = -\langle [\boldsymbol{\varphi}_\alpha + \eta_\alpha (\mathbf{w} - \mathbf{v}_\alpha)] \cdot \mathbf{e}_\alpha \rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned}
$$

$$
\begin{aligned}
&= -\left\langle \left[\boldsymbol{\varphi}_\alpha + \left[\frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} + \frac{\eta_\alpha}{\rho_\alpha} - \frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \right] \rho_\alpha \left(\mathbf{w} - \mathbf{v}_\alpha\right) \right] \cdot \mathbf{e}_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega} \\
&= -\frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} A \overset{\alpha\rightarrow}{M}_M - \left\langle \left[\boldsymbol{\varphi}_\alpha + \left[\frac{\eta_\alpha}{\rho_\alpha} - \frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \right] \rho_\alpha \left(\mathbf{w} - \mathbf{v}_\alpha\right) \right] \cdot \mathbf{e}_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned} \tag{2.50}
$$

We can define the last quantity in eqn (2.50) as

$$
A \overset{\alpha\rightarrow}{\Phi}_M = \left\langle \left[\boldsymbol{\varphi}_\alpha + \left[\frac{\eta_\alpha}{\rho_\alpha} - \frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \right] \rho_\alpha \left(\mathbf{w} - \mathbf{v}_\alpha\right) \right] \cdot \mathbf{e}_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega} \tag{2.51}
$$

which reduces eqn (2.50) to

$$
\begin{aligned}
&-\langle \mathbf{e}_\alpha \cdot \mathbf{w} \eta_\alpha \rangle_{\Gamma_{\alpha M},\Omega} + \langle \mathbf{e}_\alpha \cdot \mathbf{v}_\alpha \eta_\alpha \rangle_{\Gamma_{\alpha M},\Omega} - \langle \mathbf{e}_\alpha \cdot \boldsymbol{\varphi}_\alpha \rangle_{\Gamma_{\alpha M},\Omega} \\
&\quad = -\left(\frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} A \overset{\alpha\rightarrow}{M}_M + A \overset{\alpha\rightarrow}{\Phi}_M \right)
\end{aligned} \tag{2.52}
$$

Now we can collect all of the defined terms from eqn (2.40) to form the macroscale entropy equation:

$$
\begin{aligned}
\langle \mathcal{S}_\alpha \rangle_{\Omega_\alpha,\Omega} &= \frac{\partial^{\backprime}}{\partial t} \left(\eta^{\overline{\overline{\alpha}}} A \right) + \nabla^{\backprime} \cdot \left(\eta^{\overline{\overline{\alpha}}} \mathbf{v}^{\overline{\alpha}} A \right) - \nabla^{\backprime} \cdot \left(\epsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} A \right) \\
&\quad - \sum_{\beta \in \mathcal{J}_{c\alpha}} \left(\frac{\eta_\alpha^{\overline{\overline{\beta}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \overset{\beta\rightarrow\alpha}{M} A + \overset{\beta\rightarrow\alpha}{\Phi} A \right) \\
&\quad - \left(\frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \overset{\alpha\rightarrow}{M}_M A + \overset{\alpha\rightarrow}{\Phi}_M A \right) - \epsilon^{\overline{\overline{\alpha}}} b^\alpha A = \Lambda^{\overline{\overline{\alpha}}} A \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned} \tag{2.53}
$$

Summing the entropy balance eqn (2.53) over all entities yields an entropy inequality which satisfies the second law of thermodynamics [17]. This yields the

macroscale entropy balance equation

$$\sum_{\alpha\in\mathcal{I}} \langle \mathcal{S}_\alpha \rangle_{\Omega_\alpha,\Omega} = \sum_{\alpha\in\mathcal{I}} \left[\frac{\partial^{\backslash\!\backslash}}{\partial t}\left(\eta^{\overline{\overline{\alpha}}} A\right) + \nabla^{\backslash\!\backslash}\!\cdot \left(\eta^{\overline{\overline{\alpha}}} \mathbf{v}^{\overline{\alpha}} A\right) - \nabla^{\backslash\!\backslash}\!\cdot \left(\epsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} A\right) \right.$$
$$\left. - \left(\frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \overset{\alpha\rightarrow}{M}_M A + \overset{\alpha\rightarrow}{\Phi}_M A \right) - \epsilon^{\overline{\overline{\alpha}}} b^\alpha A \right] = \Lambda^{\overline{\overline{\alpha}}} A \geq 0 \quad \text{for } \alpha \in \mathcal{I} \quad (2.54)$$

Comparing Eq. (2.53) with Eq. (2.54), it is important to point out that when summing over all entities the inter-entity exchange terms cancel (this exchange is equal and opposite), but the edge terms remain. Eq. (2.54) can be written in material derivative form as

$$A\mathcal{S}^{\overline{\overline{\alpha}}} = \sum_{\alpha\in\mathcal{I}} \left(\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(\eta^{\overline{\overline{\alpha}}} A\right) + \left(\eta^{\overline{\overline{\alpha}}} A\right) \mathbf{I}^{\backslash\!\backslash}\!:\!\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backslash\!\backslash}\!\cdot \left(\epsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} A\right) \right.$$
$$\left. - \left(\frac{\eta_M^{\overline{\overline{\alpha}}}}{\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha} \overset{\alpha\rightarrow}{M}_M A + \overset{\alpha\rightarrow}{\Phi}_M A \right) - \epsilon^{\overline{\overline{\alpha}}} b^\alpha A \right) = \Lambda^{\overline{\overline{\alpha}}} A \geq 0 \quad \text{for } \alpha \in \mathcal{I} \quad (2.55)$$

2.3.5 Thermodynamic Equations

The thermodynamic properties of system entities contribute to the overall system behavior and provide equally important information for model development as that contributed by the conservation and balance equations [23]. The laws of thermodynamics describe how energy delocalizes or spreads; gradients in composition, temperature, and pressure, among others drive dynamic, or non-equilibrium system behavior [56]. Real world systems are often away from equilibrium, and the entropy producing dissipative processes that occur as systems tend toward an

equilibrium state are those that we would like to describe.

The established classical thermodynamic theory is somewhat of a misnomer, in that it describes systems at equilibrium, but doesn't describe system evolution between time-independent equilibrium states at which the entropy production rate is zero. For this reason, non-equilibrium thermodynamic theory is needed; this is an area of research that is still ongoing. The effort to extend classical thermodynamics has led to multiple diverging theoretical approaches including classical irreversible thermodynamics (CIT), extended irreversible thermodynamics (EIT), rational thermodynamics (RT), rational extended thermodynamics (RET), and the theory of internal variables (TIV) [23].

The TCAT framework is flexible in terms of incorporating a non-equilibrium thermodynamic theory for model development, yet up to the present CIT theory (which is the simplest extension of classical Gibbsian equilibrium thermodynamics) has proved sufficient in guiding closure relations and keeping conservation and thermodynamic principles consistent within a given model. In other words, many systems are consistent with CIT such that a more sophisticated theory is unnecessary. Information regarding basic classical thermodynamic theory and the non-equilibirium thermodynamic theories mentioned can be found in many good resources ([9, 13, 33, 36, 52]), but won't be given further attention here; the necessary elements for this work will be presented below. As before, we will start with microscale theory, and work to average up to the macroscale. The definitions of the microscale and macroscale remain consistent with those discussed in the

introduction, and depart from the typical thermodynamic language in which the microscale refers to the molecular scale, and the macroscale describes the smallest continuum scale [23].

2.3.5.1 Fluid Phase Thermodynamics

In natural porous medium systems, the most common components are the fluids, air and water, and some indigenous solid which forms a connected matrix. Put simply, fluids and solids respond differently to applied forces, and therefore deform differently which necessitates different thermodynamic descriptions for each. For the system studied here the solid is assumed to behave like a highly viscous fluid and can therefore be described within the same framework. However, if this assumption is not made solid phase deformation, which is dependent on the type of solid (elastic or inelastic), would have to be accounted for differently. Resources that explicitly account for solid phase dynamics are available elsewhere [23, 28].

The fundamental microscale thermodynamic equation for a fluid phase can be written as

$$\mathbb{S}_\alpha = \mathbb{S}_\alpha \left(\mathbb{E}_\alpha, \mathbb{V}_\alpha, \mathbb{M}_\alpha \right) \tag{2.56}$$

or, conversely

$$\mathbb{E}_\alpha = \mathbb{E}_\alpha \left(\mathbb{S}_\alpha, \mathbb{V}_\alpha, \mathbb{M}_\alpha \right) \tag{2.57}$$

where the functions $\mathbb{S}_\alpha$ and $\mathbb{E}_\alpha$ are the phase entropy and internal energy respectively, while the extensive variables $\mathbb{V}_\alpha$ and $\mathbb{M}_\alpha$ are the phase volume and mass.

The entropy and internal energy functions can be inverted, meaning eqns (2.56) and (2.57) are equally valid. It's important to note that the phase composition is not being considered in these equations, i.e. the dependence on phase mass is considered rather than individual species mass.

Normalizing Eq. (2.57) by volume yields

$$E_\alpha = \mathbb{E}_\alpha \left(\eta_\alpha, 1, \rho_\alpha\right) \tag{2.58}$$

where

$$\eta_\alpha = \frac{\mathbb{S}_\alpha}{\mathbb{V}_\alpha} \tag{2.59}$$

The microscale Euler equation for the intensive form of the fundamental equation, eqn (2.58), can be written as

$$E_\alpha = \theta_\alpha \eta_\alpha + \rho_\alpha \mu_\alpha - p_\alpha \tag{2.60}$$

where the intensive thermodynamic variables of temperature θ_α, chemical potential μ_α, and pressure p_α appear. These are defined as

$$\theta_\alpha = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{S}_\alpha}\right)_{\mathbb{V}_\alpha, \mathbb{M}_\alpha} \tag{2.61}$$

$$p_\alpha = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{V}_\alpha}\right)_{\mathbb{S}_\alpha, \mathbb{M}_\alpha} \tag{2.62}$$

and

$$\mu_\alpha = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{M}_\alpha}\right)_{\mathbb{S}_\alpha, \mathbb{V}_\alpha} \tag{2.63}$$

where the subscripts outside of the parenthesis are used to explicitly indicate which variables are being held constant. This is common practice in thermodynamics, as many alternative energy forms (potentials) exist that are used when other functional forms are more convenient for experimentation and measurement [36].

Applying an averaging operator to all terms yields

$$\langle E_\alpha \rangle_{\Omega_\alpha, \Omega} = \langle \theta_\alpha \eta_\alpha + \rho_\alpha \mu_\alpha - p_\alpha \rangle_{\Omega_\alpha, \Omega} \tag{2.64}$$

Evaluation of the averaging operators term by term yields

$$\langle E_\alpha \rangle_{\Omega_\alpha, \Omega} = E^{\overline{\overline{\alpha}}} A \tag{2.65}$$

Next, we have the entropy and temperature term

$$\langle \theta_\alpha \eta_\alpha \rangle_{\Omega_\alpha, \Omega} = A \eta^{\overline{\overline{\alpha}}} \langle \theta_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \eta_\alpha} = \theta^{\overline{\overline{\alpha}}} \eta^{\overline{\overline{\alpha}}} A \tag{2.66}$$

where

$$\langle \eta_\alpha \rangle_{\Omega_\alpha, \Omega} = \eta^{\overline{\overline{\alpha}}} A \tag{2.67}$$

and

$$\langle \theta_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \eta_\alpha} = \theta^{\overline{\overline{\alpha}}} \tag{2.68}$$

Then we have the chemical potential and density term

$$\langle \rho_\alpha \mu_\alpha \rangle_{\Omega_\alpha,\Omega} = \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mu^{\overline{\alpha}} A \tag{2.69}$$

where

$$\langle \rho_\alpha \rangle_{\Omega_\alpha,\Omega} = \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \tag{2.70}$$

and

$$\langle \mu_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha} = \mu^{\overline{\alpha}} \tag{2.71}$$

Finally, the pressure term can be defined as

$$\langle p_\alpha \rangle_{\Omega_\alpha,\Omega} = \epsilon^{\overline{\overline{\alpha}}} p^\alpha A \tag{2.72}$$

which means the macroscale Euler equation for internal energy is

$$E^{\overline{\overline{\alpha}}} = \theta^{\overline{\overline{\alpha}}} \eta^{\overline{\overline{\alpha}}} + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mu^{\overline{\alpha}} - \epsilon^{\overline{\overline{\alpha}}} p^\alpha \tag{2.73}$$

In order to get a macroscale form of the Gibbs-Duhem equation, we will first differentiate Eq. (2.60) which yields

$$\mathrm{d}E_\alpha = \theta_\alpha \, \mathrm{d}\eta_\alpha + \eta_\alpha \, \mathrm{d}\theta_\alpha + \rho_\alpha \, \mathrm{d}\mu_\alpha + \mu_\alpha \, \mathrm{d}\rho_\alpha - \mathrm{d}p_\alpha \tag{2.74}$$

The first differential of eqn (2.58) is

$$\mathrm{d}E_\alpha = \theta_\alpha \,\mathrm{d}\eta_\alpha + \mu_\alpha \,\mathrm{d}\rho_\alpha \tag{2.75}$$

Subtracting Eq. (2.75) from Eq. (2.74) yields the microscale Gibbs-Duhem equation

$$0 = \eta_\alpha \,\mathrm{d}\theta_\alpha + \rho_\alpha \,\mathrm{d}\mu_\alpha - \,\mathrm{d}p_\alpha \tag{2.76}$$

which will be useful when manipulating the averaged thermodynamics. Eq. (2.75) can be rewritten by adding and subtracting macroscale variables as follows

$$\mathrm{d}E_\alpha = \theta^{\overline{\overline{\alpha}}} \,\mathrm{d}\eta_\alpha + \mu^{\overline{\alpha}} \,\mathrm{d}\rho_\alpha + \left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right) \,\mathrm{d}\eta_\alpha + \left(\mu_\alpha - \mu^{\overline{\alpha}}\right) \,\mathrm{d}\rho_\alpha \tag{2.77}$$

Using the product rule the last two terms in Eq. (2.77) can be expanded which yields

$$\begin{aligned} \mathrm{d}E_\alpha = \theta^{\overline{\overline{\alpha}}} \,\mathrm{d}\eta_\alpha + \mu^{\overline{\alpha}} \,\mathrm{d}\rho_\alpha + \,\mathrm{d}\left[\eta_\alpha \left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)\right] + \,\mathrm{d}\left[\rho_\alpha \left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right] \\ - \eta_\alpha \,\mathrm{d}\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right) - \rho_\alpha \,\mathrm{d}\left(\mu_\alpha - \mu^{\overline{\alpha}}\right) \end{aligned} \tag{2.78}$$

We would like to get Eq. (2.78) into material derivative form in order to incorporate the thermodynamics into the entropy inequality along with the conservation

equations. This can be accomplished by rewriting Eq. (2.78) as

$$
\begin{aligned}
&\frac{\partial E_\alpha}{\partial t} + \mathbf{v}^{\overline{\alpha}}\cdot\nabla E_\alpha - \theta^{\overline{\overline{\alpha}}}\frac{\partial \eta_\alpha}{\partial t} - \mathbf{v}^{\overline{\alpha}}\cdot\theta^{\overline{\overline{\alpha}}}\nabla\eta_\alpha - \mu^{\overline{\alpha}}\frac{\partial \rho_\alpha}{\partial t} + \mathbf{v}^{\overline{\alpha}}\cdot\nabla\rho_\alpha \\
&- \frac{\partial}{\partial t}\left[\eta_\alpha\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)\right] - \mathbf{v}^{\overline{\alpha}}\cdot\nabla\left[\eta_\alpha\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)\right] \\
&- \frac{\partial}{\partial t}\left[\rho_\alpha\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right] - \mathbf{v}^{\overline{\alpha}}\cdot\nabla\left[\rho_\alpha\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right] - \eta_\alpha\frac{\partial\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)}{\partial t} \\
&- \mathbf{v}^{\overline{\alpha}}\cdot\left[\eta_\alpha\nabla\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)\right] + \rho_\alpha\frac{\partial(\mu_\alpha - \mu^{\overline{\alpha}})}{\partial t} + \mathbf{v}^{\overline{\alpha}}\cdot\left[\rho_\alpha\nabla\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right] = 0 \qquad (2.79)
\end{aligned}
$$

Now, we can use the transport and gradient theorems from the [3,(1,0),2] family on the time and space derivatives to obtain a thermodynamic equation which includes macroscale quantities averaged from the microscale. Applying eqns (2.4) and (2.6) yields

$$
\begin{aligned}
&\frac{\partial^{\backprime}}{\partial t}\left(\langle E_\alpha\rangle_{\Omega_\alpha,\Omega}\right) - \sum_{\beta\in\mathcal{J}_{c\alpha}}\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta E_\alpha\rangle_{\Omega_\beta,\Omega} - \langle\mathbf{e}\cdot\mathbf{w}E_\alpha\rangle_{\Gamma_{\alpha M},\Omega} + \mathbf{v}^{\overline{\alpha}}\cdot\nabla^{\backprime}\langle E_\alpha\rangle_{\Omega_\alpha,\Omega} \\
&+ \sum_{\beta\in\mathcal{J}_{c\alpha}}\mathbf{v}^{\overline{\alpha}}\cdot\langle\mathbf{n}_\alpha E_\alpha\rangle_{\Omega_\beta,\Omega} + \mathbf{v}^{\overline{\alpha}}\cdot\langle\mathbf{e}E_\alpha\rangle_{\Gamma_{\alpha M},\Omega} - \theta^{\overline{\overline{\alpha}}}\frac{\partial^{\backprime}}{\partial t}\left(\langle\eta_\alpha\rangle_{\Omega_\alpha,\Omega}\right) \\
&+ \sum_{\beta\in\mathcal{J}_{c\alpha}}\theta^{\overline{\overline{\alpha}}}\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\eta_\alpha\rangle_{\Omega_\beta,\Omega} + \theta^{\overline{\overline{\alpha}}}\langle\mathbf{e}\cdot\mathbf{w}\eta_\alpha\rangle_{\Gamma_{\alpha M},\Omega} - \mu^{\overline{\alpha}}\frac{\partial^{\backprime}}{\partial t}\left(\langle\rho_\alpha\rangle_{\Omega_\alpha,\Omega}\right) \\
&+ \sum_{\beta\in\mathcal{J}_{c\alpha}}\mu^{\overline{\alpha}}\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\rho_\alpha\rangle_{\Omega_\beta,\Omega} + \mu^{\overline{\alpha}}\langle\mathbf{e}\cdot\mathbf{w}\rho_\alpha\rangle_{\Gamma_{\alpha M},\Omega} + \sum_{\beta\in\mathcal{J}_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left[\eta_\alpha\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Omega_\beta,\Omega} \\
&+ \left\langle\mathbf{e}\cdot\mathbf{w}\left[\eta_\alpha\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Gamma_{\alpha M},\Omega} + \sum_{\beta\in\mathcal{J}_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left[\rho_\alpha\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right]\right\rangle_{\Omega_\beta,\Omega} \\
&+ \left\langle\mathbf{e}\cdot\mathbf{w}\left[\rho_\alpha\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right]\right\rangle_{\Gamma_{\alpha M},\Omega} + \left\langle\eta_\alpha\frac{\partial\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)}{\partial t}\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\rho_\alpha\frac{\partial(\mu_\alpha - \mu^{\overline{\alpha}})}{\partial t}\right\rangle_{\Omega_\alpha,\Omega}
\end{aligned}
$$

$$
\begin{aligned}
&- \mathbf{v}^{\overline{\alpha}}\cdot\left(\theta^{\overline{\overline{\alpha}}}\nabla\!\!\!\!\backslash\langle\eta_\alpha\rangle_{\Omega_\alpha,\Omega}\right) - \mathbf{v}^{\overline{\alpha}}\cdot\left(\mu^{\overline{\alpha}}\nabla\!\!\!\!\backslash\langle\rho_\alpha\rangle_{\Omega_\alpha,\Omega}\right) - \sum_{\beta\in\mathcal{I}_{c\alpha}} \mathbf{v}^{\overline{\alpha}}\cdot\left(\theta^{\overline{\overline{\alpha}}}\langle\mathbf{n}_\alpha\eta_\alpha\rangle_{\Omega_\beta,\Omega}\right)\\
&- \mathbf{v}^{\overline{\alpha}}\cdot\left(\theta^{\overline{\overline{\alpha}}}\langle\mathbf{e}\eta_\alpha\rangle_{\Gamma_{\alpha M},\Omega}\right) - \sum_{\beta\in\mathcal{I}_{c\alpha}} \mathbf{v}^{\overline{\alpha}}\cdot\left(\mu^{\overline{\alpha}}\langle\mathbf{n}_\alpha\rho_\alpha\rangle_{\Omega_\beta,\Omega}\right) - \mathbf{v}^{\overline{\alpha}}\cdot\left(\mu^{\overline{\alpha}}\langle\mathbf{e}\rho_\alpha\rangle_{\Gamma_{\alpha M},\Omega}\right)\\
&- \sum_{\beta\in\mathcal{I}_{c\alpha}} \mathbf{v}^{\overline{\alpha}}\cdot\left\langle\mathbf{n}_\alpha\left[\eta_\alpha\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Omega_\beta,\Omega} - \mathbf{v}^{\overline{\alpha}}\cdot\left\langle\mathbf{e}\left[\eta_\alpha\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Gamma_{\alpha M},\Omega}\\
&+ \left\langle\eta_\alpha\nabla\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)\right\rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \mathbf{v}^{\overline{\alpha}}\cdot\left\langle\mathbf{n}_\alpha\left[\rho_\alpha\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)\right]\right\rangle_{\Omega_\beta,\Omega}\\
&- \mathbf{v}^{\overline{\alpha}}\cdot\left\langle\mathbf{e}\left[\rho_\alpha\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)\right]\right\rangle_{\Gamma_{\alpha M},\Omega} + \left\langle\rho_\alpha\nabla\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} = 0
\end{aligned}
\tag{2.80}
$$

Grouping like terms, evaluating averages when possible, and combining terms to form material derivatives yields

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t} + \left\langle\eta_\alpha\frac{\mathrm{D}^{\overline{\alpha}}\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}\\
&+ \left\langle\rho_\alpha\frac{\mathrm{D}^{\overline{\alpha}}\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} + \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_\beta\right)E_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&+ \left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{w}\right)E_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \theta^{\overline{\overline{\alpha}}}\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_\beta\right)\eta_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&- \theta^{\overline{\overline{\alpha}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{w}\right)\eta_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \mu^{\overline{\alpha}}\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_\beta\right)\rho_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&- \mu^{\overline{\alpha}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{w}\right)\rho_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_\beta\right)\left[\eta_\alpha\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Omega_\beta,\Omega}\\
&- \left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{w}\right)\left[\eta_\alpha\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Gamma_{\alpha M},\Omega}\\
&- \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_\beta\right)\left[\rho_\alpha\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)\right]\right\rangle_{\Omega_\beta,\Omega}\\
&- \left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{w}\right)\left[\rho_\alpha\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)\right]\right\rangle_{\Gamma_{\alpha M},\Omega} = 0
\end{aligned}
\tag{2.81}
$$

Using Eq. (2.73), Eq. (2.81) can be rewritten as

$$\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t} + \left\langle \eta_{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}\left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}$$
$$+ \left\langle \rho_{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}\left(\mu_{\alpha} - \mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_{\alpha}\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}_{\beta}\right)p_{\alpha}\right\rangle_{\Omega_{\beta},\Omega}$$
$$- \left\langle \mathbf{e}\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{w}\right)p_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega} = 0 \tag{2.82}$$

Eq. (2.82) can be simplified for use in the formulation of the constrained entropy inequality using the identity

$$\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} = \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} + \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\cdot\nabla^{\backprime} \tag{2.83}$$

where the mass-averaged solid phase velocity $\mathbf{v}^{\overline{s}}$ can be introduced which is used to reference the material derivatives and velocities to a common frame. Eq. (2.83) and the Gibbs-Duhem equation (eqn (2.76)) can be used to rewrite Eq. (2.82) as

$$\begin{aligned}
A\mathcal{T}_{*}^{\overline{\overline{\alpha}}} =& \frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t} \\
&+ \left\langle \eta_{\alpha}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t} + \rho_{\alpha}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\alpha} - \mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega} \\
&- \left[\eta^{\overline{\overline{\alpha}}}A\nabla^{\backprime}\theta^{\overline{\overline{\alpha}}} + \rho^{\alpha}A\nabla^{\backprime}\mu^{\overline{\alpha}} - \nabla^{\backprime}\left(\epsilon^{\overline{\overline{\alpha}}}p^{\alpha}A\right)\right]\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \\
&+ \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle p_{\alpha}\left(\mathbf{v}_{\beta} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{\alpha}\right\rangle_{\Omega_{\beta},\Omega} \\
&- \left\langle p_{\alpha}\left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right)\cdot\mathbf{e}\right\rangle_{\Gamma_{\alpha M},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned} \tag{2.84}$$

Averaging operators remain on the deviation terms and two pressure terms in Eq. (2.84), and they will be left in this form for now. This is the final form of the thermodynamics for a fluid phase which will be incorporated into the augmented entropy inequality.

2.3.5.2 Solid Phase Thermodynamics

As previously mentioned, the solid phase will be treated as a highly viscous fluid; therefore, the thermodynamics for a fluid phase Eq. (2.84) applies.

2.3.5.3 Interface Thermodynamics

The procedure for deriving the thermodynamics for the interface is analogous to that of the phase, but surficial operators will be used, and the functional dependence of internal energy will change slightly. The thermodynamic relation for the microscale internal energy per unit area which comes from the fundamental equation (eqn (2.58)) can be written as

$$E_\alpha = \theta_\alpha \eta_\alpha + \rho_\alpha \mu_\alpha + \gamma_\alpha \tag{2.85}$$

for an interface; here the interfacial tension γ_α replaces the pressure term in the phase equation (eqn (2.60)), and is defined as

$$\gamma_\alpha = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{A}_\alpha}\right)_{\mathbb{S}_\alpha, \mathbb{M}_\alpha} \quad \text{for } \alpha \in \mathcal{I}_\mathrm{I} \tag{2.86}$$

where $\mathbb{A}_\alpha$ is the interfacial area. Interfaces are two-dimensional entities meaning $\mathbb{A}_\alpha$ will replace $\mathbb{V}_\alpha$ as an extensive variable in the definition of temperature and chemical potential as well, such that

$$\theta_\alpha = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{S}_\alpha}\right)_{\mathbb{A}_\alpha, \mathbb{M}_\alpha} \quad \text{for } \alpha \in \mathcal{I}_\mathrm{I} \tag{2.87}$$

and

$$\mu_\alpha = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{M}_\alpha}\right)_{\mathbb{S}_\alpha, \mathbb{A}_\alpha} \quad \text{for } \alpha \in \mathcal{I}_\mathrm{I} \tag{2.88}$$

Applying an averaging operator to all terms in Eq. (2.85) yields

$$\langle E_\alpha \rangle_{\Omega_\alpha, \Omega} = \langle \theta_\alpha \eta_\alpha + \rho_\alpha \mu_\alpha + \gamma_\alpha \rangle_{\Omega_\alpha, \Omega} \tag{2.89}$$

We can evaluate the averaging operators in Eq. (2.89) in accordance with the definitions established for the phase equation, and define the macroscale interfacial tension as follows

$$\langle \gamma_\alpha \rangle_{\Omega_\alpha, \Omega} = \epsilon^{\overline{\overline{\alpha}}} \gamma^\alpha A \tag{2.90}$$

Eq. (2.90) can be used to write the macroscale Euler equation for internal energy per area as

$$E^{\overline{\overline{\alpha}}} = \theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mu^{\overline{\alpha}} + \epsilon^{\overline{\overline{\alpha}}}\gamma^{\alpha} \tag{2.91}$$

Similarly, the Gibbs-Duhem equation for an interface can be written as

$$0 = \eta_{\alpha}\,\mathrm{d}\theta_{\alpha} + \rho_{\alpha}\,\mathrm{d}\mu_{\alpha} + \,\mathrm{d}\gamma_{\alpha} \tag{2.92}$$

The definition for the material derivative that acts on a surface and is referenced to the solid phase velocity is

$$\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t} = \frac{\partial'}{\partial t} + \mathbf{v}^{\overline{s}}\boldsymbol{\cdot}\nabla' \quad \text{for } \mathbf{x} \in \Omega_{\alpha}, \alpha \in \mathcal{I}_{\mathrm{I}} \tag{2.93}$$

Eq. (2.93) is related to the material derivative via the identity

$$\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} = \frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t} + \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\nabla - \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}}\right)\boldsymbol{\cdot}\left(\mathbf{I} - \mathbf{I}'_{\alpha}\right)\boldsymbol{\cdot}\nabla \quad \text{for } \mathbf{x} \in \Omega_{\alpha}, \alpha \in \mathcal{I}_{\mathrm{I}} \tag{2.94}$$

Using eqns (2.92)–(2.94), applying the transport and gradient theorems (eqns (2.4) and (2.6)) to Eq. (2.79), and combining like terms yields the final expression

$$\begin{aligned} A\mathcal{T}_{*}^{\overline{\overline{\alpha}}} =& \frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t} \\ &+ \left\langle \eta_{\alpha}\frac{\mathrm{D}'^{\overline{s}}\left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t} + \rho_{\alpha}\frac{\mathrm{D}'^{\overline{s}}\left(\mu_{\alpha} - \mu^{\overline{\alpha}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \end{aligned}$$

$$
\begin{aligned}
&- \left[\eta^{\overline{\overline{\alpha}}} A \nabla^{\backprime} \theta^{\overline{\overline{\alpha}}} + \rho^{\alpha} A \nabla^{\backprime} \mu^{\overline{\alpha}} + \nabla^{\backprime} \cdot \langle \mathbf{l}'_{\alpha} \gamma_{\alpha} \rangle_{\Omega_{\alpha},\Omega}\right] \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \\
&+ \nabla^{\backprime} \cdot \left\langle \left(\mathbf{I} - \mathbf{l}'_{\alpha}\right) \cdot \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{\alpha}}\right) \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \left(\mathbf{I} - \mathbf{l}'_{\alpha}\right) \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} : \mathbf{d}^{\overline{\overline{\alpha}}} \\
&+ \left\langle \nabla \cdot \mathbf{l}'_{\alpha} \cdot \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}}\right) \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \eta_{\alpha} \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{I} - \mathbf{l}'_{\alpha}\right) \right\rangle_{\Omega_{\alpha},\Omega} \cdot \nabla \theta^{\overline{\overline{\alpha}}} \\
&+ \left\langle \rho_{\alpha} \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathbf{I} - \mathbf{l}'_{\alpha}\right) \right\rangle_{\Omega_{\alpha},\Omega} \cdot \nabla \mu^{\overline{\alpha}} - \left\langle \gamma_{\alpha} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right) \cdot \mathbf{n}_{\alpha} \right\rangle_{\Omega_{wns},\Omega} \\
&+ \left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right) \gamma_{\alpha} \right\rangle_{\Gamma_{\alpha M},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{I}}
\end{aligned}
\tag{2.95}
$$

where $\mathbf{v}_{wns}$ is the velocity of the common curve.

2.3.5.4 Common Curve Thermodynamics

The process of deriving the common curve equation is analogous to the fluid and interface procedures. Using the fundamental equation eqn (2.58) and normalizing by $\mathbb{L}_{\alpha}$ for a one-dimensional entity, we get an expression with variables defined in terms of $\mathbb{L}_{\alpha}$ instead of $\mathbb{V}_{\alpha}$ or $\mathbb{A}_{\alpha}$, as for phases or interfaces. Moving from Eq. (2.95), the variable γ_{α} is now the lineal tension and is opposite in sign to the interfacial tension; it is defined as

$$
-\gamma_{\alpha} = \left(\frac{\partial \mathbb{E}_{\alpha}}{\partial \mathbb{L}_{\alpha}}\right)_{\mathbb{S}_{\alpha},\mathbb{M}_{\alpha}} \qquad \text{for } \alpha \in \mathcal{I}_{\mathrm{C}} \tag{2.96}
$$

Additionally, now the curvilinear operators designated by $''$ will be used. Using these changes and the transport and gradient theorems (eqns (2.4) and (2.6)), Eq.

(2.95) can be modified to write the common curve equation

$$
\begin{aligned}
A\mathcal{T}_*^{\overline{\overline{\alpha}}} = & \frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t} - \mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t} \\
& + \left\langle \eta_\alpha \frac{\mathrm{D}''^{\overline{s}}\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t} + \rho_\alpha \frac{\mathrm{D}''^{\overline{s}}\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \\
& - \left[\eta^{\overline{\overline{\alpha}}}A\nabla\backslash\theta^{\overline{\overline{\alpha}}} + \rho^\alpha A\nabla\backslash\mu^{\overline{\alpha}} - \nabla\backslash\cdot\langle \mathbf{l}'_\alpha\gamma_\alpha\rangle_{\Omega_\alpha,\Omega}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \\
& - \nabla\backslash\cdot\left\langle\left(\mathbf{I} - \mathbf{l}''_\alpha\right)\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega} \\
& - \left\langle\left(\mathbf{I} - \mathbf{l}''_\alpha\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{\alpha}}} - \left\langle\nabla\cdot\mathbf{l}''_\alpha\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega} \\
& + \left\langle\eta_\alpha\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I} - \mathbf{l}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}} \\
& + \left\langle\eta_\alpha\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I} - \mathbf{l}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}} \\
& + \left\langle\rho_\alpha\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I} - \mathbf{l}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{\alpha}} \\
& - \left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right)\gamma_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{C}}
\end{aligned}
\tag{2.97}
$$

2.4 Augmented Entropy Inequality

Now that we have all of the macroscale conservation equations, the entropy inequality, and the macroscale thermodynamics, we can write an augmented entropy inequality (AEI). We know that the material derivatives contained within the aforementioned equations will equal zero at equilibrium, but even a small distance away from equilibrium this is not guaranteed; therefore, using Lagrange multipliers we can augment the EI to eliminate the material derivatives while still satisfying all of the individual conservation and thermodynamic equations

[18]. Technically, the Lagrange multipliers are arbitrary as they multiply equations which are each equal to zero, but if they are carefully selected they will cancel most of the material derivatives. The entropy inequality augmented with Lagrange multipliers can be written as

$$\sum_{\alpha\in\mathcal{I}} \left(\mathcal{S}^{\overline{\overline{\alpha}}} + \lambda^{\alpha}_{\mathcal{M}}\mathcal{M}^{\overline{\overline{\alpha}}} + \boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}\boldsymbol{\cdot}\boldsymbol{\mathcal{P}}^{\overline{\overline{\alpha}}} + \lambda^{\alpha}_{\mathcal{E}}\mathcal{E}^{\overline{\overline{\alpha}}} + \lambda^{\alpha}_{\mathcal{T}}\mathcal{T}^{\overline{\overline{\alpha}}}\right) = \Lambda^{\overline{\overline{\alpha}}} \geq 0 \tag{2.98}$$

Substituting the corresponding equations into Eq. (2.98) for each of the system entities yields

$$\begin{aligned}
&\sum_{\alpha\in\mathcal{I}} \left[\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(\eta^{\overline{\overline{\alpha}}}A\right) + \left(\eta^{\overline{\overline{\alpha}}}A\right)\mathbf{l}^{\backprime}\mathbf{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backprime}\boldsymbol{\cdot}\left(\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A\right)\right.\\
&\left. - \left(\frac{\eta^{\overline{\overline{\alpha}}}_{M}}{\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}}\overset{\alpha\rightarrow}{M}_{M}A + \overset{\alpha\rightarrow}{\Phi}_{M}A\right) - \epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A\right]\\
&+ \sum_{\alpha\in\mathcal{I}} \lambda^{\alpha}_{\mathcal{M}}\left[\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A)}{\mathrm{D}t} + (\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A)\mathbf{l}^{\backprime}\mathbf{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \sum_{\beta\in\mathcal{I}^{-}_{c\alpha}} \overset{\beta\rightarrow\alpha}{A\,M} + A\overset{\alpha\rightarrow}{M}_{M}\right]\\
&+ \sum_{\alpha\in\mathcal{I}} \boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}\boldsymbol{\cdot}\left[\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}A)}{\mathrm{D}t} + \left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}A\right)\mathbf{l}^{\backprime}\mathbf{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backprime}\boldsymbol{\cdot}(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A) - \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}A\right.\\
&\left. - \sum_{\beta\in\mathcal{I}_{c\alpha}} \mathbf{v}^{\overline{\overline{\alpha,\beta}}}\overset{\beta\rightarrow\alpha}{M}A - \sum_{\beta\in\mathcal{I}_{c\alpha}} \overset{\beta\rightarrow\alpha}{\mathbf{T}}A + \mathbf{v}^{\overline{\alpha}}_{M}\overset{\alpha\rightarrow}{M}_{M}A + \overset{\alpha\rightarrow}{\mathbf{T}}_{M}A\right]\\
&+ \sum_{\alpha\in\mathcal{I}} \lambda^{\alpha}_{\mathcal{E}}\left[\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\alpha}} + K^{\overline{\overline{\alpha}}}_{E} + \psi^{\overline{\alpha}}\right]\right)\right.\\
&\left. + \left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\alpha}} + K^{\overline{\overline{\alpha}}}_{E} + \psi^{\overline{\alpha}}\right]\right)\mathbf{l}^{\backprime}\mathbf{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backprime}\boldsymbol{\cdot}\left(A\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\alpha}} + A\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right)\right.\\
&- \sum_{\beta\in\mathcal{I}_{c\alpha}} \left(\left[\overline{E}^{\overline{\overline{\alpha,\beta}}} + \frac{1}{2}\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\overline{\alpha,\beta}}} + K^{\overline{\overline{\alpha,\beta}}}_{E} + \psi^{\overline{\overline{\alpha,\beta}}}\right]\overset{\beta\rightarrow\alpha}{A\,M} + \overset{\beta\rightarrow\alpha}{A\,\mathbf{T}}\boldsymbol{\cdot}\mathbf{v}^{\overline{\overline{\alpha,\beta}}} + \overset{\beta\rightarrow\alpha}{A\,Q}\right)
\end{aligned}$$

$$
-\left(\left(\overline{E}_M^{\overline{\overline{\alpha}}}+\frac{1}{2}\mathbf{v}_M^{\overline{\overline{\alpha}}}\cdot\mathbf{v}_M^{\overline{\overline{\alpha}}}+K_{EM}^{\overline{\overline{\alpha}}}+\psi_M^{\overline{\alpha}}\right)A\overset{\alpha\rightarrow}{M}_M+A\overset{\alpha\rightarrow}{\mathbf{T}}_M\cdot\mathbf{v}_M^{\overline{\alpha}}+A\overset{\alpha\rightarrow}{Q}_M\right)
$$

$$
-\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A-\left\langle\rho_\alpha\frac{\partial^{(n)}\psi_\alpha}{\partial t}\right\rangle_{\Omega_\alpha,\Omega}+\left\langle\mathbf{v}_\alpha\cdot\left(\mathbf{I}-\mathbf{I}_\alpha^{(n)}\right)\cdot\mathbf{g}_\alpha\right\rangle_{\Omega_\alpha,\Omega}\Bigg]
$$

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\lambda_{\mathcal{T}}^{\alpha}\Bigg[\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}
$$

$$
+\left\langle\eta_\alpha\frac{\mathrm{D}^{\overline{s}}\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}+\rho_\alpha\frac{\mathrm{D}^{\overline{s}}\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}
$$

$$
-\left[\eta^{\overline{\overline{\alpha}}}A\nabla^{\backprime}\theta^{\overline{\overline{\alpha}}}+\rho^{\alpha}A\nabla^{\backprime}\mu^{\overline{\alpha}}-\nabla^{\backprime}\left(\epsilon^{\overline{\overline{\alpha}}}p^{\alpha}A\right)\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)
$$

$$
+\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\left\langle p_\alpha\left(\mathbf{v}_\beta-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}-\left\langle p_\alpha\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\cdot\mathbf{e}\right\rangle_{\Gamma_{\alpha M},\Omega}\Bigg]
$$

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\lambda_{\mathcal{T}}^{\alpha}\Bigg[\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}
$$

$$
+\left\langle\eta_\alpha\frac{\mathrm{D}'^{\overline{s}}\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}+\rho_\alpha\frac{\mathrm{D}'^{\overline{s}}\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}
$$

$$
-\left[\eta^{\overline{\overline{\alpha}}}A\nabla^{\backprime}\theta^{\overline{\overline{\alpha}}}+\rho^{\alpha}A\nabla^{\backprime}\mu^{\overline{\alpha}}+\nabla^{\backprime}\cdot\langle\mathbf{I}'_\alpha\gamma_\alpha\rangle_{\Omega_\alpha,\Omega}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)
$$

$$
+\nabla^{\backprime}\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}+\left\langle\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{\alpha}}}
$$

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

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

$$
-\left\langle\gamma_\alpha\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_{wns},\Omega}+\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}\Bigg]
$$

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{C}}}\lambda_{\mathcal{T}}^{\alpha}\Bigg[\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}
$$

$$
+\left\langle\eta_\alpha\frac{\mathrm{D}''^{\overline{s}}\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}+\rho_\alpha\frac{\mathrm{D}''^{\overline{s}}\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}
$$

$$
-\left[\eta^{\overline{\overline{\alpha}}}A\nabla^{\backprime}\theta^{\overline{\overline{\alpha}}}+\rho^{\alpha}A\nabla^{\backprime}\mu^{\overline{\alpha}}-\nabla^{\backprime}\cdot\langle\mathbf{I}'_\alpha\gamma_\alpha\rangle_{\Omega_\alpha,\Omega}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)
$$

$$
\begin{aligned}
&-\nabla^{\backslash\backslash}\cdot\left\langle\left(\mathbf{I}-\mathbf{I}''_{\alpha}\right)\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{\alpha}}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}-\left\langle\left(\mathbf{I}-\mathbf{I}''_{\alpha}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}:\mathbf{d}^{\overline{\overline{\alpha}}}\\
&-\left\langle\nabla\cdot\mathbf{I}''_{\alpha}\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\\
&+\left\langle\eta_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}+\left\langle\rho_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\mu^{\overline{\alpha}}\\
&-\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega}\Big]\\
&=\Lambda^{\overline{\overline{\alpha}}}A\geq 0
\end{aligned}
\tag{2.99}
$$

Selecting the Lagrange multipliers such that the material derivatives vanish is accomplished by looking at each derivative separately. Solving for the multipliers becomes much easier when they are chosen in a particular order, starting with the thermodynamic Lagrange multipliers and the entropy time derivatives as shown below.

1. <u>Entropy Time Derivatives:</u>

$$
\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}\lambda^{\alpha}_{\mathcal{T}}=0 \tag{2.100}
$$

The equations for each of the entities ($\alpha=\{w,n,s,wn,ws,ns,wns\}$) have the same form, so for compactness we will remain in generic notation; however, it's important to remember that a Lagrange multiplier exists for each entity. Solving Eq. (2.100) for the Lagrange multiplier gives

$$
\lambda^{\alpha}_{\mathcal{T}}=\frac{1}{\theta^{\overline{\overline{\alpha}}}} \tag{2.101}
$$

2. Energy Time Derivatives:

In order to solve for the energy Lagrange multipliers it is necessary to rearrange the energy material derivative. This is accomplished by using the product rule and splitting up the material derivative as follows

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right]\right)}{\mathrm{D}t} \\
&=\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}+\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}\right)}{\mathrm{D}t}+\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\left[K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right]\right)}{\mathrm{D}t} \\
&=\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}+\mathbf{v}^{\overline{\alpha}}\cdot\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{v}^{\overline{\alpha}}\right)}{\mathrm{D}t} \\
&+\left(K_E^{\overline{\overline{\alpha}}}-\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\frac{\mathrm{D}^{\overline{\alpha}}\left(K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)}{\mathrm{D}t}
\end{aligned}
\tag{2.102}
$$

Now we can isolate the internal energy material derivative which appears in the energy and thermodynamic equations; this gives

$$
\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}\lambda_{\mathcal{E}}^{\alpha}+\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}\lambda_{\mathcal{T}}^{\alpha}=0 \tag{2.103}
$$

which means

$$
\lambda_{\mathcal{E}}^{\alpha}=-\lambda_{\mathcal{T}}^{\alpha} \tag{2.104}
$$

Therefore, the energy Lagrange multiplier is

$$
\lambda_{\mathcal{E}}^{\alpha}=-\frac{1}{\theta^{\overline{\overline{\alpha}}}} \tag{2.105}
$$

3. <u>Momentum Time Derivatives:</u>

$$\boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}\cdot\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{v}^{\overline{\alpha}}\right)}{\mathrm{D}t}+\lambda^{\alpha}_{\mathcal{E}}\mathbf{v}^{\overline{\alpha}}\cdot\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{v}^{\overline{\alpha}}\right)}{\mathrm{D}t}=0 \tag{2.106}$$

which simplifies to

$$\boldsymbol{\lambda}^{\alpha}_{\mathcal{T}}+\lambda^{\alpha}_{\mathcal{E}}\mathbf{v}^{\overline{\alpha}}=0 \tag{2.107}$$

This means the momentum time derivative is

$$\boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}=\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}} \tag{2.108}$$

4. <u>Mass Time Derivatives:</u>

Mass time derivatives appear in the mass, momentum, and energy equations; it is for this reason that these time derivatives are eliminated last. At this point we have definitions for the momentum and energy Lagrange multipliers, so solving for the mass multiplier is much easier. We have

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}\lambda^{\alpha}_{\mathcal{M}}-\mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}\lambda^{\alpha}_{\mathcal{T}}\\&+\left(K^{\overline{\overline{\alpha}}}_{E}-\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}\lambda^{\alpha}_{\mathcal{E}}=0\end{aligned} \tag{2.109}$$

which simplifies to

$$\lambda^{\alpha}_{\mathcal{M}}-\mu^{\overline{\alpha}}\lambda^{\alpha}_{\mathcal{T}}+\left(K^{\overline{\overline{\alpha}}}_{E}+\psi^{\overline{\alpha}}-\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}\right)\lambda^{\alpha}_{\mathcal{E}}=0 \tag{2.110}$$

Substituting in the definitions of the momentum and energy Lagrange multipliers gives

$$\lambda^{\alpha}_{\mathcal{M}} = \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(K^{\overline{\overline{\alpha}}}_{E} + \psi^{\overline{\alpha}} + \mu^{\overline{\alpha}} - \frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}\right) \tag{2.111}$$

The remaining material derivatives that could not be eliminated via Lagrange multipliers will survive into the constrained entropy inequality; these derivatives include the body force potential and the kinetic energy due to velocity fluctuations.

Now we can substitute the definitions of the Lagrange multipliers into Eq. (2.99) which gives the expanded AEI where the phase, interface, and common curve terms are labeled to make the equation more readable. The expanded equation without any algebraic manipulations is

Phase Terms:

$$\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(\eta^{\overline{\overline{\alpha}}}A\right) + \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \left(\eta^{\overline{\overline{\alpha}}}A\right)\mathbf{l}^{\backprime}\!:\!\mathbf{d}^{\overline{\overline{\alpha}}} - \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A - \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A\right)$$

$$+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \overline{\eta}^{\overline{\overline{\alpha}}}_{M}\overset{\alpha\rightarrow}{M}_{M}A + \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \overset{\alpha\rightarrow}{\Phi}_{M}A$$

$$+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}} + K^{\overline{\overline{\alpha}}}_{E} + \psi^{\overline{\alpha}} - \frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}\right)\left[\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{l}^{\backprime}\!:\!\mathbf{d}^{\overline{\overline{\alpha}}}\right.$$

$$\left. - \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \overset{\beta\rightarrow\alpha}{M}A + \overset{\alpha\rightarrow}{M}_{M}A\right]$$

$$+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\cdot\left[\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}A\right)}{\mathrm{D}t} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}A\mathbf{l}^{\backprime}\!:\!\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right) - \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}A\right]$$

$$+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\cdot\left[-\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \mathbf{v}^{\overline{\overline{\alpha,\beta}}}\overset{\beta\rightarrow\alpha}{M}A - \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \overset{\beta\rightarrow\alpha}{\mathbf{T}}A + \mathbf{v}^{\overline{\alpha}}_{M}\overset{\alpha\rightarrow}{M}_{M}A + \overset{\alpha\rightarrow}{\mathbf{T}}_{M}A\right]$$

$$
\begin{aligned}
&- \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} \left[E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \left(\frac{\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}}}{2} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) \right] \right. \\
&\left. + \left[E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \left(\frac{\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}}}{2} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) \right] \mathbf{I}^{\backslash\backslash} : \mathbf{d}^{\overline{\overline{\alpha}}} \right\} \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \left[\epsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{\alpha}}} A + \nabla^{\backslash\backslash} \cdot \left(\epsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} \cdot \mathbf{v}^{\overline{\alpha}} A \right) \right] + \left\langle \rho_{\alpha} \frac{\partial \psi_{\alpha}}{\partial t} \right\rangle_{\Omega_{\alpha},\Omega} \right\} \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \left(\overline{E}^{\overline{\overline{\alpha,\beta}}} + \frac{1}{2} \mathbf{v}^{\overline{\overline{\alpha,\beta}}} \cdot \mathbf{v}^{\overline{\overline{\alpha,\beta}}} + K_E^{\overline{\overline{\alpha,\beta}}} + \psi^{\overline{\overline{\alpha,\beta}}} \right) \overset{\beta\to\alpha}{M} A \right\} \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \mathbf{v}^{\overline{\overline{\alpha,\beta}}} \cdot \overset{\beta\to\alpha}{\mathbf{T}} A + \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \overset{\beta\to\alpha}{Q} A \right\} \\
&- \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \left(\overline{E}_M^{\overline{\overline{\alpha}}} + \frac{1}{2} \mathbf{v}_M^{\overline{\overline{\alpha}}} \cdot \mathbf{v}_M^{\overline{\overline{\alpha}}} + K_{EM}^{\overline{\overline{\alpha}}} + \psi_M^{\overline{\alpha}} \right) \overset{\alpha\to}{M}_M A + \mathbf{v}_M^{\overline{\alpha}} \cdot \overset{\alpha\to}{\mathbf{T}}_M A + \overset{\alpha\to}{Q}_M A \right\} \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\frac{\mathrm{D}^{\overline{\alpha}} \left(E^{\overline{\overline{\alpha}}} A \right)}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}} \frac{\mathrm{D}^{\overline{\alpha}} \left(\eta^{\overline{\overline{\alpha}}} A \right)}{\mathrm{D}t} - \mu^{\overline{\alpha}} \frac{\mathrm{D}^{\overline{\alpha}} \left(\epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \right)}{\mathrm{D}t} \right] \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\left\langle \eta_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}} \right)}{\mathrm{D}t} + \rho_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{\alpha} - \mu^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right] \\
&- \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) \cdot \left[\eta^{\overline{\overline{\alpha}}} A \nabla^{\backslash\backslash} \theta^{\overline{\overline{\alpha}}} + \epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \nabla^{\backslash\backslash} \mu^{\overline{\alpha}} - \nabla^{\backslash\backslash} \left(\epsilon^{\overline{\overline{\alpha}}} p^{\alpha} A \right) \right] \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}^{-}} \left\langle p_{\alpha} \left(\mathbf{v}_{\beta} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_{\alpha} \right\rangle_{\Omega_{\beta},\Omega} - \sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w} \right) p_{\alpha} \right\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned}
$$

Interface Terms:

$$
\begin{aligned}
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} \left(\eta^{\overline{\overline{\alpha}}} A \right) + \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \left(\eta^{\overline{\overline{\alpha}}} A \right) \mathbf{I}^{\backslash\backslash} : \mathbf{d}^{\overline{\overline{\alpha}}} - \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \epsilon^{\overline{\overline{\alpha}}} b^{\alpha} A - \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \nabla^{\backslash\backslash} \cdot \left(\epsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} A \right) \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \overline{\eta}_M^{\overline{\overline{\alpha}}} \overset{\alpha\to}{M}_M A + \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \overset{\alpha\to}{\Phi}_M A \\
&+ \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\mu^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} - \frac{1}{2} \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} \right) \left[\frac{\mathrm{D}^{\overline{\alpha}} \left(\epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \right)}{\mathrm{D}t} + \epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \mathbf{I}^{\backslash\backslash} : \mathbf{d}^{\overline{\overline{\alpha}}} \right. \\
&\left. - \sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}} \overset{\beta\to\alpha}{M} A + \overset{\alpha\to}{M}_M A \right]
\end{aligned}
$$

$$
\begin{aligned}
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\cdot\left[\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}A\right)}{\mathrm{D}t}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}A\mathbf{l}^{\backprime}\mathbf{:d}^{\overline{\overline{\alpha}}}-\nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right)-\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}A\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\cdot\left[-\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\overset{\beta\to\alpha}{M}A-\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\overset{\beta\to\alpha}{\mathbf{T}}A+\mathbf{v}^{\overline{\alpha}}_{M}\overset{\alpha\to}{M}_{M}A+\overset{\alpha\to}{\mathbf{T}}_{M}A\right]\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left[E^{\overline{\overline{\alpha}}}A+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\left(\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right]\right.\\
&\left.+\left[E^{\overline{\overline{\alpha}}}A+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\left(\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right]\mathbf{l}^{\backprime}\mathbf{:d}^{\overline{\overline{\alpha}}}\right\}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\left[\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A+\nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A+\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}A\right)\right]+\left\langle\rho_{\alpha}\frac{\partial'\psi_{\alpha}}{\partial t}\right\rangle_{\Omega_{\alpha},\Omega}\right\}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_{\alpha}\mathbf{v}_{\alpha}\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\cdot\mathbf{g}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\left(\overline{E}^{\overline{\overline{\alpha,\beta}}}+\frac{1}{2}\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\beta}}}+K_{E}^{\overline{\overline{\alpha,\beta}}}+\psi^{\overline{\overline{\alpha,\beta}}}\right)\overset{\beta\to\alpha}{M}A\right\}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\cdot\overset{\beta\to\alpha}{\mathbf{T}}A+\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\overset{\beta\to\alpha}{Q}A\right\}\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\left(\overline{E}^{\overline{\overline{\alpha}}}_{M}+\frac{1}{2}\mathbf{v}^{\overline{\overline{\alpha}}}_{M}\cdot\mathbf{v}^{\overline{\overline{\alpha}}}_{M}+K^{\overline{\overline{\alpha}}}_{EM}+\psi^{\overline{\alpha}}_{M}\right)\overset{\alpha\to}{M}_{M}A+\mathbf{v}^{\overline{\alpha}}_{M}\cdot\overset{\alpha\to}{\mathbf{T}}_{M}A+\overset{\alpha\to}{Q}_{M}A\right\}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\frac{\mathrm{D}^{\overline{\alpha}}\left(E^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\eta^{\overline{\overline{\alpha}}}A\right)}{\mathrm{D}t}-\mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\eta_{\alpha}\frac{\mathrm{D}'^{\overline{s}}\left(\theta_{\alpha}-\theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}+\rho_{\alpha}\frac{\mathrm{D}'^{\overline{s}}\left(\mu_{\alpha}-\mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\right]\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\cdot\left[\eta^{\overline{\overline{\alpha}}}A\nabla^{\backprime}\theta^{\overline{\overline{\alpha}}}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\nabla^{\backprime}\mu^{\overline{\alpha}}+\nabla^{\backprime}\cdot\left\langle\mathbf{I}'_{\alpha}\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\nabla^{\backprime}\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{\alpha}}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}+\left\langle\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\mathbf{:d}^{\overline{\overline{\alpha}}}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\nabla\cdot\mathbf{I}'_{\alpha}\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\eta_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\mu^{\overline{\alpha}}
\end{aligned}
$$

$$- \sum_{\alpha \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\langle \gamma_\alpha \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_{wns},\Omega} + \sum_{\alpha \in \mathcal{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w} \right) \gamma_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega}$$

Common Curve Terms:

$$+ \frac{\mathrm{D}^{\overline{wns}}}{\mathrm{D}t} \left(\eta^{\overline{\overline{wns}}} A \right) + \left(\eta^{\overline{\overline{wns}}} A \right) \mathbf{I}'' : \mathbf{d}^{\overline{\overline{wns}}} - \epsilon^{\overline{\overline{wns}}} b^{wns} A$$

$$- \nabla'' \cdot \left(\epsilon^{\overline{\overline{wns}}} \boldsymbol{\varphi}^{\overline{\overline{wns}}} A \right) + \overline{\eta}_M^{\overline{\overline{wns}}} \overset{wns\rightarrow}{M}_M A + \overset{wns\rightarrow}{\Phi}_M A$$

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left(\mu^{\overline{wns}} + K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}} - \frac{1}{2} \mathbf{v}^{\overline{wns}} \cdot \mathbf{v}^{\overline{wns}} \right) \left[\frac{\mathrm{D}^{\overline{wns}} \left(\epsilon^{\overline{\overline{wns}}} \rho^{wns} A \right)}{\mathrm{D}t} \right.$$

$$\left. + \epsilon^{\overline{\overline{wns}}} \rho^{wns} A \mathbf{I}'' : \mathbf{d}^{\overline{\overline{wns}}} \right]$$

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left(\mu^{\overline{wns}} + K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}} - \frac{1}{2} \mathbf{v}^{\overline{wns}} \cdot \mathbf{v}^{\overline{wns}} \right) \left[- \sum_{\beta \in \mathcal{I}_{cwns}} \overset{\beta \rightarrow wns}{M} A + \overset{wns\rightarrow}{M}_M A \right]$$

$$+ \frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}} \cdot \left[\frac{\mathrm{D}^{\overline{wns}} \left(\epsilon^{\overline{\overline{wns}}} \rho^{wns} \mathbf{v}^{\overline{wns}} A \right)}{\mathrm{D}t} + \epsilon^{\overline{\overline{wns}}} \rho^{wns} \mathbf{v}^{\overline{wns}} A \mathbf{I}'' : \mathbf{d}^{\overline{\overline{wns}}} \right.$$

$$\left. - \nabla'' \cdot \left(\epsilon^{\overline{\overline{wns}}} \mathbf{t}^{\overline{\overline{wns}}} A \right) - \epsilon^{\overline{\overline{wns}}} \rho^{wns} \mathbf{g}^{\overline{wns}} A \right]$$

$$+ \frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}} \cdot \left[- \sum_{\beta \in \mathcal{I}_{c\alpha}} \mathbf{v}^{\overline{\overline{wns,\beta}}} \overset{\beta \rightarrow wns}{M} A - \sum_{\beta \in \mathcal{I}_{cwns}} \overset{\beta \rightarrow wns}{\mathbf{T}} A + \mathbf{v}_M^{\overline{\overline{wns}}} \overset{wns\rightarrow}{M}_M A + \overset{wns\rightarrow}{\mathbf{T}}_M A \right]$$

$$- \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \frac{\mathrm{D}^{\overline{wns}}}{\mathrm{D}t} \left[E^{\overline{\overline{wns}}} A + \epsilon^{\overline{\overline{wns}}} \rho^{wns} A \left(\frac{1}{2} \mathbf{v}^{\overline{wns}} \cdot \mathbf{v}^{\overline{wns}} + K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}} \right) \right] \right\}$$

$$- \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \left[E^{\overline{\overline{wns}}} A + \epsilon^{\overline{\overline{wns}}} \rho^{wns} A \left(\frac{1}{2} \mathbf{v}^{\overline{wns}} \cdot \mathbf{v}^{\overline{wns}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) \right] \mathbf{I}'' : \mathbf{d}^{\overline{\overline{wns}}} \right\}$$

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left\{ \left[\epsilon^{\overline{\overline{wns}}} h^{\overline{\overline{wns}}} A + \nabla'' \cdot \left(\epsilon^{\overline{\overline{wns}}} \mathbf{q}^{\overline{\overline{wns}}} A + \epsilon^{\overline{\overline{wns}}} \mathbf{t}^{\overline{\overline{wns}}} \cdot \mathbf{v}^{\overline{wns}} A \right) \right] \right.$$

$$\left. + \left\langle \rho_{wns} \frac{\partial'' \psi_{wns}}{\partial t} \right\rangle_{\Omega_{wns},\Omega} \right\}$$

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

$$+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left\{ \sum_{\beta \in \mathcal{I}_{cwns}} \left(\overline{E}^{\overline{\overline{wns,\beta}}} + \frac{1}{2} \mathbf{v}^{\overline{\overline{wns,\beta}}} \cdot \mathbf{v}^{\overline{\overline{wns,\beta}}} + K_E^{\overline{\overline{wns,\beta}}} + \psi^{\overline{\overline{wns,\beta}}} \right) \overset{\beta \rightarrow wns}{M} A \right\}$$

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\sum_{\beta\in\mathfrak{I}_{cwns}}\mathbf{v}^{\overline{\overline{wns,\beta}}}\cdot\overset{\beta\to wns}{\mathbf{T}}A+\sum_{\beta\in\mathfrak{I}_{cwns}}\overset{\beta\to wns}{Q}A\right\}\\
&-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\{\left(\overline{E}_M^{\overline{\overline{wns}}}+\frac{1}{2}\mathbf{v}_M^{\overline{\overline{wns}}}\cdot\mathbf{v}_M^{\overline{\overline{wns}}}+K_{EM}^{\overline{\overline{wns}}}+\psi_M^{\overline{\overline{wns}}}\right)\overset{wns\to}{M}_M A+\mathbf{v}_M^{\overline{\overline{wns}}}\cdot\overset{wns\to}{\mathbf{T}}_M A+\overset{wns\to}{Q}_M A\right\}\\
&+\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\frac{\mathrm{D}^{\overline{wns}}\left(E^{\overline{\overline{wns}}}A\right)}{\mathrm{D}t}-\theta^{\overline{\overline{wns}}}\frac{\mathrm{D}^{\overline{wns}}\left(\eta^{\overline{\overline{wns}}}A\right)}{\mathrm{D}t}-\mu^{\overline{\overline{wns}}}\frac{\mathrm{D}^{\overline{wns}}\left(\epsilon^{\overline{\overline{wns}}}\rho^{wns}A\right)}{\mathrm{D}t}\right]\\
&+\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\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}\right]\\
&-\frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\cdot\left[\eta^{\overline{\overline{wns}}}A\nabla\!\!\!\!\backslash\,\theta^{\overline{\overline{wns}}}+\epsilon^{\overline{\overline{wns}}}\rho^{wns}A\nabla\!\!\!\!\backslash\,\mu^{\overline{wns}}+\nabla\!\!\!\!\backslash\cdot\langle\mathbf{I}''_{wns}\gamma_{wns}\rangle_{\Omega_{wns},\Omega}\right]\\
&-\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\nabla\!\!\!\!\backslash\cdot\left\langle\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}+\left\langle\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{wns}}}\right]\\
&-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\nabla\cdot\mathbf{I}''_{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\eta_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\theta^{\overline{\overline{wns}}}\\
&+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\mu^{\overline{wns}}\\
&-\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wns}\right\rangle_{\Gamma_{wnsM},\Omega}=A\Lambda^{\overline{\overline{\alpha}}}\geq 0
\end{aligned}
\tag{2.112}
$$

2.5 Constrained Entropy Inequality

Within the TCAT framework, formulating the constrained entropy inequality (CEI) is the final exact expression, limited only by the documented primary restrictions. The CEI is one of the most important equations derived with the TCAT approach because from the CEI secondary restrictions and approximations are applied which lead to a simplified entropy inequality (SEI), closure relations, and finally a closed model [18]. In other words, the CEI is a starting point for a large set of possible closed models, and is an equation to return to when a cho-

sen set of approximations and closure relations fails to produce a model which describes a given system adequately. We would like to derive a CEI which is composed of force-flux pairs (entropy generation terms due to irreversible processes) that vanish at equilibrium [18].

Forming the CEI from Eq. (2.112) requires a significant number of manipulations, most of which include combining like terms, and using the product rule to expand terms with the goal of getting terms in a force-flux form. While these algebraic manipulations are technically simple, they can be far from intuitive; further guidance is available in [23].

Eq. (2.112) contains the terms

$$
\begin{aligned}
\text{Terms} &= -\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\cdot\nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right) + \nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}A\right) \\
&= -\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\cdot\nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right) + \nabla^{\backprime}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right)\cdot\mathbf{v}^{\overline{\alpha}} + \nabla^{\backprime}\mathbf{v}^{\overline{\alpha}}\colon\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right) \\
&= \mathbf{l}^{\backprime}\cdot\nabla\mathbf{v}^{\overline{\alpha}}\colon\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right) \\
&= \mathbf{l}^{\backprime}\cdot\mathbf{d}^{\overline{\overline{\alpha}}}\colon\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right) \\
&= \left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{l}^{\backprime}A\right)\colon\mathbf{d}^{\overline{\overline{\alpha}}}
\end{aligned}
\tag{2.113}
$$

where the product rule was used moving from the first line of Eq. (2.113) to the second, the first two terms in line two cancel, and finally the remaining term can be reexpressed to a convenient final form. This form is convenient because we are left with the rate of strain tensor (a force) multiplying a quantity which can be considered a flux term. The type of manipulations present in Eq. (2.113) are

typical of those that will be utilized to get a final CEI. Another useful manipulation involves the macroscale Euler equation

$$E^{\overline{\overline{\alpha}}} = \theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mu^{\overline{\alpha}} - \epsilon^{\overline{\overline{\alpha}}}p^{\alpha} \tag{2.114}$$

Eq. (2.114) can be used to combine terms, along with Eq. (2.113). For example, we can collect like terms in Eq. (2.112), and simplify using Eq. (2.114) which gives

$$\begin{aligned}\text{Combined Terms} &= \frac{1}{\theta^{\overline{\overline{\alpha}}}}A\left[\left(\theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}} - E^{\overline{\overline{\alpha}}} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mu^{\overline{\alpha}}\right)\mathbf{I}^{\backprime} + \mathbf{t}^{\overline{\overline{\alpha}}}\right]:\mathbf{d}^{\overline{\overline{\alpha}}} \\ &= \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\epsilon^{\overline{\overline{\alpha}}}p^{\alpha}\mathbf{I}^{\backprime}A + \epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}A\right]:\mathbf{d}^{\overline{\overline{\alpha}}}\end{aligned} \tag{2.115}$$

We can manipulate the exchange terms by introducing a reference velocity $\mathbf{v}^{\overline{s}}$ and grouping like terms. Additionally, the relationship between phase to interface and interface to phase transfer as stated by eqn (2.116) will be used to group terms.

$$\overset{\alpha\to\alpha\beta}{X} = -\overset{\alpha\beta\to\alpha}{X} \tag{2.116}$$

Further rearrangement and cancelation of like terms can be used in conjunction with Eq. (2.116) to rewrite Eq. (2.112) as

Phase Terms:

$$\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[p^{\alpha}\mathbf{I}^{\backprime}A + \epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{I}^{\backprime}A\right]:\mathbf{d}^{\overline{\overline{\alpha}}}$$

$$
-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\left\{\epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A\right.\right.
$$

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

$$
-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\cdot\left[\eta^{\overline{\overline{\alpha}}}A\nabla^{\backprime}\theta^{\overline{\overline{\alpha}}}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\nabla^{\backprime}\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}\right)\right.
$$

$$
\left.+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{g}^{\overline{\alpha}}-\nabla^{\backprime}\left(\epsilon^{\overline{\overline{\alpha}}}Ap^{\alpha}\right)\right]
$$

$$
-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\nabla^{\backprime}\cdot\left[\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A-\frac{\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A}{\theta^{\overline{\overline{\alpha}}}}\right]-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\left[\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A\cdot\nabla^{\backprime}\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)\right]
$$

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\left[\overset{\alpha\rightarrow}{\Phi}_{M}A-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\alpha\rightarrow}{Q}_{M}A\right]
$$

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\mu^{\overline{\alpha}}+\overline{\eta}_{M}^{\overline{\overline{\alpha}}}\theta^{\overline{\overline{\alpha}}}-\overline{E}_{M}^{\overline{\overline{\alpha}}}+K_{E}^{\overline{\overline{\alpha}}}-K_{EM}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}-\psi_{M}^{\overline{\alpha}}\right.
$$

$$
\left.-\frac{1}{2}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\right]\overset{\alpha\rightarrow}{M}_{M}A
$$

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\overset{\alpha\rightarrow\beta}{M}A\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\frac{1}{\theta^{\overline{\overline{\beta}}}}\left(\mu^{\overline{\beta}}+K_{E}^{\overline{\overline{\beta}}}+\psi^{\overline{\beta}}\right)\right]
$$

$$
-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\left[\left(\overline{E}_{\alpha}^{\overline{\beta}}+\overline{K}_{E\alpha}^{\overline{\overline{\beta}}}+\overline{\psi}_{\alpha}^{\overline{\beta}}\right)\overset{\alpha\rightarrow\beta}{M}A+\overset{\alpha\rightarrow\beta}{Q}A+\left(\mathbf{v}_{\alpha}^{\overline{\beta}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{\alpha\rightarrow\beta}{\mathbf{T}}A\right.
$$

$$
\left.+\frac{1}{2}\left(\mathbf{v}_{\alpha}^{\overline{\beta}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_{\alpha}^{\overline{\beta}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\rightarrow\beta}{M}A\right]\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}-\frac{1}{\theta^{\overline{\overline{\beta}}}}\right)
$$

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

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}^{-}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\alpha\rightarrow\beta}{\mathbf{T}}A-\frac{1}{2}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\rightarrow\beta}{M}A+\left(\mathbf{v}_{\alpha}^{\overline{\beta}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\rightarrow\beta}{M}A\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)
$$

$$
-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega}
$$

Interface Terms:

$$
+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left(\left\langle-\mathbf{l}_{\alpha}'\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\cdot\mathbf{l}^{\backprime}+\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{l}^{\backprime}A\right):\mathbf{d}^{\overline{\overline{\alpha}}}\right]
$$

$$
\begin{aligned}
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \Bigg\{\epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\Bigg[\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A\\
&+\Bigg\langle\eta_{\alpha}\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}\left(\theta_{\alpha}-\theta^{\overline{\overline{\alpha}}}\right)+\rho_{\alpha}\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}\left(\mu_{\alpha}+\psi_{\alpha}-\mu^{\overline{\alpha}}-K_{E}^{\overline{\overline{\alpha}}}-\psi^{\overline{\alpha}}\right)\Bigg\rangle_{\Omega_{\alpha},\Omega}\Bigg]\Bigg\}\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \nabla\!\!\!\backslash\!\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A-\frac{\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A}{\theta^{\overline{\overline{\alpha}}}}\right)\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\cdot\Big\{\langle\eta_{\alpha}\mathbf{I}'_{\alpha}\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\!\!\!\backslash\theta^{\overline{\overline{\alpha}}}+\langle\rho_{\alpha}\mathbf{I}'_{\alpha}\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\!\!\!\backslash\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\\
&+\nabla\!\!\!\backslash\cdot\langle\mathbf{I}'_{\alpha}\gamma_{\alpha}\rangle_{\Omega_{\alpha},\Omega}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}A\Big\}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \left[-\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A\cdot\nabla\!\!\!\backslash\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\rho_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\cdot\nabla\left(K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_{\alpha},\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\nabla\!\!\!\backslash\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{\alpha}}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\eta_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\rho_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\mu^{\overline{\alpha}}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\rho_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\cdot\mathbf{g}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\nabla\cdot\mathbf{I}'_{\alpha}\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{1}{\theta^{\overline{\overline{\alpha}}}}\Big[\mu^{\overline{\alpha}}+\overline{\eta}_{M}^{\overline{\overline{\alpha}}}\theta^{\overline{\overline{\alpha}}}-\overline{E}_{M}^{\overline{\overline{\alpha}}}+K_{E}^{\overline{\overline{\alpha}}}-K_{EM}^{\overline{\overline{\alpha}}}\\
&+\psi^{\overline{\alpha}}-\psi_{M}^{\overline{\alpha}}-\frac{1}{2}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\Big]\overset{\alpha\rightarrow}{M}_{M}A\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_{M}^{\overline{\alpha}}\right)}{\theta^{\overline{\overline{\alpha}}}}\cdot\overset{\alpha\rightarrow}{\mathbf{T}}_{M}A+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \left[\overset{\alpha\rightarrow}{\Phi}_{M}A-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\alpha\rightarrow}{Q}_{M}A\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\ \overset{\alpha\rightarrow wns}{M}A\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mu^{\overline{wns}}+K_{E}^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right]
\end{aligned}
$$

$$
-\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\left[\left(\overline{E}_{\alpha}^{\overline{wns}}+\overline{K}_{E\alpha}^{\overline{\overline{wns}}}+\overline{\psi}_{\alpha}^{\overline{wns}}\right)\overset{\alpha\to wns}{M}A+\overset{\alpha\to wns}{Q}A+\left(\mathbf{v}_{\alpha}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\cdot\overset{\alpha\to wns}{\mathbf{T}}A\right.
$$

$$
+\frac{1}{2}\left(\mathbf{v}_{\alpha}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{v}_{\alpha}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\to wns}{M}A
$$

$$
\left.+\left\langle\gamma_{\alpha}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{\alpha}\right\rangle_{\Omega_{wns},\Omega}\right]\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)
$$

$$
+\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\overset{\alpha\to wns}{\mathbf{T}}A-\frac{1}{2}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\to wns}{M}A+\left(\mathbf{v}_{\alpha}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\to wns}{M}A\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)
$$

$$
-\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\sum_{\beta\in\mathcal{J}_{c\alpha}^{+}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\overset{\beta\to\alpha}{\mathbf{T}}A-\frac{1}{2}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\overset{\beta\to\alpha}{M}A+\left(\mathbf{v}_{\beta}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\overset{\beta\to\alpha}{M}A\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)
$$

$$
+\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega}
$$

Common Curve Terms:

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\left\langle\mathbf{l}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\cdot\mathbf{l}''+\epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{l}''A\right]:\mathbf{d}^{\overline{\overline{wns}}}
$$

$$
-\left\{\epsilon^{\overline{\overline{wns}}}b^{wns}A-\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\epsilon^{\overline{\overline{wns}}}h^{\overline{\overline{wns}}}A\right.\right.
$$

$$
+\left\langle\eta_{wns}\frac{\mathrm{D}''^{\overline{s}}}{\mathrm{D}t}\left(\theta_{wns}-\theta^{\overline{\overline{wns}}}\right)\right.
$$

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

$$
-\nabla''\cdot\left(\epsilon^{\overline{\overline{wns}}}\boldsymbol{\varphi}^{\overline{\overline{wns}}}A-\frac{\epsilon^{\overline{\overline{wns}}}\mathbf{q}^{\overline{\overline{wns}}}A}{\theta^{\overline{\overline{wns}}}}\right)
$$

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

$$
+\left\langle\rho_{wns}\mathbf{l}''_{wns}\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla''\left(\mu^{\overline{wns}}+K_{E}^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)
$$

$$
\left.-\nabla''\cdot\left\langle\mathbf{l}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}+\epsilon^{\overline{\overline{wns}}}\rho^{wns}\mathbf{g}^{\overline{wns}}A\right\}
$$

$$
-\epsilon^{\overline{\overline{wns}}}\mathbf{q}^{\overline{\overline{wns}}}A\cdot\nabla''\left(\frac{1}{\theta^{\overline{\overline{wns}}}}\right)
$$

$$
+\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\cdot\left(\mathbf{I}-\mathbf{l}''_{wns}\right)\cdot\nabla\left(K_{E}^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right\rangle_{\Omega_{wns},\Omega}\right]
$$

$$
\begin{aligned}
&- \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\nabla^{\backslash\backslash} \cdot \left\langle \left(\mathbf{I} - \mathbf{I}''_{wns} \right) \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}} \right) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega} \right] \\
&+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\left\langle \eta_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}} \right) \cdot \left(\mathbf{I} - \mathbf{I}''_{wns} \right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \theta^{\overline{\overline{wns}}} \right] \\
&+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\left\langle \rho_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}} \right) \cdot \left(\mathbf{I} - \mathbf{I}''_{wns} \right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \mu^{\overline{wns}} \right] \\
&+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\left\langle \rho_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{I} - \mathbf{I}''_{wns} \right) \cdot \mathbf{g}_{wns} \right\rangle_{\Omega_{wns},\Omega} \right] \\
&- \frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \nabla \cdot \mathbf{I}''_{wns} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega} \\
&+ \overset{wns\rightarrow}{\Phi}_M A - \frac{1}{\theta^{\overline{\overline{wns}}}} \overset{wns\rightarrow}{Q}_M A + \frac{\left(\mathbf{v}^{\overline{wns}} - \mathbf{v}_M^{\overline{wns}} \right)}{\theta^{\overline{\overline{wns}}}} \cdot \overset{wns\rightarrow}{\mathbf{T}}_M A \\
&+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\mu^{\overline{wns}} + \overline{\eta}_M^{\overline{\overline{wns}}} \theta^{\overline{\overline{wns}}} - \overline{E}_M^{\overline{\overline{wns}}} + K_E^{\overline{\overline{wns}}} - K_{EM}^{\overline{\overline{wns}}} + \psi^{\overline{wns}} - \psi_M^{\overline{wns}} \right. \\
&\left. - \frac{1}{2} \left(\mathbf{v}^{\overline{wns}} - \mathbf{v}_M^{\overline{wns}} \right) \cdot \left(\mathbf{v}^{\overline{wns}} - \mathbf{v}_M^{\overline{wns}} \right) \right] \overset{wns\rightarrow}{M}_M A \\
&- \sum_{\beta \in \mathfrak{I}^+_{cwns}} \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\overset{\beta\rightarrow wns}{\mathbf{T}} A - \frac{1}{2} \left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}} \right) \overset{\beta\rightarrow wns}{M} A \right. \\
&\left. + \left(\mathbf{v}_\beta^{\overline{wns}} - \mathbf{v}^{\overline{s}} \right) \overset{\beta\rightarrow wns}{M} A \right] \cdot \left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}} \right) \\
&- \frac{1}{\theta^{\overline{\overline{wns}}}} \left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w} \right) \gamma_{wns} \right\rangle_{\Gamma_{wnsM},\Omega} \\
&= A \Lambda^{\overline{\overline{\alpha}}} \geq 0
\end{aligned}
\tag{2.117}
$$

Eq. (2.117) will be considered the final form of the CEI for this work. With the CEI secondary restrictions and approximations can be introduced to formulate a simplified entropy inequality comprised only of force-flux pairs.

2.6 Simplified Entropy Inequality

With Eq. (2.117) we have exhausted the available exact algebraic manipulations to achieve a form of the entropy inequality that is in strictly force-flux form, the

SEI. The simplifications and approximations introduced to derive the SEI serve to reduce the generality of the CEI and arrive at a system-specific equation that can serve as a guide for positing closure relations; therefore, it supports a hierarchy of possible closed models. Secondary restrictions, which narrow down the system of interest, and SEI approximations, which are physically guided mathematical approximations, will be introduced systematically to show how each restriction can further simplify the entropy inequality to attain a final SEI.

It is important to note that many approximations that are made to reduce the CEI to an SEI are guided by equilibrium conditions. Using variational methods it's possible to derive conditions which apply at equilibrium at the microscale and then the macroscale; these conditions are important to identify in order to formulate a model that satisfies equilibrium thermodynamics, in addition to being helpful for positing closure relations to yield a solvable model. One logical result of this analysis is the condition that the temperature gradient in a system is zero at equilibrium, but many other conditions are less straightforward [23].

Other guides in moving from the CEI to the SEI are the evolution equations which describe the changes in geometric properties such as porosity, fluid saturations, and specific entity measures $\epsilon^{\overline{\overline{\alpha}}}$. The evolution of these quantities cannot be derived using the conservation or thermodynamic equations, but instead relies upon differential geometry considerations [23]. The derivation of a full set of equilibrium conditions and evolution equations necessary to guide SEI approximations is beyond the scope of this work, and instead the resources [18, 23, 28] are relied

upon while the necessary results will be presented here.

Secondary Restriction 1 (Isothermal, No Mass Exchange)

- The temperature of the system is constant, meaning $\theta^{\overline{\overline{\alpha}}} = \theta \quad \text{for } \alpha \in \mathcal{I}$

- There is no mass exchange between entities, i.e. all terms of the form $\overset{\alpha\to\beta}{M} = 0 \quad \text{for } \alpha \in \mathcal{I}, \beta \in \mathcal{I}^{-}_{c\alpha}$

Using Secondary Restriction 1 the CEI (Eq. (2.117)) can be simplified to

Phase Terms:

$$\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \frac{1}{\theta}\left[p^{\alpha}\mathbf{I}^{\backprime}A + \epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{I}^{\backprime}A\right]:\mathbf{d}^{\overline{\overline{\alpha}}}$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\left\{\epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A - \frac{1}{\theta}\left[\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A + \left\langle \rho_{\alpha}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\alpha}+\psi_{\alpha}-\mu^{\overline{\alpha}}-\psi^{\overline{\alpha}}-K_E^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\right]\right\}$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\frac{1}{\theta}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\cdot\left[\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\nabla^{\backprime}\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}\right)+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{g}^{\overline{\alpha}}-\nabla^{\backprime}\left(\epsilon^{\overline{\overline{\alpha}}}Ap^{\alpha}\right)\right]$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\nabla^{\backprime}\cdot\left[\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A-\frac{\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A}{\theta}\right]+\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\left[\overset{\alpha\to}{\Phi}_M A-\frac{1}{\theta}\overset{\alpha\to}{Q}_M A\right]+\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_M^{\overline{\alpha}}\right)}{\theta^{\overline{\overline{\alpha}}}}\cdot\overset{\alpha\to}{\mathbf{T}}_M A$$

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

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega}$$

Interface Terms:

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\left(\left\langle-\mathbf{I}'_{\alpha}\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\cdot\mathbf{I}^{\backprime}+\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{I}^{\backprime}A\right):\mathbf{d}^{\overline{\overline{\alpha}}}\right]$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\left\{\epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A-\frac{1}{\theta}\left[\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A+\left\langle\rho_{\alpha}\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}\left(\mu_{\alpha}+\psi_{\alpha}-\mu^{\overline{\alpha}}-K_E^{\overline{\overline{\alpha}}}-\psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_{\alpha},\Omega}\right]\right\}$$

$$
\begin{aligned}
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \nabla^{\backslash\!\backslash}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A-\frac{\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A}{\theta}\right)\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\cdot\Big\{\langle\rho_\alpha\mathbf{l}'_\alpha\rangle_{\Omega_\alpha,\Omega}\cdot\nabla^{\backslash\!\backslash}\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\\
&+\nabla^{\backslash\!\backslash}\cdot\langle\mathbf{l}'_\alpha\gamma_\alpha\rangle_{\Omega_\alpha,\Omega}+\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\mathbf{g}^{\overline{\alpha}}A\Big\}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{l}'_\alpha\right)\cdot\nabla\left(K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left[\nabla^{\backslash\!\backslash}\cdot\left\langle\left(\mathbf{I}-\mathbf{l}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{l}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{\alpha}}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{l}'_\alpha\right)\cdot\mathbf{g}_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left\langle\nabla\cdot\mathbf{l}'_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\\
&+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_M^{\overline{\alpha}}\right)}{\theta}\cdot\overset{\alpha\rightarrow}{\mathbf{T}}_M A+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\left[\overset{\alpha\rightarrow}{\Phi}_M A-\frac{1}{\theta}\overset{\alpha\rightarrow}{Q}_M A\right]\\
&-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \frac{1}{\theta}\left\langle\gamma_\alpha\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_{wns},\Omega}+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned}
$$

Common Curve Terms:

$$
\begin{aligned}
&+\frac{1}{\theta}\left[\langle\mathbf{l}''_{wns}\gamma_{wns}\rangle_{\Omega_{wns},\Omega}\cdot\mathbf{l}^{\backslash\!\backslash}+\epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{l}^{\backslash\!\backslash}A\right]:\mathbf{d}^{\overline{\overline{wns}}}\\
&-\Bigg\{\epsilon^{\overline{\overline{wns}}}b^{wns}A-\frac{1}{\theta}\Bigg[\epsilon^{\overline{\overline{wns}}}h^{\overline{\overline{wns}}}A\\
&+\left\langle\rho_{wns}\frac{\mathrm{D}''^{\overline{s}}}{\mathrm{D}t}\left(\mu_{wns}+\psi_{wns}-\mu^{\overline{wns}}-K_E^{\overline{\overline{wns}}}-\psi^{\overline{wns}}\right)\right\rangle_{\Omega_{wns},\Omega}\Bigg]\Bigg\}\\
&-\nabla^{\backslash\!\backslash}\cdot\left(\epsilon^{\overline{\overline{wns}}}\boldsymbol{\varphi}^{\overline{\overline{wns}}}A-\frac{\epsilon^{\overline{\overline{wns}}}\mathbf{q}^{\overline{\overline{wns}}}A}{\theta}\right)\\
&-\frac{1}{\theta}\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\cdot\Big\{\langle\rho_{wns}\mathbf{l}''_{wns}\rangle_{\Omega_{wns},\Omega}\cdot\nabla^{\backslash\!\backslash}\left(\mu^{\overline{wns}}+K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)
\end{aligned}
$$

$$
\begin{aligned}
&-\nabla^{\backslash\backslash}\cdot\langle \mathbf{I}''_{wns}\gamma_{wns}\rangle_{\Omega_{wns},\Omega} + \epsilon^{\overline{\overline{wns}}}\rho^{wns}\mathbf{g}^{\overline{wns}}A\Big\} \\
&+\frac{1}{\theta}\left[\left\langle \rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\nabla\left(K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right\rangle_{\Omega_{wns},\Omega}\right] \\
&-\frac{1}{\theta}\left[\nabla^{\backslash\backslash}\cdot\left\langle\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\right] \\
&+\frac{1}{\theta}\left[\left\langle \rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\mu^{\overline{wns}}\right] \\
&+\frac{1}{\theta}\left[\left\langle \rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\mathbf{g}_{wns}\right\rangle_{\Omega_{wns},\Omega}\right] \\
&-\frac{1}{\theta}\left\langle \nabla\cdot\mathbf{I}''_{wns}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega} \\
&+\overset{wns\rightarrow}{\Phi}_M A-\frac{1}{\theta}\overset{wns\rightarrow}{Q}_M A+\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}_M^{\overline{wns}}\right)}{\theta}\cdot\overset{wns\rightarrow}{\mathbf{T}}_M A \\
&-\sum_{\beta\in\mathcal{J}_{cwns}}\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{\overline{wns,\beta}}}\right)}{\theta}\cdot\overset{\beta\rightarrow wns}{\mathbf{T}}A \\
&-\sum_{\alpha\in\mathcal{J}_{\mathrm{P}}}\sum_{\beta\in\mathcal{J}_{c\alpha}}\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\right)}{\theta^{\overline{\overline{\alpha}}}}\cdot\overset{\beta\rightarrow\alpha}{\mathbf{T}}A-\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\sum_{\beta\in\mathcal{J}_{c\alpha}}\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\right)}{\theta^{\overline{\overline{\alpha}}}}\cdot\overset{\beta\rightarrow\alpha}{\mathbf{T}}A \\
&-\frac{1}{\theta}\left\langle \mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wns}\right\rangle_{\Gamma_{wnsM},\Omega} \\
&=A\Lambda^{\overline{\overline{\alpha}}}\geq 0
\end{aligned}
\tag{2.118}
$$

SEI Approximation 1 (Macroscopically Simple System)

- The entropy source and the heat source plus the deviation terms balance each other such that the following relation applies

$$
\begin{aligned}
&\epsilon^{\overline{\overline{\alpha}}}b^{\alpha}A-\frac{1}{\theta}\left[\epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}A+\left\langle \rho_{\alpha}\frac{\mathrm{D}^{(n)\overline{s}}}{\mathrm{D}t}\left(\mu_{\alpha}+\psi_{\alpha}-\mu^{\overline{\alpha}}-K_E^{\overline{\overline{\alpha}}}-\psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_{\alpha},\Omega}\right] \\
&\qquad=0\quad\text{for }\alpha\in\mathcal{J}
\end{aligned}
\tag{2.119}
$$

- The entropy and non-advective heat and mechanical energy flux terms balance such that

$$\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}A - \frac{\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A}{\theta^{\overline{\overline{\alpha}}}} = 0 \quad \text{for } \alpha \in \mathcal{J} \tag{2.120}$$

- The corresponding exchange terms at the megascale boundary balance such that

$$\left[\overset{\alpha\rightarrow}{\Phi}_M A - \frac{1}{\theta}\overset{\alpha\rightarrow}{Q}_M A\right] = 0 \quad \text{for } \alpha \in \mathcal{J} \tag{2.121}$$

Using SEI approximation 1, Eq. (2.118) can be written as

Phase Terms:

$$\sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \frac{1}{\theta}\left[p^{\alpha}\mathbf{I}^{\backprime}A + \epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{I}^{\backprime}A\right]:\mathbf{d}^{\overline{\overline{\alpha}}}$$

$$-\sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \frac{1}{\theta}\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\cdot\left[\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\nabla^{\backprime}\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}}\right) + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{g}^{\overline{\alpha}} - \nabla^{\backprime}\left(\epsilon^{\overline{\overline{\alpha}}}Ap^{\alpha}\right)\right]$$

$$+\frac{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}_M^{\overline{\alpha}}\right)}{\theta^{\overline{\overline{\alpha}}}}\cdot\overset{\alpha\rightarrow}{\mathbf{T}}_M A$$

$$+\sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \frac{1}{\theta}\sum_{\beta\in\mathcal{J}_{\mathrm{c}\alpha}^{-}} \left\langle p_{\alpha}\left(\mathbf{v}_{\beta} - \mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_{\alpha}\right\rangle_{\Omega_{\beta},\Omega}$$

$$-\sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right)p_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega}$$

Interface Terms:

$$+\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}} \frac{1}{\theta}\left[\left(\left\langle-\mathbf{I}_{\alpha}'\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\cdot\mathbf{I}^{\backprime} + \epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{I}^{\backprime}A\right):\mathbf{d}^{\overline{\overline{\alpha}}}\right]$$

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

$$\left.+\nabla^{\backprime}\cdot\left\langle\mathbf{I}_{\alpha}'\gamma_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}A\right\}$$

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\cdot\nabla\left(K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}\right]$$

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\nabla^{\backprime}\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]$$

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{\alpha}}\right]$$

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\cdot\mathbf{g}_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]$$

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

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_M^{\overline{\alpha}}\right)}{\theta}\cdot\overset{\alpha\rightarrow}{\mathbf{T}}_M A$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left\langle\gamma_\alpha\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_{wns},\Omega}+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}$$

Common Curve Terms:

$$+\frac{1}{\theta}\left[\left\langle\mathbf{I}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\cdot\mathbf{I}^{\backprime}+\epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{I}^{\backprime}A\right]:\mathbf{d}^{\overline{\overline{wns}}}$$

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

$$\left.-\nabla^{\backprime}\cdot\left\langle\mathbf{I}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}+\epsilon^{\overline{\overline{wns}}}\rho^{wns}\mathbf{g}^{\overline{wns}}A\right\}$$

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

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

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

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

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

$$+\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}_M^{\overline{wns}}\right)}{\theta}\cdot\overset{wns\rightarrow}{\mathbf{T}}_M A-\sum_{\beta\in\mathcal{I}_{cwns}}\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{\overline{wns,\beta}}}\right)}{\theta}\cdot\overset{\beta\rightarrow wns}{\mathbf{T}}A$$

$$
\begin{aligned}
&- \sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \sum_{\beta\in\mathcal{J}_{c\alpha}} \frac{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{\overline{\alpha,\beta}}}\right)}{\theta^{\overline{\overline{\alpha}}}} \cdot \overset{\beta\to\alpha}{\mathbf{T}} A - \sum_{\alpha\in\mathcal{J}_{\mathrm{I}}} \sum_{\beta\in\mathcal{J}_{c\alpha}} \frac{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{\overline{\alpha,\beta}}}\right)}{\theta^{\overline{\overline{\alpha}}}} \cdot \overset{\beta\to\alpha}{\mathbf{T}} A \\
&- \frac{1}{\theta} \left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right) \gamma_{wns} \right\rangle_{\Gamma_{wnsM},\Omega} \\
&= A\Lambda^{\overline{\overline{\alpha}}} \geq 0
\end{aligned}
\tag{2.122}
$$

Secondary Restriction 2 (Velocity Conditions)

- The solid is immobile such that $\mathbf{v}^{\overline{s}} = 0$
- The average horizontal velocity is zero
- Fluid-solid interface velocities averaged over a fluid phase, and fluid phase velocities averaged over fluid-solid interfaces, are zero, i.e. $\mathbf{v}^{\overline{\overline{\alpha,\beta}}} = 0$ for $\alpha = w, n,\ \beta = ws, ns$
- Macroscale Fluid-solid interface velocities are zero such that $\mathbf{v}^{\overline{ws}} = \mathbf{v}^{\overline{ns}} = 0$

SEI Approximation 2 (Velocity Difference Terms)

- Expressions involving the product of microscale quantities and the difference $(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})$ for $\alpha \in \mathcal{J}$ are assumed to be negligible [23].

Using these restrictions and approximations Eq. (2.122) becomes

Phase Terms:

$$
\begin{aligned}
&\sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \frac{1}{\theta} \left[p^{\alpha} \mathbf{I}^{\backprime} A + \epsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} \cdot \mathbf{I}^{\backprime} A \right] : \mathbf{d}^{\overline{\overline{\alpha}}} \\
&- \sum_{\alpha\in\mathcal{J}_{\mathrm{P}}} \frac{1}{\theta} \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \cdot \left[\epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \nabla^{\backprime} \left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} \right) + \epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} A \mathbf{g}^{\overline{\alpha}} - \nabla^{\backprime} \left(\epsilon^{\overline{\overline{\alpha}}} A p^{\alpha} \right) \right]
\end{aligned}
$$

$$+\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_M^{\overline{\alpha}}\right)}{\theta^{\overline{\overline{\alpha}}}}\cdot\overset{\alpha\rightarrow}{\mathbf{T}}_M A$$

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

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)p_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}}\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\right)}{\theta}\cdot\overset{\beta\rightarrow\alpha}{\mathbf{T}}A$$

Interface Terms:

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\left(\left\langle-\mathbf{l}'_\alpha\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\cdot\mathbf{l}^{\backslash\backslash}+\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{l}^{\backslash\backslash}A\right):\mathbf{d}^{\overline{\overline{\alpha}}}\right]$$

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

$$\left.+\nabla^{\backslash\backslash}\cdot\left\langle\mathbf{l}'_\alpha\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}+\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\mathbf{g}^{\overline{\alpha}}A\right\}$$

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left[\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_\alpha\right)\cdot\mathbf{g}_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]$$

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

$$+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}_M^{\overline{\alpha}}\right)}{\theta}\cdot\overset{\alpha\rightarrow}{\mathbf{T}}_M A$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta}\left\langle\gamma_\alpha\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_{wns},\Omega}+\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}$$

$$-\sum_{\alpha\in\mathcal{I}_{\mathrm{I}}}\sum_{\beta\in\mathcal{I}_{\mathrm{c}\alpha}}\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{\overline{\alpha,\beta}}}\right)}{\theta}\cdot\overset{\beta\rightarrow\alpha}{\mathbf{T}}A$$

Common Curve Terms:

$$+\frac{1}{\theta}\left[\left\langle\mathbf{l}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\cdot\mathbf{l}^{\backslash\backslash}+\epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{l}^{\backslash\backslash}A\right]:\mathbf{d}^{\overline{\overline{wns}}}$$

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

$$
\begin{aligned}
&-\nabla^{\backprime}\cdot\langle \mathbf{I}''_{wns}\gamma_{wns}\rangle_{\Omega_{wns},\Omega} + \epsilon^{\overline{\overline{wns}}}\rho^{wns}\mathbf{g}^{\overline{wns}}A\Big\} \\
&+\frac{1}{\theta}\left[\left\langle \rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\mathbf{g}_{wns}\right\rangle_{\Omega_{wns},\Omega}\right] \\
&-\frac{1}{\theta}\left\langle \nabla\cdot\mathbf{I}''_{wns}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega} \\
&+\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}_M^{\overline{wns}}\right)}{\theta}\cdot\overset{wns\rightarrow}{\mathbf{T}_M}A - \sum_{\beta\in\mathcal{I}_{cwns}}\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{\overline{wns,\beta}}}\right)}{\theta}\cdot\overset{\beta\rightarrow wns}{\mathbf{T}}A \\
&-\frac{1}{\theta}\left\langle \mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wns}\right\rangle_{\Gamma_{wnsM},\Omega} \\
&= A\Lambda^{\overline{\overline{\alpha}}} \geq 0
\end{aligned}
\tag{2.123}
$$

Now we can expand the summations in Eq. (2.123) to make further simplifications. Additionally, the two phases which comprise each interface have normal vectors that are in opposite directions such that the following relation applies

$$
\mathbf{n}_\beta = -\mathbf{n}_\alpha \quad \text{for } \mathbf{x}\in\Omega_{\alpha\beta},\ \alpha,\beta\in\mathcal{I}_{\mathrm{P}} \tag{2.124}
$$

Using Eq. (2.124), and remembering that for this three phase system $\mathcal{I}_{\mathrm{P}} = \{w,n,s\}$, $\mathcal{I}_{\mathrm{I}} = \{wn,ns,ws\}$, and $\mathcal{I}_{\mathrm{C}} = \{wns\}$, the summations in Eq. (2.123) can be expanded, which yields

$$
\begin{aligned}
&\frac{1}{\theta}\left[p^w\mathbf{I}^{\backprime}A + \epsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}\cdot\mathbf{I}^{\backprime}A\right]:\mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta}\left[p^n\mathbf{I}^{\backprime}A + \epsilon^{\overline{\overline{n}}}\mathbf{t}^{\overline{\overline{n}}}\cdot\mathbf{I}^{\backprime}A\right]:\mathbf{d}^{\overline{\overline{n}}} \\
&-\frac{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left[\epsilon^{\overline{\overline{w}}}\rho^w A\nabla^{\backprime}\left(\mu^{\overline{w}}+\psi^{\overline{w}}+K_E^{\overline{\overline{w}}}\right) + \epsilon^{\overline{\overline{w}}}\rho^w A\mathbf{g}^{\overline{w}} - \nabla^{\backprime}\left(\epsilon^{\overline{\overline{w}}}Ap^w\right)\right] \\
&-\frac{\left(\mathbf{v}^{\overline{n}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left[\epsilon^{\overline{\overline{n}}}\rho^n A\nabla^{\backprime}\left(\mu^{\overline{n}}+\psi^{\overline{n}}+K_E^{\overline{\overline{n}}}\right) + \epsilon^{\overline{\overline{n}}}\rho^n A\mathbf{g}^{\overline{n}} - \nabla^{\backprime}\left(\epsilon^{\overline{\overline{n}}}Ap^n\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\overset{w\rightarrow}{\mathbf{T}}_M A+\frac{\left(\mathbf{v}^{\overline{n}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\overset{n\rightarrow}{\mathbf{T}}_M A\\
&+\frac{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{\overline{w},\overline{wn}}}\right)}{\theta}\cdot\overset{w\rightarrow wn}{\mathbf{T}}A+\frac{\left(\mathbf{v}^{\overline{n}}-\mathbf{v}^{\overline{\overline{n},\overline{wn}}}\right)}{\theta}\cdot\overset{n\rightarrow wn}{\mathbf{T}}A\\
&-\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)p_w\right\rangle_{\Gamma_{wM},\Omega}-\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)p_n\right\rangle_{\Gamma_{nM},\Omega}-\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)p_s\right\rangle_{\Gamma_{sM},\Omega}\\
&+\frac{1}{\theta}\left[\left(\left\langle-\mathbf{l}'_{wn}\gamma_{wn}\right\rangle_{\Omega_{wn},\Omega}\cdot\mathbf{l}''+\epsilon^{\overline{\overline{wn}}}\mathbf{t}^{\overline{\overline{wn}}}\cdot\mathbf{l}''A\right):\mathbf{d}^{\overline{\overline{wn}}}\right]\\
&-\frac{\left(\mathbf{v}^{\overline{wn}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left\{\left\langle\rho_{wn}\mathbf{l}'_{wn}\right\rangle_{\Omega_{wn},\Omega}\cdot\nabla''\left(\mu^{\overline{wn}}+K_E^{\overline{\overline{wn}}}+\psi^{\overline{wn}}\right)\right.\\
&\left.+\nabla''\cdot\left\langle\mathbf{l}'_{wn}\gamma_{wn}\right\rangle_{\Omega_{wn},\Omega}+\epsilon^{\overline{\overline{wn}}}\rho^{wn}\mathbf{g}^{\overline{wn}}A\right\}\\
&+\frac{\left(\mathbf{v}^{\overline{wn}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\overset{wn\rightarrow}{\mathbf{T}}_M A+\frac{\left(\mathbf{v}^{\overline{wn}}-\mathbf{v}^{\overline{\overline{wn},\overline{w}}}\right)}{\theta}\cdot\overset{w\rightarrow wn}{\mathbf{T}}A+\frac{\left(\mathbf{v}^{\overline{wn}}-\mathbf{v}^{\overline{\overline{wn},\overline{n}}}\right)}{\theta}\cdot\overset{n\rightarrow wn}{\mathbf{T}}A\\
&+\frac{1}{\theta}\left\langle\left[\left(p_w-p_n\right)\cdot\mathbf{n}_w+\gamma_{wn}\left(\nabla\cdot\mathbf{l}'_{wn}\right)+\rho_{wn}\mathbf{g}_{wn}\cdot\left(\mathbf{l}-\mathbf{l}'_{wn}\right)\right]\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}\\
&+\frac{1}{\theta}\left\langle\left[\left(p_w-p_s\right)\cdot\mathbf{n}_w+\gamma_{ws}\left(\nabla\cdot\mathbf{l}'_{ws}\right)+\rho_{ws}\mathbf{g}_{ws}\cdot\left(\mathbf{l}-\mathbf{l}'_{ws}\right)\right]\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega}\\
&+\frac{1}{\theta}\left\langle\left[\left(p_n-p_s\right)\cdot\mathbf{n}_n+\gamma_{ns}\left(\nabla\cdot\mathbf{l}'_{ns}\right)+\rho_{ns}\mathbf{g}_{ns}\cdot\left(\mathbf{l}-\mathbf{l}'_{ns}\right)\right]\cdot\left(\mathbf{v}_{ns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ns},\Omega}\\
&+\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wn}\right\rangle_{\Gamma_{wnM},\Omega}-\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{ns}\right\rangle_{\Gamma_{nsM},\Omega}\\
&-\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{ws}\right\rangle_{\Gamma_{wsM},\Omega}\\
&+\frac{1}{\theta}\left[\left\langle\mathbf{l}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\cdot\mathbf{l}''+\epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{l}''A\right]:\mathbf{d}^{\overline{\overline{wns}}}\\
&-\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left\{\left\langle\rho_{wns}\mathbf{l}''_{wns}\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla''\left(\mu^{\overline{wns}}+K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right.\\
&\left.-\nabla''\cdot\left\langle\mathbf{l}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}+\epsilon^{\overline{\overline{wns}}}\rho^{wns}\mathbf{g}^{\overline{wns}}A\right\}\\
&-\frac{1}{\theta}\left\langle\left[\gamma_{wn}\mathbf{n}_{wn}+\gamma_{ws}\mathbf{n}_{ws}+\gamma_{ns}\mathbf{n}_{ns}+\gamma_{wns}\left(\nabla\cdot\mathbf{l}''_{wns}\right)\right.\right.\\
&\left.\left.-\rho_{wns}\mathbf{g}_{wns}\cdot\left(\mathbf{l}-\mathbf{l}''_{wns}\right)\right]\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\\
&+\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\overset{wns\rightarrow}{\mathbf{T}}_M A-\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{\overline{wns},\overline{wn}}}\right)}{\theta}\cdot\overset{wn\rightarrow wns}{\mathbf{T}}A\\
&-\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wns}\right\rangle_{\Gamma_{wnsM},\Omega}
\end{aligned}
$$

$$= A\Lambda \geq 0 \tag{2.125}$$

Microscale averages over the interfaces and the common curve have been grouped, and subsequently require further attention. The following relations for the surface divergence and unit surface tensor prove useful in rearranging terms that are averaged over an interface.

$$\mathbf{I} - \mathbf{I}'_{\alpha\beta} = \mathbf{n}_\alpha \mathbf{n}_\alpha \quad \text{for } \mathbf{x} \in \Omega_{\alpha\beta},\ \alpha, \beta \in \mathcal{I}_{\mathrm{P}} \tag{2.126}$$

and

$$\nabla' \cdot \mathbf{I}'_{\alpha\beta} = -\left(\nabla' \cdot \mathbf{n}_\alpha\right) \mathbf{n}_\alpha \quad \text{for } \mathbf{x} \in \Omega_{\alpha\beta},\ \alpha, \beta \in \mathcal{I}_{\mathrm{P}} \tag{2.127}$$

Using Eqs. (2.126) and (2.127), we know

$$\begin{aligned}
&\frac{1}{\theta}\left\langle \left[\left(p_w - p_n\right) \cdot \mathbf{n}_w + \gamma_{wn}\left(\nabla' \cdot \mathbf{I}'_{wn}\right) + \rho_{wn}\mathbf{g}_{wn} \cdot \left(\mathbf{I} - \mathbf{I}'_{wn}\right)\right] \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wn},\Omega} \\
&\quad = \frac{1}{\theta}\left\langle \left(p_w - p_n + \gamma_{wn}\nabla' \cdot \mathbf{n}_w + \rho_{wn}\mathbf{g}_{wn} \cdot \mathbf{n}_w\right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wn},\Omega} \\
&\quad = \frac{1}{\theta}\left\langle \left(P_{wn} - \gamma_{wn} J_w\right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{wn},\Omega}
\end{aligned} \tag{2.128}$$

where we have defined

$$P_{wn} = p_w - p_n + \rho_{wn}\mathbf{g}_{wn} \cdot \mathbf{n}_w \tag{2.129}$$

and the microscale curvature

$$J_w = \nabla' \cdot \mathbf{n}_w \tag{2.130}$$

We can now define macroscale averages of these terms as

$$P^{wn} = p_w^{wn} - p_n^{wn} + \rho^{wn} \left(\mathbf{g}_{wn} \cdot \mathbf{n}_w\right)^{\overline{wn}} = \langle P_{wn} \rangle_{\Omega_{wn}, \Omega_{wn}} \tag{2.131}$$

and

$$J_w^{wn} = \langle J_w \rangle_{\Omega_{wn}, \Omega_{wn}} \tag{2.132}$$

Expanding Eq. (2.128) by adding and subtracting these macroscale quantities as we have done before yields

$$\begin{aligned}
&\frac{1}{\theta} \left\langle \left(P_{wn} - \gamma_{wn} J_w\right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wn}, \Omega} \\
&= \frac{1}{\theta} \Big\langle \left([P^{wn} + (P_{wn} - P^{wn})] - [\gamma^{wn} + (\gamma_{wn} - \gamma^{wn})] \right. \\
&\left. [J_w^{wn} + (J_w - J_w^{wn})] \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right) \Big\rangle_{\Omega_{wn}, \Omega} \\
&= \frac{1}{\theta} \left(P^{wn} - \gamma^{wn} J_w^{wn}\right) \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wn}, \Omega} \\
&- \left\langle \gamma^{wn} \left(J_w - J_w^{wn}\right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wn}, \Omega} \\
&+ \left\langle \left(P_{wn} - P^{wn}\right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wn}, \Omega} \\
&- \left\langle \left(\gamma_{wn} - \gamma^{wn}\right) J_w \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wn}, \Omega}
\end{aligned} \tag{2.133}$$

Eq. (2.133) can be condensed by defining some new variables:

$$e_J^{\overline{\overline{wn}}} = \left\langle \gamma^{wn} \left(J_w - J_w^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \tag{2.134}$$

$$e_P^{\overline{\overline{wn}}} = \left\langle \left(P_{wn} - P^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \tag{2.135}$$

and

$$e_\gamma^{\overline{\overline{wn}}} = \left\langle J_w \left(\gamma_{wn} - \gamma^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \tag{2.136}$$

where eqns (2.134)–(2.136) represent deviation terms between microscale and macroscale variables [23]. Now Eq. (2.133) can be rewritten as

$$\begin{aligned} &\frac{1}{\theta} \left\langle \left(P_{wn} - \gamma_{wn} J_w \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \\ &\quad = \frac{1}{\theta} \left[\left(P^{wn} - \gamma^{wn} J_w^{wn} \right) \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} - e_J^{\overline{\overline{wn}}} + e_P^{\overline{\overline{wn}}} - e_\gamma^{\overline{\overline{wn}}} \right] \end{aligned} \tag{2.137}$$

The terms that appear in Eq. (2.137) can be simplified using an additional set of SEI approximations.

SEI Approximation 3 (Fluid-Fluid Interface Conditions)

- The average of the velocity difference can be approximated as

$$\left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} = \frac{\mathrm{D}^{\overline{s}} \epsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{ws}}} \frac{\mathrm{D}^{\overline{s}} \epsilon}{\mathrm{D}t} \tag{2.138}$$

where

$$\chi_s^{\overline{\overline{\alpha s}}} = \langle 1 \rangle_{\Omega_{\alpha s},\Gamma_s} \quad \text{for } \alpha s \in \mathcal{I}_{\mathrm{I}}, \alpha \in \mathcal{I}_f \tag{2.139}$$

and

$$\epsilon^{\overline{\overline{s}}} = 1 - \epsilon \tag{2.140}$$

Eq. (2.139) is the wetted fraction, or the fraction of the solid surface that is wet by the α fluid phase forming the αs interface [23], and ϵ is the porosity, which is defined as

$$\epsilon = \sum_{\alpha \in \mathcal{I}_f} \epsilon^{\overline{\overline{\alpha}}} = \epsilon^{\overline{\overline{w}}} + \epsilon^{\overline{\overline{n}}} \tag{2.141}$$

- Now, approximating the $e^{\overline{\overline{wn}}}$ terms in Eq. (2.137) we can say that $e_J^{\overline{\overline{wn}}}$ (the term accounting for changes in the curvature of the interface) can be written as a first-order approximation in the deviation from equilibrium. Introducing a positive coefficient $\hat{k}^{wn}$, and $\epsilon_{eq}^{\overline{\overline{wn}}}$, which is the area of the interface at equilibrium, we can write

$$e_J^{\overline{\overline{wn}}} = -\hat{k}^{wn}\gamma^{wn}\left(\epsilon^{\overline{\overline{wn}}} - \epsilon_{eq}^{\overline{\overline{wn}}}\right) \tag{2.142}$$

where

$$\epsilon_{eq}^{\overline{\overline{wn}}} = \epsilon_{eq}^{\overline{\overline{wn}}}\left(s^{\overline{\overline{w}}}, J_w^{wn}\right) \tag{2.143}$$

In Eq. (2.143), $s^{\overline{\overline{w}}}$ is the saturation of the wetting phase; in general, the fluid saturation is defined as

$$s^{\overline{\overline{\alpha}}} = \langle 1 \rangle_{\Omega_\alpha, \Omega_f} \quad \text{for } \alpha \in \mathcal{I}_\mathrm{f} \tag{2.144}$$

Eq. (2.141) can be interpreted as the relaxation rate of the wn interface due to changes in curvature of the interface [23].

- We know that $e_P^{\overline{\overline{wn}}}$ and $e_\gamma^{\overline{\overline{wn}}}$ will be much smaller than $e_J^{\overline{\overline{wn}}}$ in that the relaxation rates due to the pressure and interfacial tension changes at the interface will occur much faster than the relaxation rate due to curvature changes. For this reason, $e_P^{\overline{\overline{wn}}}$ and $e_\gamma^{\overline{\overline{wn}}}$ will both be approximated such that they are equal to zero.

Using SEI approximation 3, Eq. (2.137) becomes

$$\begin{aligned}
&\frac{1}{\theta}\left[\left(P^{wn}-\gamma^{wn}J_w^{wn}\right)\left\langle \mathbf{n}_w\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}-e_J^{\overline{\overline{wn}}}+e_P^{\overline{\overline{wn}}}-e_\gamma^{\overline{\overline{wn}}}\right]\\
&=\frac{1}{\theta}\left(P^{wn}-\gamma^{wn}J_w^{wn}\right)\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}-\chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t}\right]+\frac{1}{\theta}\hat{k}^{wn}\gamma^{wn}\left(\epsilon^{\overline{\overline{wn}}}-\epsilon_{eq}^{\overline{\overline{wn}}}\right)
\end{aligned}\tag{2.145}$$

which is now in terms of all macroscale quantities. From equilibrium conditions defined at the macroscale [28], we know

$$P^{wn}-\gamma^{wn}J_w^{wn}=0\ \rightarrow\ 0=\frac{\gamma^{wn}J_w^{wn}}{P^{wn}}-1\tag{2.146}$$

at equilibrium, so we can define another coefficient $\hat{k}_1^{wn}$ such that

$$\hat{k}^{wn}=\left(\frac{\gamma^{wn}J_w^{wn}}{P^{wn}}-1\right)\hat{k}_1^{wn}\tag{2.147}$$

Using this coefficient in Eq. (2.145) we can write

$$\frac{1}{\theta}\left(P^{wn}-\gamma^{wn}J_w^{wn}\right)\left[\frac{\mathrm{D}^{\bar{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}-\chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\bar{s}}\epsilon}{\mathrm{D}t}\right]+\frac{1}{\theta}\hat{k}^{wn}\gamma^{wn}\left(\epsilon^{\overline{\overline{wn}}}-\epsilon_{eq}^{\overline{\overline{wn}}}\right)$$
$$=\frac{1}{\theta}\left(P^{wn}-\gamma^{wn}J_w^{wn}\right)\left[\frac{\mathrm{D}^{\bar{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}-\chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\bar{s}}\epsilon}{\mathrm{D}t}-\frac{\gamma^{wn}}{P^{wn}}\hat{k}_1^{wn}\left(\epsilon^{\overline{\overline{wn}}}-\epsilon_{eq}^{\overline{\overline{wn}}}\right)\right] \tag{2.148}$$

where we will substitute the definition of P^{wn} into Eq. (2.148) for subsequent use. In arriving at Eq. (2.148), some sophisticated assumptions were made regarding the capillary effects at the fluid-fluid interface which are beyond the scope of this work; more detailed information regarding capillary pressure dynamics is available [22].

Similarly, the ws and ns interfaces terms will take the form

$$\frac{1}{\theta}\left(p_\alpha^{\alpha s}+\left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right)_s^{\alpha s}+\rho^{\alpha s}\left(\mathbf{g}_{\alpha s}\cdot\mathbf{n}_s\right)_s^{\bar{\alpha}s}+\gamma^{\alpha s}J_s^{\alpha s}\right)\chi_s^{\bar{\bar{\alpha}}s}\frac{\mathrm{D}^{\bar{s}}\epsilon}{\mathrm{D}t}\quad\text{for }\alpha\in\mathcal{I}_\mathrm{f} \tag{2.149}$$

Although fluid-solid interfaces are inherently different than fluid-fluid interfaces based on solid deformation properties, Eq. (2.149) will be taken to be valid. A full derivation of Eq. (2.149) exists in [23].

At the common curve we can also use some geometric relationships to simplify Eq. (2.125). The terms which need to be evaluated are

$$\begin{aligned}\text{Terms}=&\frac{1}{\theta}\Big\langle\left[\gamma_{wn}\mathbf{n}_{wn}+\gamma_{ws}\mathbf{n}_{ws}+\gamma_{ns}\mathbf{n}_{ns}+\gamma_{wns}\left(\nabla\cdot\mathbf{I}''_{wns}\right)\right.\\&\left.-\rho_{wns}\mathbf{g}_{wns}\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right]\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\Big\rangle_{\Omega_{wns},\Omega}\end{aligned} \tag{2.150}$$

In this analysis we will make the assumption that the solid is smooth such that it has a unique normal direction at every point on the surface, which means the normal vectors for the fluid-solid interfaces and for the solid phase can be related as follows

$$\mathbf{n}_{ns} = -\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{2.151}$$

$$\mathbf{n}_{wn} = \cos \boldsymbol{\varphi}_{ws,wn} \mathbf{n}_{ws} - \sin \boldsymbol{\varphi}_{ws,wn} \mathbf{n}_{s} \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{2.152}$$

where $\boldsymbol{\varphi}_{ws,ws}$ is the contact angle between the ws and wn interfaces. Additionally, along the common curve the following relation holds

$$\nabla \cdot \mathbf{l}''_{wns} = \kappa_{Nwns} \mathbf{n}_{s} + \kappa_{Gwns} \mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{2.153}$$

where κ_{Nwns} is the normal curvature, and κ_{Gwns} is the geodesic curvature. The unit vectors normal to the common curve can be related as follows

$$\mathbf{I} - \mathbf{l}''_{wns} = \mathbf{n}_{s} \mathbf{n}_{s} + \mathbf{n}_{ws} \mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{2.154}$$

Eq. (2.154), along with Eqs. (2.151)–(2.153) can be used to rewrite Eq. (2.150) as

$$\frac{1}{\theta} \Big\langle \left[\gamma_{wn} \mathbf{n}_{wn} + \gamma_{ws} \mathbf{n}_{ws} + \gamma_{ns} \mathbf{n}_{ns} + \gamma_{wns} \left(\nabla \cdot \mathbf{l}''_{wns} \right) \right.$$

$$
\begin{aligned}
&-\rho_{wns}\mathbf{g}_{wns}\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)]\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{wns},\Omega}\\
&=\frac{1}{\theta}\Big\langle\left(\gamma_{wn}\cos\boldsymbol{\varphi}_{ws,wn}+\gamma_{ws}-\gamma_{ns}+\gamma_{wns}\kappa_{Gwns}\right.\\
&\left.-\rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{ws}\right)\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{wns},\Omega}\\
&-\frac{1}{\theta}\langle\left(\gamma_{wn}\sin\boldsymbol{\varphi}_{ws,wn}-\gamma_{wns}\kappa_{Nwns}+\rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{s}\right)\mathbf{n}_{s}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{wns},\Omega}
\end{aligned}
\tag{2.155}
$$

The following approximation can be made at this point:

SEI Approximation 4 (Common Curve Conditions)

- The product of factors in the averages over wns can be rewritten as averages of the product of factors.

- The following approximations are valid

$$
\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=A\left(\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_{s}^{\overline{\overline{ws}}}}{\mathrm{D}t}
\tag{2.156}
$$

  and

$$
\left\langle\mathbf{n}_{s}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=-A\frac{\epsilon^{\overline{\overline{wns}}}}{\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t}
\tag{2.157}
$$

- The correlations of γ_{wn} with $\cos\boldsymbol{\varphi}_{ws,wn}$ and $\sin\boldsymbol{\varphi}_{ws,wn}$ are negligible.

- The correlations of γ_{wns} with κ_{Gwns} and κ_{Nwns} are negligible.

- Negligible correlations imply that the average of the product of the factors can be written as the product of the averages.

Using SEI approximation 4, Eq. (2.155) can be written as

$$
\begin{aligned}
&\frac{1}{\theta}\Big\langle \big(\gamma_{wn}\cos\boldsymbol{\varphi}_{ws,wn}+\gamma_{ws}-\gamma_{ns}+\gamma_{wns}\kappa_{Gwns} \\
&-\rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{ws}\big)\,\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{wns},\Omega} \\
&-\frac{1}{\theta}\big\langle\big(\gamma_{wn}\sin\boldsymbol{\varphi}_{ws,wn}-\gamma_{wns}\kappa_{Nwns}+\rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{s}\big)\,\mathbf{n}_{s}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\big\rangle_{\Omega_{wns},\Omega} \\
&=\frac{1}{\theta}A\left[\gamma_{wn}^{wns}\cos\boldsymbol{\varphi}^{\overline{\overline{ws},\overline{wn}}}+\gamma_{ws}^{wns}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_{G}^{\overline{\overline{wns}}}\right. \\
&\left.-\rho^{wns}\left(\mathbf{g}_{wns}\cdot\mathbf{n}_{ws}\right)^{\overline{wns}}\right]\left(\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_{s}^{\overline{\overline{ws}}}}{\mathrm{D}t} \\
&+\frac{1}{\theta}A\left[\gamma_{wn}^{wns}\sin\boldsymbol{\varphi}^{\overline{\overline{ws},\overline{wn}}}-\gamma^{wns}\kappa_{N}^{\overline{\overline{wns}}}+\rho^{wns}\left(\mathbf{g}_{wns}\cdot\mathbf{n}_{s}\right)^{\overline{wns}}\right]\frac{\epsilon^{\overline{\overline{wns}}}}{\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t}
\end{aligned}
\tag{2.158}
$$

We can also make use of the geometric orientation tensors when simplifying interface and common curve terms. These are

$$
\mathbf{G}_{\alpha}=\mathbf{I}-\mathbf{I}'_{\alpha}\quad\text{for }\alpha\in\mathcal{I}_{\mathrm{I}} \tag{2.159}
$$

and

$$
\mathbf{G}_{wns}=\mathbf{I}-\mathbf{I}''_{wns} \tag{2.160}
$$

SEI Approximation 5 (Geometric Orientation Tensor Products)

- For a general microscsale property f_{α}, the following relations apply

$$
\langle\mathbf{G}_{\alpha}f_{\alpha}\rangle_{\Omega_{\alpha},\Omega}=\epsilon^{\overline{\overline{\alpha}}}\mathbf{G}^{\alpha}f^{\alpha}A \tag{2.161}
$$

and

$$\langle \mathbf{G}_{wns} f_{wns} \rangle_{\Omega_{wns},\Omega} = \epsilon^{\overline{\overline{wns}}} \mathbf{G}^{wns} f^{wns} A \tag{2.162}$$

where $\mathbf{G}$ are symmetric tensors which provide a measure of the average orientation of a surface or a curve [23]. Making the approximations in Eqs. (2.161) and (2.162) on the products appearing in Eq. (2.125) implies that the geometric orientation tensors are independent of the properties f_α that they multiply; therefore, the average of products can be split into a product of averages. If these products are found to be dependent via experimentation then SEI approximation 5 would no longer be valid.

An additional restriction will be imposed to limit the system of interest:

Secondary Restriction 3 (Massless Interfaces and Common Curves)

- The interfaces and the common curve will be considered massless such that

  $\rho^\alpha = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{I}} \text{ and } \mathcal{J}_{\mathrm{C}}$

Using the outlined approximations and making use of secondary restriction 3, Eq. (2.125) becomes

$$\begin{aligned}
&\frac{1}{\theta}\left[p^w \mathbf{I}^{\backslash\backslash} A + \epsilon^{\overline{\overline{w}}} \mathbf{t}^{\overline{\overline{w}}} \cdot \mathbf{I}^{\backslash\backslash} A\right] : \mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta}\left[p^n \mathbf{I}^{\backslash\backslash} A + \epsilon^{\overline{\overline{n}}} \mathbf{t}^{\overline{\overline{n}}} \cdot \mathbf{I}^{\backslash\backslash} A\right] : \mathbf{d}^{\overline{\overline{n}}} \\
&- \frac{(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}})}{\theta} \cdot \left[\epsilon^{\overline{\overline{w}}} \rho^w A \nabla^{\backslash\backslash}\left(\mu^{\overline{w}} + \psi^{\overline{w}} + K_E^{\overline{\overline{w}}}\right) + \epsilon^{\overline{\overline{w}}} \rho^w A \mathbf{g}^{\overline{w}} - \nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{w}}} A p^w\right) - {}^{w\to wn}\mathbf{T} A\right] \\
&- \frac{(\mathbf{v}^{\overline{n}} - \mathbf{v}^{\overline{s}})}{\theta} \cdot \left[\epsilon^{\overline{\overline{n}}} \rho^n A \nabla^{\backslash\backslash}\left(\mu^{\overline{n}} + \psi^{\overline{n}} + K_E^{\overline{\overline{n}}}\right) + \epsilon^{\overline{\overline{n}}} \rho^n A \mathbf{g}^{\overline{n}} - \nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{n}}} A p^n\right) - {}^{n\to wn}\mathbf{T} A\right] \\
&+ \frac{(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}})}{\theta} \cdot {}^{w\to}\mathbf{T}_M A + \frac{(\mathbf{v}^{\overline{n}} - \mathbf{v}^{\overline{s}})}{\theta} \cdot {}^{n\to}\mathbf{T}_M A \\
&- \frac{1}{\theta}\left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right) p_w \right\rangle_{\Gamma_{wM},\Omega} - \frac{1}{\theta}\left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right) p_n \right\rangle_{\Gamma_{nM},\Omega} - \frac{1}{\theta}\left\langle \mathbf{e} \cdot \left(\mathbf{v}^{\overline{s}} - \mathbf{w}\right) p_s \right\rangle_{\Gamma_{sM},\Omega}
\end{aligned}$$

$$
\begin{aligned}
&+ \frac{1}{\theta}\left[\left(-\left(\mathbf{I}-\mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}\cdot\mathbf{I}^{\backslash\backslash}A+\epsilon^{\overline{\overline{wn}}}\mathbf{t}^{\overline{\overline{wn}}}\cdot\mathbf{I}^{\backslash\backslash}A\right):\mathbf{d}^{\overline{\overline{wn}}}\right] \\
&- \frac{\left(\mathbf{v}^{\overline{wn}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left\{\nabla^{\backslash\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}A\right]+\sum_{wn\in\mathcal{I}_{c\alpha}^{+}}{}^{wn\to\alpha}\mathbf{T}\,A-{}^{wn\to wns}\mathbf{T}\,A\right\} \\
&+ \frac{\left(\mathbf{v}^{\overline{wn}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot{}^{wn\to}\mathbf{T}_{M}A \\
&+ \frac{1}{\theta}\left(p_{w}^{wn}-p_{n}^{wn}-\gamma^{wn}J_{w}^{wn}\right)A\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}-\chi_{s}^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t}-\frac{\gamma^{wn}\hat{k}_{1}^{wn}\left(\epsilon^{\overline{\overline{wn}}}-\epsilon_{eq}^{\overline{\overline{wn}}}\right)}{p_{w}^{wn}-p_{n}^{wn}}\right] \\
&+ \frac{1}{\theta}\left(p_{w}^{ws}-p_{s}^{ws}-\gamma^{ws}J_{w}^{ws}\right)A\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}-\chi_{s}^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t}-\frac{\gamma^{ws}\hat{k}_{1}^{ws}\left(\epsilon^{\overline{\overline{ws}}}-\epsilon_{eq}^{\overline{\overline{ws}}}\right)}{p_{w}^{ws}-p_{s}^{ws}}\right] \\
&+ \frac{1}{\theta}\left(p_{n}^{ns}-p_{s}^{ns}-\gamma^{ns}J_{w}^{ns}\right)A\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{n}}}}{\mathrm{D}t}-\chi_{s}^{\overline{\overline{ns}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t}-\frac{\gamma^{ns}\hat{k}_{1}^{ns}\left(\epsilon^{\overline{\overline{ns}}}-\epsilon_{eq}^{\overline{\overline{ns}}}\right)}{p_{w}^{ns}-p_{n}^{ns}}\right] \\
&+ \frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wn}\right\rangle_{\Gamma_{wnM},\Omega}+\frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{ns}\right\rangle_{\Gamma_{nsM},\Omega} \\
&+ \frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{ws}\right\rangle_{\Gamma_{wsM},\Omega} \\
&+ \frac{1}{\theta}\left[\left(\mathbf{I}-\mathbf{G}^{wns}\right)\epsilon^{\overline{\overline{wns}}}\gamma^{wns}\cdot\mathbf{I}^{\backslash\backslash}A+\epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{I}^{\backslash\backslash}A\right]:\mathbf{d}^{\overline{\overline{wns}}} \\
&+ \frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left\{\nabla^{\backslash\backslash}\cdot\left(\mathbf{I}-\mathbf{G}^{wns}\right)\epsilon^{\overline{\overline{wns}}}\gamma^{wns}A-{}^{wn\to wns}\mathbf{T}\,A\right\} \\
&- \frac{1}{\theta}A\left[\gamma_{wn}^{wns}\cos\boldsymbol{\varphi}^{\overline{\overline{ws,wn}}}+\gamma_{ws}^{wns}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_{G}^{\overline{\overline{wns}}}\right]\left(\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_{s}^{\overline{\overline{ws}}}}{\mathrm{D}t} \\
&- \frac{1}{\theta}A\left[\gamma_{wn}^{wns}\sin\boldsymbol{\varphi}^{\overline{\overline{ws,wn}}}-\gamma^{wns}\kappa_{N}^{\overline{\overline{wns}}}\right]\frac{\epsilon^{\overline{\overline{wns}}}}{\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t} \\
&+ \frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}{\theta}\cdot{}^{wns\to}\mathbf{T}_{M}A \\
&- \frac{1}{\theta}\left\langle\mathbf{e}\cdot\left(\mathbf{v}^{\overline{s}}-\mathbf{w}\right)\gamma_{wns}\right\rangle_{\Gamma_{wnsM},\Omega} \\
&= A\Lambda\geq 0
\end{aligned}
\tag{2.163}
$$

The final secondary restriction is

Secondary Restriction 4 (System Specification)

- The RAV will be considered a rigid column such that the velocity of the boundary $\mathbf{w} = 0$.

Additionally, the observation can be made that

$$\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t} = 0 \tag{2.164}$$

because

$$\epsilon = 1 - \epsilon^{\overline{\overline{s}}} = \text{constant} \tag{2.165}$$

Using secondary restriction 4, and Eqs. (2.164) and (2.165), Eq. (2.163) becomes the final simplified entropy inequality

$$\begin{aligned}
&\frac{1}{\theta}\left[p^{w}\mathbf{I}^{\backslash\backslash}A + \epsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}\cdot\mathbf{I}^{\backslash\backslash}A\right]:\mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta}\left[p^{n}\mathbf{I}^{\backslash\backslash}A + \epsilon^{\overline{\overline{n}}}\mathbf{t}^{\overline{\overline{n}}}\cdot\mathbf{I}^{\backslash\backslash}A\right]:\mathbf{d}^{\overline{\overline{n}}} \\
&+ \frac{1}{\theta}\left[\left(-\left(\mathbf{I} - \mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}\cdot\mathbf{I}^{\backslash\backslash}A + \epsilon^{\overline{\overline{wn}}}\mathbf{t}^{\overline{\overline{wn}}}\cdot\mathbf{I}^{\backslash\backslash}A\right):\mathbf{d}^{\overline{\overline{wn}}}\right] \\
&+ \frac{1}{\theta}\left[\left(\mathbf{I} - \mathbf{G}^{wns}\right)\epsilon^{\overline{\overline{wns}}}\gamma^{wns}\cdot\mathbf{I}^{\backslash\backslash}A + \epsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}\cdot\mathbf{I}^{\backslash\backslash}A\right]:\mathbf{d}^{\overline{\overline{wns}}} \\
&- \frac{\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left[\epsilon^{\overline{\overline{w}}}\rho^{w}A\nabla^{\backslash\backslash}\left(\mu^{\overline{w}} + \psi^{\overline{w}} + K_{E}^{\overline{\overline{w}}}\right) + \epsilon^{\overline{\overline{w}}}\rho^{w}A\mathbf{g}^{\overline{w}}\right. \\
&\left.-\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{w}}}Ap^{w}\right) - \overset{w\rightarrow}{\mathbf{T}}_{M}A + \overset{w\rightarrow wn}{\mathbf{T}}A\right] \\
&- \frac{\left(\mathbf{v}^{\overline{n}} - \mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left[\epsilon^{\overline{\overline{n}}}\rho^{n}A\nabla^{\backslash\backslash}\left(\mu^{\overline{n}} + \psi^{\overline{n}} + K_{E}^{\overline{\overline{n}}}\right) + \epsilon^{\overline{\overline{n}}}\rho^{n}A\mathbf{g}^{\overline{n}}\right. \\
&\left.-\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{n}}}Ap^{n}\right) - \overset{n\rightarrow}{\mathbf{T}}_{M}A + \overset{n\rightarrow wn}{\mathbf{T}}A\right] \\
&+ \frac{1}{\theta}\left(p_{w}^{wn} - p_{n}^{wn} - \gamma^{wn}J_{w}^{wn}\right)A\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \frac{\gamma^{wn}\hat{k}_{1}^{wn}\left(\epsilon^{\overline{\overline{wn}}} - \epsilon_{eq}^{\overline{\overline{wn}}}\right)}{p_{w}^{wn} - p_{n}^{wn}}\right] \\
&- \frac{\left(\mathbf{v}^{\overline{wn}} - \mathbf{v}^{\overline{s}}\right)}{\theta}\cdot\left\{\nabla^{\backslash\backslash}\cdot\left[\left(\mathbf{I} - \mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}A\right] + \overset{wn\rightarrow}{\mathbf{T}}_{M}A + \sum_{wn\in\mathcal{I}_{c\alpha}^{+}}\overset{wn\rightarrow\alpha}{\mathbf{T}}A - \overset{wn\rightarrow wns}{\mathbf{T}}A\right\}
\end{aligned}$$

$$
\begin{aligned}
&+ \frac{\left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right)}{\theta} \cdot \left\{ \nabla^{\backprime} \cdot \left(\mathbf{I} - \mathbf{G}^{wns}\right) \epsilon^{\overline{\overline{wns}}} \gamma^{wns} A + \overset{wns\rightarrow}{\mathbf{T}_M} A - \overset{wn\rightarrow wns}{\mathbf{T}} A \right\} \\
&- \frac{1}{\theta} A \left[\gamma_{wn}^{wns} \cos \boldsymbol{\varphi}^{\overline{\overline{ws,wn}}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns} \kappa_G^{\overline{\overline{wns}}} \right] \left(\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}} \right) \frac{\mathrm{D}^{\overline{s}} \chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} \\
&= A\Lambda \geq 0
\end{aligned}
\tag{2.166}
$$

The efficacy of Eq. (2.166) in describing a system of interest is subject to the validity of the approximations made to form it. Each of the approximations can be verified via computational and/or experimental approaches at the microscale and can then be adjusted if necessary.

2.7 Closure Relations

Now we have a Simplified Entropy Inequality (SEI) which is comprised of force-flux pairs that are zero at equilibrium, and away from equilibrium they are non-negative quantities which can contribute to entropy generation. We need to specify closure relations for the force-flux pairs which satisfy these two conditions, and to do so we will use a conjugate force-flux closure scheme where the fluxes are linear functions of the forces. A full cross-coupled closure scheme is also possible if cross-coupling effects are considered to be significant, but the simpler conjugate force-flux closure will be used here; additional information regarding cross-coupled closure exists in [23]. The SEI (Eq. (2.166)) is used to guide the selection of non-unique closure relations which ultimately produce closed thermodynamically consistent models [27].

Although many restrictions and approximations were applied to produce the

SEI, it is still a general equation which supports a hierarchy of closed models which are system specific, and depend on the level of refinement that is desired. Here we are considering two-fluid-phase flow in a porous medium as the system of interest; a system which is often modeled by the classic Richards' equation.

Eq. (2.166) contains fluxes multiplied by the rate of strain tensors. Considering the fact that the macroscale stress tensor depends on interphase interactions more than macroscale velocity gradients, we will use the approximation that the forces have a zero-order dependence on the rate of strain. This means that the fluxes can be written as

$$\mathbf{t}^{\overline{\overline{w}}} \cdot \mathbf{I}^{\backslash\backslash} = -p^{w} \mathbf{I}^{\backslash\backslash} \tag{2.167}$$

$$\mathbf{t}^{\overline{\overline{n}}} \cdot \mathbf{I}^{\backslash\backslash} = -p^{n} \mathbf{I}^{\backslash\backslash} \tag{2.168}$$

$$\mathbf{t}^{\overline{\overline{wn}}} \cdot \mathbf{I}^{\backslash\backslash} = \left(\mathbf{I} - \mathbf{G}^{wn}\right) \gamma^{wn} \cdot \mathbf{I}^{\backslash\backslash} \tag{2.169}$$

and

$$\mathbf{t}^{\overline{\overline{wns}}} \cdot \mathbf{I}^{\backslash\backslash} = -\left(\mathbf{I} - \mathbf{G}^{wns}\right) \gamma^{wns} \cdot \mathbf{I}^{\backslash\backslash} \tag{2.170}$$

Eqs. (2.167)–(2.170) physically mean that the flow is being modeled as macroscopically inviscid. These approximations simplify Eq. (2.166) to

$$\begin{aligned}
&-\frac{1}{\theta}\Big[\epsilon^{\overline{\overline{w}}} \rho^{w} A \nabla^{\backslash\backslash}\left(\mu^{\overline{w}} + \psi^{\overline{w}} + K_{E}^{\overline{\overline{w}}}\right) + \epsilon^{\overline{\overline{w}}} \rho^{w} A \mathbf{g}^{\backslash\backslash \overline{w}} \\
&-\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{w}}} A p^{w}\right) - \overset{w\rightarrow}{\mathbf{T}}_{M} A + \overset{w\rightarrow wn}{\mathbf{T}} A\Big] \cdot \left(\mathbf{v}^{\backslash\backslash \overline{\overline{w}}} - \mathbf{v}^{\backslash\backslash \overline{\overline{s}}}\right) \\
&-\frac{1}{\theta}\Big[\epsilon^{\overline{\overline{n}}} \rho^{n} A \nabla^{\backslash\backslash}\left(\mu^{\overline{n}} + \psi^{\overline{n}} + K_{E}^{\overline{\overline{n}}}\right) + \epsilon^{\overline{\overline{n}}} \rho^{n} A \mathbf{g}^{\backslash\backslash \overline{n}}
\end{aligned}$$

$$
\begin{aligned}
&-\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{n}}}Ap^{n}\right)-\overset{n\rightarrow}{\mathbf{T}}_{M}A+\overset{n\rightarrow wn}{\mathbf{T}}A\Big]\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{n}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&+\frac{1}{\theta}\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}A-\frac{\gamma^{wn}\hat{k}_{1}^{wn}\left(\epsilon^{\overline{\overline{wn}}}-\epsilon_{eq}^{\overline{\overline{wn}}}\right)}{p_{w}^{wn}-p_{n}^{wn}}A\right]\left(p_{w}^{wn}-p_{n}^{wn}-\gamma^{wn}J_{w}^{wn}\right)\\
&-\frac{1}{\theta}\left\{\nabla^{\backslash\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}A\right]+\overset{wn\rightarrow}{\mathbf{T}}_{M}A\right.\\
&\left.+\sum_{wn\in\mathcal{I}_{c\alpha}^{+}}\overset{wn\rightarrow\alpha}{\mathbf{T}}A-\overset{wn\rightarrow wns}{\mathbf{T}}A\right\}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{wn}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&+\frac{1}{\theta}\left\{\nabla^{\backslash\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wns}\right)\epsilon^{\overline{\overline{wns}}}\gamma^{wns}A\right]+\overset{wns\rightarrow}{\mathbf{T}}_{M}A-\overset{wn\rightarrow wns}{\mathbf{T}}A\right\}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{wns}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&-\frac{1}{\theta}\left(\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_{s}^{\overline{\overline{ws}}}}{\mathrm{D}t}A\left[\gamma_{wn}^{wns}\cos\boldsymbol{\varphi}^{\overline{\overline{ws,wn}}}+\gamma_{ws}^{wns}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_{G}^{\overline{\overline{wns}}}\right]\\
&=A\Lambda\geq 0
\end{aligned}
\tag{2.171}
$$

It should be noted that the velocity vectors only have components in the macroscale direction; the horizontal components are assumed to be zero as previously mentioned. The $\backslash\backslash$ notation was introduced for vector quantities to indicate that only macroscale components survive; this notation is consistent with the notation for the macroscale operators that has been used throughout this study. The flux terms in Eq. (2.171) which are multiplied by the velocities relative to the solid-phase velocity will be approximated as first-order dependent as follows

$$
\begin{aligned}
&-\epsilon^{\overline{\overline{w}}}\rho^{w}A\nabla^{\backslash\backslash}\left(\mu^{\overline{w}}+\psi^{\overline{w}}\right)-\epsilon^{\overline{\overline{w}}}\rho^{w}A\mathbf{g}^{\backslash\backslash\overline{w}}+\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{w}}}Ap^{w}\right)+\overset{w\rightarrow}{\mathbf{T}}_{M}A+\overset{w\rightarrow wn}{\mathbf{T}}A\\
&\qquad=A\hat{\mathbf{R}}^{\backslash\backslash w}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{w}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)
\end{aligned}
\tag{2.172}
$$

$$-\epsilon^{\overline{\overline{n}}}\rho^n A\nabla^{\backslash\!\backslash}\left(\mu^{\overline{n}}+\psi^{\overline{n}}\right)-\epsilon^{\overline{\overline{n}}}\rho^n A\mathbf{g}^{\backslash\!\backslash\overline{n}}+\nabla^{\backslash\!\backslash}\left(\epsilon^{\overline{\overline{n}}}Ap^n\right)+\overset{n\rightarrow}{\mathbf{T}}_M A+\overset{n\rightarrow wn}{\mathbf{T}}A$$
$$=A\hat{\mathbf{R}}^{\backslash\!\backslash n}\cdot\left(\mathbf{v}^{\backslash\!\backslash\overline{\overline{n}}}-\mathbf{v}^{\backslash\!\backslash\overline{\overline{s}}}\right) \tag{2.173}$$

where $\hat{\mathbf{R}}^{\backslash\!\backslash\alpha}$ are resistance coefficients which are in general, symmetric second-order positive, semi-definite tensors [23]. Additionally, the $K_E^{\overline{\overline{\alpha}}}$ terms were neglected from Eqs. (2.172) and (2.173) because of higher order smallness. For the interface and common curve we have

$$\nabla^{\backslash\!\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}A\right]+\overset{wn\rightarrow}{\mathbf{T}}_M A+\sum_{wn\in\mathfrak{I}_{c\alpha}^{+}}\overset{wn\rightarrow\alpha}{\mathbf{T}}A-\overset{wn\rightarrow wns}{\mathbf{T}}A$$
$$=-A\hat{\mathbf{R}}^{\backslash\!\backslash wn}\cdot\left(\mathbf{v}^{\backslash\!\backslash\overline{\overline{wn}}}-\mathbf{v}^{\backslash\!\backslash\overline{\overline{s}}}\right) \tag{2.174}$$

and

$$\nabla^{\backslash\!\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wns}\right)\epsilon^{\overline{\overline{wns}}}\gamma^{wns}A\right]+\overset{wns\rightarrow}{\mathbf{T}}_M A-\overset{wn\rightarrow wns}{\mathbf{T}}A$$
$$=A\hat{\mathbf{R}}^{\backslash\!\backslash wns}\cdot\left(\mathbf{v}^{\backslash\!\backslash\overline{\overline{wns}}}-\mathbf{v}^{\backslash\!\backslash\overline{\overline{s}}}\right) \tag{2.175}$$

Cross-coupling effects could be considered when positing the approximations in Eqs. (2.172)–(2.175) which would incorporate the effects of adjacent entities through the use of a more general resistance tensors $\hat{\mathbf{R}}_{\alpha}^{\backslash\!\backslash\alpha}$ and $\hat{\mathbf{R}}_{\beta}^{\backslash\!\backslash\alpha}$ summed over

the relevant connected set; this is the approach presented in [23]. However, cross-coupling will be neglected here.

A first-order closure relationship is also posited for the flux describing changes in volume fraction where the corresponding force relates the relaxation of capillary pressure to its equilibrium value. This approximation is

$$\frac{\mathrm{D}^{\bar{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \frac{\gamma^{wn}\hat{k}_1^{wn}\left(\epsilon^{\overline{\overline{wn}}} - \epsilon_{eq}^{\overline{\overline{wn}}}\right)}{p_w^{wn} - p_n^{wn}} = \hat{c}^{wn}\left(p_w^{wn} - p_n^{wn} - \gamma^{wn}J_w^{wn}\right) \tag{2.176}$$

We'll go further by assuming that the volume fraction and interface kinematics occur at a much shorter time scale then the system physics, which means the pressure at the interface will always be balanced such that

$$p_w^{wn} - p_n^{wn} = \gamma^{wn}J_w^{wn} \tag{2.177}$$

The last force-flux pair in Eq. (2.166) describes a balance of surface tension forces at the common curve, tangent to the solid. A first-order dependence of the flux on the force yields the approximation

$$\frac{\mathrm{D}^{\bar{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} = -\hat{c}^{wns}\left[\gamma_{wn}^{wns}\cos\boldsymbol{\varphi}^{\overline{\overline{ws,wn}}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right] \tag{2.178}$$

where $\hat{c}^{wns}$ is a closure coefficient. Following the simplifications made at the wn

interface, Eq. (2.178) will be further simplified to a steady state condition

$$\left[\gamma_{wn}^{wns}\cos\boldsymbol{\varphi}^{\overline{\overline{ws,wn}}}+\gamma_{ws}^{wns}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right]=0 \tag{2.179}$$

2.8 Model Formulation

In order to formulate a closed model, the closure relations, along with the documented restrictions and approximations will be applied to the conservation of mass and momentum equations.

2.8.1 Closed Conservation Equations

2.8.1.1 Mass Conservation

The interfaces and common curve are massless, there is no interentity mass exchange, and the solid is immobile, so the only non-trivial mass conservation equations are for the wetting and non-wetting phases; these take the form

$$\frac{\mathrm{D}^{\overline{\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\mathrm{D}t}+\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)\mathbf{I}^{\shortparallel}\mathbf{:d}^{\overline{\overline{\alpha}}}=0 \quad \text{for } \alpha\in\{w,n\} \tag{2.180}$$

2.8.1.2 Momentum Conservation

The properties of the interfaces and common curve are not being modeled, so the momentum conservation equations for these entities reduce to a trivial condition. If we were considering cross-coupling between the movement of the interface and the adjacent phases, or the common curve and the adjacent interfaces due to

inter-entity momentum transfer, then these equations would include resistance tensor terms accounting for this interaction; these tensors would appear in Eqs. (2.174) and (2.175). However, since these entities are considered massless, and no inter-entity momentum transfer terms survived in the SEI, we have no momentum conservation equations for the interfaces or common curve.

Additionally, we are considering an immobile solid treated as a highly viscous fluid, so solid-phase deformation is not being modeling. In this case, the solid-phase conservation of momentum, which is often accounted for by employing a total system momentum conservation equation, isn't needed. This leaves the conservation equations for the fluid phases which are

$$\frac{\mathrm{D}^{\overline{w}}\left(\epsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{v}^{\backslash\backslash\overline{\overline{w}}}A\right)}{\mathrm{D}t}+\left(\epsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{v}^{\backslash\backslash\overline{\overline{w}}}A\right)\mathbf{I}^{\backslash\backslash}\mathbf{:d}^{\overline{\overline{w}}}+\epsilon^{\overline{\overline{w}}}\rho^{w}A\nabla^{\backslash\backslash}\left(\mu^{\overline{w}}+\psi^{\overline{w}}\right)$$
$$+A\hat{\mathbf{R}}_{w}^{\backslash\backslash w}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{w}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)=0 \tag{2.181}$$

and

$$\frac{\mathrm{D}^{\overline{n}}\left(\epsilon^{\overline{\overline{n}}}\rho^{n}\mathbf{v}^{\backslash\backslash\overline{\overline{n}}}A\right)}{\mathrm{D}t}+\left(\epsilon^{\overline{\overline{n}}}\rho^{n}\mathbf{v}^{\backslash\backslash\overline{\overline{n}}}A\right)\mathbf{I}^{\backslash\backslash}\mathbf{:d}^{\overline{\overline{n}}}+\epsilon^{\overline{\overline{n}}}\rho^{n}A\nabla^{\backslash\backslash}\left(\mu^{\overline{n}}+\psi^{\overline{n}}\right)$$
$$+A\hat{\mathbf{R}}_{n}^{\backslash\backslash n}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{n}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)=0 \tag{2.182}$$

For slow flow the inertial terms drop out and Eqs. (2.181) and (2.182) become

$$\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\nabla^{\backslash\backslash}\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)+A\hat{\mathbf{R}}_{\alpha}^{\backslash\backslash\alpha}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{\alpha}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)=\mathbf{0}\quad\text{for }\alpha\in\{w,n\} \tag{2.183}$$

We would like to get an expression in terms of gravity, which can be accomplished using the relation between the body force potential and gravity at the microscale

$$\nabla^{\backslash\backslash}\psi_\alpha = -\mathbf{g}^{\backslash\backslash\overline{\alpha}} \tag{2.184}$$

Multiplying Eq. (2.184) by ρ_α, adding and subtracting the macroscale body force potential, and applying an averaging operator to yields

$$\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\nabla^{\backslash\backslash}\psi^{\overline{\alpha}} + \left\langle \rho_\alpha\nabla^{\backslash\backslash}\left(\psi_\alpha - \psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} = -\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\mathbf{g}^{\backslash\backslash\overline{\alpha}} \tag{2.185}$$

We can write the Gibbs-Duhem equation for constant temperature

$$\begin{aligned}\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\nabla^{\backslash\backslash}\mu^{\overline{\alpha}} - \epsilon^{\overline{\overline{\alpha}}}\nabla^{\backslash\backslash}p^\alpha - \left\langle\nabla^{\backslash\backslash}\left(p_\alpha - p^\alpha\right)\right\rangle_{\Omega_\alpha,\Omega} \\ + \left\langle \rho_\alpha\nabla^{\backslash\backslash}\left(\mu_\alpha - \mu^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha \in \{w,n\}\end{aligned} \tag{2.186}$$

Now, moving the last three terms in Eq. (2.186) to the right side, and adding Eq. (2.185) yields

$$\begin{aligned}\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\nabla^{\backslash\backslash}\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right) = \epsilon^{\overline{\overline{\alpha}}}\left(\nabla^{\backslash\backslash}p^\alpha - \rho^\alpha\mathbf{g}^{\backslash\backslash\overline{\alpha}}\right) + \left\langle\nabla^{\backslash\backslash}\left(p_\alpha - p^\alpha\right)\right\rangle_{\Omega_\alpha,\Omega} \\ - \left\langle \rho_\alpha\nabla^{\backslash\backslash}\left(\mu_\alpha + \psi_\alpha - \mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \alpha \in \{w,n\}\end{aligned} \tag{2.187}$$

Neglecting the deviation terms in Eq. (2.187) via the assumption that the gradients of the deviations are small, and neglecting the gradients in volume fractions

leaves the first two terms. This allows the fluid phase momentum equations for slow flow, represented inEq. (2.183), to be written as

$$\epsilon^{\overline{\overline{w}}}\left(\nabla^{\backslash\backslash}p^{w}-\rho^{w}\mathbf{g}^{\backslash\backslash\overline{w}}\right)+\hat{\mathbf{R}}^{\backslash\backslash w}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{w}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)=0 \tag{2.188}$$

and

$$\epsilon^{\overline{\overline{n}}}\left(\nabla^{\backslash\backslash}p^{n}-\rho^{n}\mathbf{g}^{\backslash\backslash\overline{n}}\right)+\hat{\mathbf{R}}^{\backslash\backslash n}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{n}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)=0 \tag{2.189}$$

Using the definition of the material derivative, the conservation of mass equations represented by Eq. (2.180) can be rewritten as

$$\frac{\partial^{\backslash\backslash}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\right)}{\partial t}+\nabla^{\backslash\backslash}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{v}^{\backslash\backslash\overline{\overline{\alpha}}}\right)=0\quad\text{for }\alpha\in\mathcal{I}_{f} \tag{2.190}$$

Using the product rule on the partial derivative yields

$$\rho^{\alpha}\frac{\partial^{\backslash\backslash}\left(\epsilon^{\overline{\overline{\alpha}}}A\right)}{\partial t}+\epsilon^{\overline{\overline{\alpha}}}A\frac{\partial^{\backslash\backslash}\rho^{\alpha}}{\partial t}+\nabla^{\backslash\backslash}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}A\mathbf{v}^{\backslash\backslash\overline{\overline{\alpha}}}\right)=0\quad\text{for }\alpha\in\mathcal{I}_{f} \tag{2.191}$$

We can also use the product rule to expand the third term in Eq. (2.191) which leaves

$$\begin{aligned}\rho^{\alpha}\frac{\partial^{\backslash\backslash}\left(\epsilon^{\overline{\overline{\alpha}}}A\right)}{\partial t}+\epsilon^{\overline{\overline{\alpha}}}A\frac{\partial^{\backslash\backslash}\rho^{\alpha}}{\partial t}+\rho^{\alpha}\nabla^{\backslash\backslash}\cdot\left(\epsilon^{\overline{\overline{\alpha}}}A\mathbf{v}^{\backslash\backslash\overline{\overline{\alpha}}}\right)&\\ +\left(\epsilon^{\overline{\overline{\alpha}}}A\mathbf{v}^{\backslash\backslash\overline{\overline{\alpha}}}\right)\cdot\nabla^{\backslash\backslash}\rho^{\alpha}=0\quad\text{for }\alpha\in\mathcal{I}_{f}&\end{aligned} \tag{2.192}$$

Considering the final term in Eq. (2.192) negligibly small compared to the first

three terms, dividing by ρ^α, and using the relationship between the porosity and saturation

$$\epsilon^{\overline{\overline{\alpha}}} = s^{\overline{\overline{\alpha}}}\epsilon \quad \text{for } \alpha \in \mathcal{I}_f \tag{2.193}$$

Eq. (2.192) can now be written as

$$\epsilon A \frac{\partial^{\backprime}\left(s^{\overline{\overline{\alpha}}}\right)}{\partial t} + \frac{s^{\overline{\overline{\alpha}}}\epsilon A}{\rho^\alpha}\frac{\partial^{\backprime}\rho^\alpha}{\partial t} + \nabla^{\backprime}\cdot\left(\epsilon s^{\overline{\overline{\alpha}}} A \mathbf{v}^{\backprime\overline{\overline{\alpha}}}\right) = 0 \quad \text{for } \alpha \in \mathcal{I}_f \tag{2.194}$$

We need to use equations of state to relate the phase densities to the macroscale fluid-phase pressures; for this isothermal system these take the form

$$\hat{\beta}^\alpha = \frac{1}{\rho^\alpha}\left(\frac{\mathrm{d}\rho^\alpha}{\mathrm{d}p^\alpha}\right) \quad \text{for } \alpha \in \mathcal{I}_f \tag{2.195}$$

where $\hat{\beta}^\alpha$ is the fluid compressibility. Substituting Eq. (2.195) into Eq. (2.194) yields

$$\epsilon\frac{\partial^{\backprime} s^{\overline{\overline{\alpha}}}}{\partial t} + s^{\overline{\overline{\alpha}}}\epsilon\hat{\beta}^\alpha\frac{\partial^{\backprime} p^\alpha}{\partial t} + \nabla^{\backprime}\cdot\left[\epsilon s^{\overline{\overline{\alpha}}}\mathbf{v}^{\backprime\overline{\overline{\alpha}}}\right] = 0 \quad \text{for } \alpha \in \mathcal{I}_f \tag{2.196}$$

We will assume that the pressure equilibrates very quickly as compared to the saturation, and we can transform the divergence term by subtracting the solid phase velocity which is equal to zero, so Eq. (2.196) becomes

$$\epsilon\frac{\partial^{\backprime} s^{\overline{\overline{\alpha}}}}{\partial t} + \nabla^{\backprime}\cdot\left[\epsilon s^{\overline{\overline{\alpha}}}\left(\mathbf{v}^{\backprime\overline{\overline{\alpha}}} - \mathbf{v}^{\backprime\overline{\overline{s}}}\right)\right] = 0 \quad \text{for } \alpha \in \mathcal{I}_f \tag{2.197}$$

This equation can be combined with the conservation of momentum equation

for the fluid phases, but first some additional simplifying assumptions will be made. We will consider the case where the porous medium is isotropic which means the resistance tensors reduces to scalars

$$\hat{\mathbf{R}}^{\backslash\backslash\alpha} = \hat{R}^{\alpha}\mathbf{I}^{\backslash\backslash} \tag{2.198}$$

Now we will define a coefficient $\hat{K}^{\alpha}$

$$\hat{K}^{\alpha} = \frac{\epsilon^{\bar{\bar{\alpha}}2}}{\hat{R}^{\alpha}} \tag{2.199}$$

where $\hat{K}^{\alpha}$ is refered to as the hydraulic conductivity. Eq. (2.199) allows Eqs. (2.188)–(2.189) to be rewritten as

$$\epsilon^{\bar{\bar{w}}}\left(\mathbf{v}^{\backslash\backslash\bar{\bar{w}}} - \mathbf{v}^{\backslash\backslash\bar{\bar{s}}}\right) = -\hat{K}^{w}\left(\nabla^{\backslash\backslash}p^{w} - \rho^{w}\mathbf{g}^{\backslash\backslash\bar{\bar{w}}}\right) \tag{2.200}$$

and

$$\epsilon^{\bar{\bar{n}}}\left(\mathbf{v}^{\backslash\backslash\bar{\bar{n}}} - \mathbf{v}^{\backslash\backslash\bar{\bar{s}}}\right) = -\hat{K}^{n}\left(\nabla^{\backslash\backslash}p^{n} - \rho^{n}\mathbf{g}^{\backslash\backslash\bar{\bar{n}}}\right) \tag{2.201}$$

Eqs. (2.200) and (2.201) are momentum equations in the so-called Darcian form; Eq. (2.201) represents the typical form of Darcy's Law [23]. Eqs. (2.200)–(2.201) can now be substituted into Eq. (2.197), which leaves

$$\epsilon\frac{\partial^{\backslash\backslash}s^{\bar{\bar{\alpha}}}}{\partial t} = \nabla^{\backslash\backslash}\cdot\left[\hat{K}^{\alpha}\left(\nabla^{\backslash\backslash}p^{\alpha} - \rho^{\alpha}\mathbf{g}^{\backslash\backslash\bar{\bar{\alpha}}}\right)\right] \quad \text{for } \alpha \in \mathcal{I}_f \tag{2.202}$$

Eq. (2.202) written for the w phase is one form of the standard Richards' equation, used to model single-fluid-phase flow in porous media with the unknowns $s^{\overline{\overline{w}}}$ and p^w. The hydraulic conductivity is a function of saturation: $\hat{K}^\alpha = \hat{K}^\alpha\left(s^{\overline{\overline{\alpha}}}\right)$, as is the capillary pressure. This means solving Eq. (2.202) requires the specification of a pressure-saturation relationship as well as a saturation-permeability relationship; two of the most common constitutive p-S-k relations will be used here, the van Genunchten Mualem (VGM) model [60], and the Brooks-Corey Burdine (BCB) model [7, 57] which will be explained in the next chapter.

Based on the pressure balance at the interface, stated by Eq. (2.177), and the fact that we we neglected any cross-coupling of the velocity when we formed the closed fluid-phase momentum equations, we will be modeling capillary pressure as a function of saturation only. As it stands we have the statement

$$p^c\left(s^{\overline{\overline{w}}}\right) = -\gamma^{wn} J_w^{wn} = p_n^{wn} - p_w^{wn} \tag{2.203}$$

However, we aren't modeling interfacial properties, so we will approximate the pressures averaged over the interface as macroscale fluid-phase pressures, meaning Eq. (2.203) becomes

$$p^c\left(s^{\overline{\overline{w}}}\right) = -\gamma^{wn} J_w^{wn} = p^n - p^w \tag{2.204}$$

2.9 Entropy Generation

The entropy producing terms which have survived thus far are

$$
\begin{aligned}
&-\frac{1}{\theta}\left[\epsilon^{\overline{\overline{w}}}\rho^{w}A\nabla^{\backslash\backslash}\left(\mu^{\overline{w}}+\psi^{\overline{w}}+K_{E}^{\overline{\overline{w}}}\right)+\epsilon^{\overline{\overline{w}}}\rho^{w}A\mathbf{g}^{\backslash\backslash\overline{w}}\right.\\
&\left.-\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{w}}}Ap^{w}\right)-\overset{w\rightarrow}{\mathbf{T}}_{M}A+\overset{w\rightarrow wn}{\mathbf{T}}A\right]\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{w}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&-\frac{1}{\theta}\left[\epsilon^{\overline{\overline{n}}}\rho^{n}A\nabla^{\backslash\backslash}\left(\mu^{\overline{n}}+\psi^{\overline{n}}+K_{E}^{\overline{\overline{n}}}\right)+\epsilon^{\overline{\overline{n}}}\rho^{n}A\mathbf{g}^{\backslash\backslash\overline{n}}\right.\\
&\left.-\nabla^{\backslash\backslash}\left(\epsilon^{\overline{\overline{n}}}Ap^{n}\right)-\overset{n\rightarrow}{\mathbf{T}}_{M}A+\overset{n\rightarrow wn}{\mathbf{T}}A\right]\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{n}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&+\frac{1}{\theta}\left[\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{w}}}}{\mathrm{D}t}A-\frac{\gamma^{wn}\hat{k}_{1}^{wn}\left(\epsilon^{\overline{\overline{wn}}}-\epsilon_{eq}^{\overline{\overline{wn}}}\right)}{p_{w}^{wn}-p_{n}^{wn}}A\right]\left(p_{w}^{wn}-p_{n}^{wn}-\gamma^{wn}J_{w}^{wn}\right)\\
&-\frac{1}{\theta}\left\{\nabla^{\backslash\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wn}\right)\epsilon^{\overline{\overline{wn}}}\gamma^{wn}A\right]+\overset{wn\rightarrow}{\mathbf{T}}_{M}A\right.\\
&\left.+\sum_{wn\in\mathcal{I}_{c\alpha}^{+}}\overset{wn\rightarrow\alpha}{\mathbf{T}}A-\overset{wn\rightarrow wns}{\mathbf{T}}A\right\}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{wn}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&+\frac{1}{\theta}\left\{\nabla^{\backslash\backslash}\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wns}\right)\epsilon^{\overline{\overline{wns}}}\gamma^{wns}A\right]+\overset{wns\rightarrow}{\mathbf{T}}_{M}A-\overset{wn\rightarrow wns}{\mathbf{T}}A\right\}\cdot\left(\mathbf{v}^{\backslash\backslash\overline{\overline{wns}}}-\mathbf{v}^{\backslash\backslash\overline{\overline{s}}}\right)\\
&-\frac{1}{\theta}\left(\epsilon^{\overline{\overline{ws}}}+\epsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_{s}^{\overline{\overline{ws}}}}{\mathrm{D}t}A\left[\gamma_{wn}^{wns}\cos\boldsymbol{\varphi}^{\overline{\overline{ws,wn}}}+\gamma_{ws}^{wns}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_{G}^{\overline{\overline{wns}}}\right]\\
&=A\Lambda\geq 0
\end{aligned}
\tag{2.205}
$$

Neglecting interface and common curve properties as we did when forming the closed conservation equations, and applying the outlined closure relations simplifies Eq. (2.205) to

$$\frac{1}{\theta}A\hat{R}^{w}\mathbf{v}^{\backprime\overline{\overline{w}}}\cdot\mathbf{v}^{\backprime\overline{\overline{w}}}+\frac{1}{\theta}A\hat{R}^{n}\mathbf{v}^{\backprime\overline{\overline{n}}}\cdot\mathbf{v}^{\backprime\overline{\overline{n}}}=A\Lambda\geq 0 \tag{2.206}$$

At this point we will consider the non-wetting phase to be passive, which is common in standard air-water two phase flow porous media models [46]. This means the non-wetting phase no longer needs to be modeled. We will also reduce the vector notation with primes to one-dimensional scalar notation; for example, $\mathbf{v}^{\backprime\overline{w}}$ will be written as $v^{\overline{w}}$. Using these conditions, Eq. (2.206) simplifies to a one-dimensional equation

$$\frac{1}{\theta}\hat{R}^{w}\left(v^{\overline{w}}\right)^{2}=\Lambda\geq 0 \tag{2.207}$$

or, using the definition of $\hat{R}^{w}$, Eq. (2.208) can be rewritten as

$$\frac{1}{\theta}\left(\frac{\epsilon^{\overline{\overline{w}}2}}{\hat{K}^{w}}\right)\left(v^{\overline{w}}\right)^{2}=\Lambda\geq 0 \tag{2.208}$$

Once a velocity field is obtained using the solution to Eq. (2.202), Eq. (2.208) can be solved for the entropy production rate $\Lambda=\Lambda\left(z,t\right)$ for position z, and time t. Using numerical integration, the global entropy production rate $\Lambda_{T}\left(t\right)$ for the system can be obtained from the values of Λ for each time t; this will be discussed further in the next chapter.

2.10 Discussion

Using the TCAT framework, a constrained entropy inequality for two-phase flow was derived using conservation, thermodynamic, and entropy balance equations averaged up from the microscale. Based on the family of averaging theorems used, the model has one dimension of macroscale variability and is megascale in the remaining dimensions. This form is useful for systems where spatial variability only needs to be accounted in one direction for such as flow in rivers or channels, or when modeling vertical infiltration through a column.

The derived two-phase flow model was reduced to RE, a standard unsaturated flow model, and a simplified entropy inequality with the goal of numerically simulating RE and verifying whether it satisfies the MEPRP. However, the CEI is general and exact and therefore provides a point of return for others to provide theoretical extensions, such as incorporating more general p-S-k relations to form a novel two-phase flow model.

CHAPTER 3

NUMERICAL SIMULATION OF RICHARDS' EQUATION

To determine whether Richards' equation satisfies the minimum entropy production rate principle, the entropy generation equation and RE will need to be discretized and numerically simulated. Two common p-S-k relations will be tested using a set of simulation conditions that have been used as a benchmark for RE; solutions using finite differences and finite elements with low-order temporal discretization, and the method of lines have been explored extensively [11, 40, 54, 58, 59]. This benchmark problem models vertical infiltration into a soil column under constant surface ponding, or surface water conditions which create a sharp infiltration front [59].

The purpose of this work is to verify the MEPRP for RE rather than improving upon existing numerical methods, so a standard mass conserving finite difference approach was formulated which uses the mixed form of RE as outlined by [11], and solved by many others [11, 40, 47, 50, 55]. This well-tested method will be briefly outlined, along with the constitutive relation formulations for the VGM and BCB models, the numerical differentiation of the pressure head field, and finally the numerical integration of the local entropy production rate. After the numerical model is summarized, the results for the two p-S-k relations will be presented and

discussed.

3.1 Preliminaries: Model Equations and p-S-k Relations

The equations derived in chapter 2 that will be used in the numerical model include Richards' equation, Darcy's Law, and the entropy generation equation; these will be collected, and expressed in a convenient form below.

1. Richards' Equation

   Using the definition of pressure head h^w:

$$h^w = \frac{p^w}{\rho^w \mathbf{g}^{\overline{w}}} \tag{3.1}$$

   Richards' equation can be written in 1-D as

$$\epsilon \frac{\partial s^{\overline{\overline{w}}}}{\partial t} = \frac{\partial}{\partial z}\left[\hat{K}^w \left(\frac{\partial h^w}{\partial z} + 1\right)\right] \tag{3.2}$$

   Eq. (3.2) can be rewritten using the definition of moisture content θ^w:

$$\theta^w = \epsilon s^{\overline{\overline{w}}} \tag{3.3}$$

   It's important to differentiate the moisture content (θ^w) from the macroscale temperature ($\theta^{\overline{\overline{\alpha}}}$) that appears in chapter two, or the system temperature (θ) which appears in the entropy generation equation, eqn (3.6). Using Eq. (3.3), Eq. (3.2) can be written in the standard 1-D mixed form of Richards'

equation

$$\frac{\partial \theta^w}{\partial t} = \frac{\partial}{\partial z}\left[\hat{K}^w\left(\frac{\partial h^w}{\partial z}+1\right)\right] \tag{3.4}$$

2. Darcy's Law

$$\epsilon^{\overline{\overline{w}}}\left(v^{\overline{w}} - v^{\overline{s}}\right) = -\hat{K}^w\left(\frac{\partial h^w}{\partial z}+1\right) \tag{3.5}$$

3. Entropy Generation

$$\frac{1}{\theta}\left(\frac{\epsilon^{\overline{\overline{w}}2}}{\hat{K}^w}\right)\left(v^{\overline{w}}\right)^2 = \Lambda \geq 0 \tag{3.6}$$

In order to solve Eq. (3.2) p-S-k relations are needed. The two that will be used here are the van Genuchten Mualem (VGM) model, and the Brooks-Corey Burdine (BCB) model. The van Genuchten (VG) pressure-saturation relationship is

$$S_e\left(h^w\right) = \frac{\theta^w - \theta_r^w}{\theta_s^w - \theta_r^w} = \left(1 - \left|\alpha_v h^w\right|^{n_v}\right)^{-m_v} \tag{3.7}$$

with

$$m_v = 1 - \frac{1}{n_v} \tag{3.8}$$

where S_e is the effective saturation, θ_r^w is the residual volumetric water content, θ_s^w is the saturated volumetric water content, and n_v and α_v are experimental coefficients. The VG relation is often paired with Mualem's saturation-permeability

relation

$$\hat{K}^w(h^w) = \hat{K}^s S_e^{0.5} \left[1 - \left(1 - S_e^{1/m_v}\right)^{m_v}\right]^2 \tag{3.9}$$

where $\hat{K}^w$ is the hydraulic conductivity of the wetting phase, and $\hat{K}^s$ is the saturated hydraulic conductivity. Together, Eqs. (3.7) and (3.9) form the VGM model. Alternatively, the Brooks-Corey pressure-saturation relation is

$$S_e\left(h^w\right) = \frac{\theta^w - \theta_r^w}{\theta_s^w - \theta_r^w} = \left(\frac{h_b^w}{h^w}\right)^{\lambda} \text{ for } h^w > h_b^w \tag{3.10}$$

where h_b^w is the air entry pressure head, and λ is an experimental coefficient called the pore size distribution index [42]. The BC relation can be paired with Burdine's saturation-permeability relation

$$\hat{K}^w(h^w) = \hat{K}^s S_e^2 \left[1 - \left(1 - S_e^{1/m_v}\right)^{m_v}\right] \tag{3.11}$$

Eqs. (3.10) and (3.11) comprise the BCB p-S-k model. The parameters in the BCB model are related to the VGM parameters via the approximate relationships [60]:

$$h_b^w \approx \frac{1}{\alpha_v} \tag{3.12}$$

and

$$\lambda \approx n_v - 1 \tag{3.13}$$

when

$$m_v = 1 - \frac{1}{n_v} \tag{3.14}$$

The simulation parameters and conditions which were used for both the VGM and BCB models are included in Table 3.1. The BCB parameters were matched with the VGM parameters using Eqs. (3.12)–(3.14).

Table 3.1: Simulation Parameters and Conditions

Variable	Problem A
Δz (m)	.00125
z (m)	[0,0.3]
h_0^w (m)	-10
h_1^w (m)	-10
h_2^w (m)	-.750
t (days)	[0,1.0]
$K_s(m/day)$	7.97
n_v	2.00
α_v	3.35
θ_s^w	.368
θ_r^w	.102
$\theta(K)$	283.15

The pressure head values listed in Table 3.1 come from the initial and boundary conditions of the form

- $h^w(z, t = 0) = h_0^w$
- $h^w(z = 0, t > 0) = h_1^w(t)$
- $h^w(z = Z, t > 0) = h_2^w(t)$

These are constant head, or Dirichlet boundary conditions, which will be incorporated into the numerical model.

3.2 Numerical Development

Richards' equation is a partial differential equation which is highly nonlinear due to the dependence of permeability on capillary pressure and saturation. Because of this nonlinearity, analytical solutions to RE are limited to very restricted systems [25]; this necessitates a numerical solution. Common numerical solutions to RE involve low-order finite difference, or finite element spatial discretizations coupled with a nonlinear iterative solution method like Newton, Picard, or Modified Picard iteration [62]. Similarly, temporal discretization is often done using a low-order fixed time-step method like backward Euler. More sophisticated approaches exist [58, 59], but a straightforward numerical model was adequate for the one-dimensional system modeled in this work.

A Modified Picard iteration scheme was chosen because it has been shown to be perfectly mass conservative [11, 62]. Finite difference approximations which use this iteration scheme were developed to discretize the spatial and temporal domain for the mixed form of RE, Eq. (3.4).

3.2.1 Finite Difference Approximations

Formulating the numerical model first requires discretizing the spatial and temporal domain into a set of interior and boundary nodes, where an approximate solution to RE will be calculated. Then the finite difference approximation is written for each node in the interior of the domain, while the boundary node treatment depends on the boundary type. In finite difference methods, functional derivatives

are replaced with finite difference operators to produce an approximation to the equation. The approximations, term by term are outlined below.

$$\frac{\partial \theta^w}{\partial t} \approx \frac{\theta^{n+1} - \theta^n}{\Delta t} \tag{3.15}$$

$$\frac{\partial h^w}{\partial z} \approx \frac{h_{i+1} - h_i}{\Delta z} \tag{3.16}$$

$$\frac{\partial \hat{K}^w}{\partial z} \approx \frac{\hat{K}_{i+1/2} - \hat{K}_{i-1/2}}{z_{i+1/2} - z_{i-1/2}} \tag{3.17}$$

$$\frac{\partial}{\partial z}\hat{K}^w \frac{\partial h}{\partial z} \approx \frac{\hat{K}_{i+1/2}\frac{h_{i+1}^{n+1} - h_i^{n+1}}{z_{i+1} - z_i} - \hat{K}_{i-1/2}\frac{h_i^{n+1} - h_{i-1}^{n+1}}{z_i - z_{i-1}}}{z_{i+1/2} - z_{i-1/2}} \tag{3.18}$$

where n designates the time level, and i designates the location in space, such that

$$t^n = n\Delta t \tag{3.19}$$

and

$$z_i = (i-1)\,\Delta z \tag{3.20}$$

with

$$\Delta z = \frac{Z}{(n_n - 1)} \text{ for } 1 \leq i \leq n_n \tag{3.21}$$

where a fixed time step Δt, and a fixed node spacing Δz will be used. The notation of [59] for the one-dimensional spatial domain $[0, Z]$ was used in Eqs. (3.20) and (3.21) which corresponds to n_n spatial nodes where approximations will be written.

In Eqs. (3.15)–(3.18) the w superscript was dropped on the right side for clarity with the discretized notation, but θ^n and θ^{n+1} in Eq. (3.15) should not be confused with the temperature.

The hydraulic conductivity in Eqs. (3.17) and (3.18) appears in between spacial nodes at $i \pm 1/2$, and will be evaluated using the average between neighboring nodes; this was established as an accurate method by [11], and [1], although other averages exist. This averaging method for $i \pm 1/2$ yields

$$K_{i-1/2}^{n+1,m} = \frac{1}{2}(K_{i-1}^{n+1,m} + K_i^{n+1,m}) \tag{3.22}$$

$$K_{i+1/2}^{n+1,m} = \frac{1}{2}(K_{i+1}^{n+1,m} + K_i^{n+1,m}) \tag{3.23}$$

Using Eqs. (3.15)–(3.18) to replace the derivatives in Richards' eqn (3.4) yields the finite difference model

$$\begin{aligned}\frac{\theta_i^{n+1} - \theta_i^n}{\Delta t} = & \frac{\hat{K}_{i+1/2}^{n+1}\left(h_{i+1}^{n+1} - h_i^{n+1}\right)}{\left(z_{i+1/2} - z_{i-1/2}\right)\left(z_{i+1} - z_i\right)} \\ & - \frac{\hat{K}_{i-1/2}^{n+1}\left(h_i^{n+1} - h_{i-1}^{n+1}\right)}{\left(z_{i+1/2} - z_{i-1/2}\right)\left(z_i - z_{i-1}\right)} + \frac{\hat{K}_{i+1/2}^{n+1} - \hat{K}_{i-1/2}^{n+1}}{z_{i+1/2} - z_{i-1/2}}\end{aligned} \tag{3.24}$$

or, in condensed form

$$\frac{\theta_i^{n+1} - \theta_i^n}{\Delta t} = \frac{\hat{K}_{i+1/2}^{n+1}\left(h_{i+1}^{n+1} - h_i^{n+1}\right)}{(\Delta z)^2} - \frac{\hat{K}_{i-1/2}^{n+1}\left(h_i^{n+1} - h_{i-1}^{n+1}\right)}{(\Delta z)^2} + \frac{\hat{K}_{i+1/2}^{n+1} - \hat{K}_{i-1/2}^{n+1}}{\Delta z} \tag{3.25}$$

This approximate form of RE (Eq. (3.25)) is still nonlinear, and therefore must be linearized and solved iteratively. The Modified Picard iterative scheme can be applied to Eq. (3.25) following the development outlined in [62], which yields

$$\frac{\theta_i^{n+1,m+1} - \theta_i^n}{\Delta t} = \frac{\hat{K}_{i+1/2}^{n+1,m}\left(h_{i+1}^{n+1,m+1} - h_i^{n+1,m+1}\right)}{(\Delta z)^2} - \frac{\hat{K}_{i-1/2}^{n+1,m}\left(h_i^{n+1,m+1} - h_{i-1}^{n+1,m+1}\right)}{(\Delta z)^2} + \frac{\hat{K}_{i+1/2}^{n+1,m} - \hat{K}_{i-1/2}^{n+1,m}}{\Delta z} \tag{3.26}$$

where m is the iteration level, which means variables at the $(m+1)$ level are the unknowns being solved for. Eq. (3.26) is then modified by expanding $\theta_i^{n+1,m+1}$ in order to yield obtain the moisture content at the current iteration level m. This is expansion is achieved using the truncated Taylor series which appears in [11, 62] as

$$\theta_i^{n+1,m+1} = \theta_i^{n+1,m} + \frac{d\theta_i^{n+1,m}}{dh}(h_i^{n+1,m+1} - h_i^{n+1,m}) + O(h^2) \tag{3.27}$$

where Eq. (3.27) can be rewritten using the definition of the specific moisture

capacity $C\left(h\right)$:

$$C^{w}\left(h^{w}\right)=\frac{\mathrm{d}\theta^{w}}{\mathrm{d}h^{w}} \tag{3.28}$$

Using Eq. (3.28), Eq. (3.27) becomes

$$\theta_{i}^{n+1,m+1}=\theta_{i}^{n+1,m}+C_{i}^{n+1,m}(h_{i}^{n+1,m+1}-h_{i}^{n+1,m})+O(h^{2}) \tag{3.29}$$

This expansion contributes to the mass conservative quality of the modified Picard method [10, 61]. Substituting Eq. (3.27) into Eq. (3.26) and rearranging terms yields the equation

$$\begin{aligned}
&-\frac{\hat{K}_{i-1/2}^{n+1,m}}{\left(\Delta z\right)^{2}}\left(h_{i-1}^{n+1,m+1}-h_{i-1}^{n+1,m}\right)\\
&+\left(\frac{\hat{K}_{i-1/2}^{n+1,m}}{\left(\Delta z\right)^{2}}+\frac{\hat{K}_{i+1/2}^{n+1,m}}{\left(\Delta z\right)^{2}}+\frac{C_{i}^{n+1,m}}{\Delta t}\right)\left(h_{i}^{n+1,m+1}-h_{i}^{n+1,m}\right)\\
&-\frac{\hat{K}_{i+1/2}^{n+1,m}}{\left(\Delta z\right)^{2}}\left(h_{i+1}^{n+1,m+1}-h_{i+1}^{n+1,m}\right)\\
&=\frac{\theta_{i}^{n}-\theta_{i}^{n+1,m}}{\Delta t}+\hat{K}_{i+1/2}^{n+1,m}\frac{\left(h_{i+1}^{n+1,m}-h_{i}^{n+1,m}\right)}{\left(\Delta z\right)^{2}}\\
&-\hat{K}_{i-1/2}^{n+1,m}\frac{\left(h_{i}^{n+1,m}-h_{i-1}^{n+1,m}\right)}{\left(\Delta z\right)^{2}}+\frac{\hat{K}_{i+1/2}^{n+1,m}-\hat{K}_{i-1/2}^{n+1,m}}{\Delta z}
\end{aligned} \tag{3.30}$$

Writing Eq. (3.30) for each node in the system yields a system of algebraic equations which can be written generally in matrix form as

$$\left[\mathbf{A}\left(\mathbf{h}^{n+1,m}\right)\right]\left[\mathbf{h}^{n+1,m+1}-\mathbf{h}^{n+1,m}\right]=\left[\mathbf{r}\left(\mathbf{h}^{n+1,m}\right)\right] \tag{3.31}$$

where the dependence of the tridiagonal coefficient matrix $\mathbf{A}$, and the residual vector $\mathbf{r}$ on the pressure is explicitly noted to reiterate that this is a nonlinear system. However, the modified Picard iterative scheme allows $\mathbf{A}$ and $\mathbf{r}$ to be written in terms of the iteration level m, which effectively linearizes the system. It should be noted that the coefficient matrix is tridiagonal because of the three point stencil of the finite difference approximations used here.

The first and last rows of the matrix system Eq. (3.31), correspond to boundary nodes which require special attention. The constant head boundary conditions, which are listed in Table 3.1, require that the equations written for the lower and upper boundaries ($i = 0$) and ($i = n_n - 1$) be modified; these nodes are shown in red in Figure 3.1. After incorporating these boundary conditions, the matrix structure of Eq. (3.31) becomes

$$\begin{bmatrix} b_1 & c_1 & 0 & 0 & \cdots & 0 \\ a_2 & b_2 & c_2 & 0 & \cdots & 0 \\ 0 & a_3 & b_3 & c_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \ddots & \\ 0 & 0 & 0 & \cdots & a_{n_n-1} & b_{n_n-1} \end{bmatrix}^{n+1,m} \begin{bmatrix} \delta h_1 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \delta h_{n_n-1} \end{bmatrix}^{n+1,m} = \begin{bmatrix} b_1 - a_1 * h_0 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ b_{n_n-1} - c_{n_n-1} * h_{n_n} \end{bmatrix}^{n+1,m}$$

where

$$\delta h^{n+1,m} = h^{n+1,m+1} - h^{n+1,m} \tag{3.32}$$

The terms a, b, and c represent the coefficients written at $(i-1)$, i, and $(i+1)$ nodes. The boundary conditions at the first and the last node become part of the next row denoted by h_0 and h_n above.

The convergence of the modified Picard scheme was established, using the criteria found in [54]:

$$\max \frac{\left|h^{n+1,m+1} - h^{n+1,m}\right|}{\left|h^{n+1,m+1}\right|} \leq 1 \times 10^{-5} \tag{3.33}$$

At this point, the system Eq. (3.32) can be solved for pressure head h^w along the column; however, what we are really interested in is the velocity field which will allow us to solve for the global entropy production rate of the system as it approaches a steady state. This can be accomplished by numerically differentiating the pressure field, and using Eq. (3.5) to solve for the velocity.

3.2.2 Numerical Differentiation of Pressure Field

A standard three-point central difference formula can be used to approximate the derivative of the pressure field as follows

$$\frac{\partial h^w}{\partial z} = \frac{h^w_{i+1} - h^w_{i-1}}{2\Delta z} + \mathcal{O}\left(\Delta z^2\right) \tag{3.34}$$

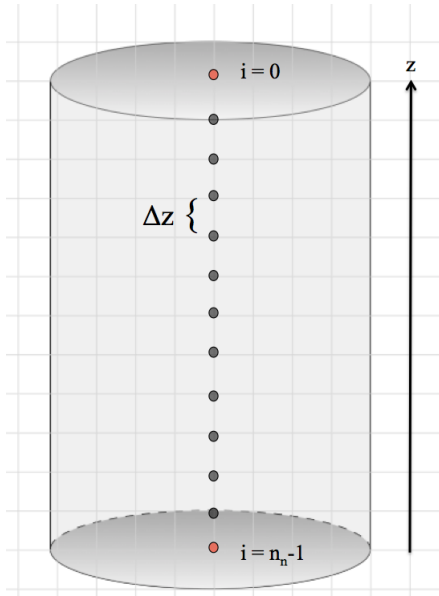

Figure 3.1: Example discretized 1-D domain for RE simulation; created using the TikZ LaTeX package.

Substituting Eq. (3.34) into Eq. (3.5) yields

$$\epsilon^{\overline{\overline{w}}} v_i^{\overline{w}} = -\hat{K}_i^w \left(\frac{h_{i+1}^w - h_{i-1}^w}{2\Delta z} + 1 \right) \tag{3.35}$$

where we can solve for the Darcy velocity $\epsilon^{\overline{\overline{w}}} \left(v^{\overline{w}}\right)_i$ at each node. It is important to verify that the solution converges as the grid spacing is decreased because if the solution was oscillatory, or had unbounded error, then the computed velocity field would propagate numerical error into the solution of the entropy generation rate. The relative error E, defined using the L_2-norm, is

$$E = \frac{\|\epsilon^{\overline{\overline{w}}} v^{\overline{w}} - \epsilon^{\overline{\overline{w}}} v_{dense}^{\overline{w}}\|_2}{\|\epsilon^{\overline{\overline{w}}} v^{\overline{w}}\|_2} \tag{3.36}$$

where v_{dense} is the dense-grid solution. Using Eq. (3.36), the relative error of the approximate velocity values can be monitored as the numerical grid is refined. We expect the global error to approach zero as the grid spacing goes to zero if the method is convergent. Additionally, the order of convergence is expected to be approximately first order, as the local truncation error of the central difference formula is second order [15] (as shown in eqn (3.34)) and can be calculated using

$$E\left(\Delta z\right) \approx C\left(\Delta z\right)^{p} \tag{3.37}$$

where p is the order of convergence, and C is a constant. Using Eq. (3.37), and the values from Table 3.2, the velocity estimate was calculated as scaling linearly with the step-size which can be seen in Figure 3.2; higher-order methods exist for better performance, but Eq. (3.34) provided a sufficient estimate for the small-scale simulations performed in this work.

Table 3.2: Velocity Convergence Analysis

grid spacing, Δz (m)	Relative Error
0.025	9.33×10^{-4}
0.0125	6.35×10^{-4}
0.00625	8.62×10^{-5}
0.000125 (dense grid)	- - -

3.2.3 Numerical Integration of Local Entropy Production Rate

Using Eq. (3.34), the Darcy velocity at each node is known. Now, we can use the entropy generation equation (eqn (3.6)) to solve for the global entropy production of the system which will be used to verify the MEPRP.

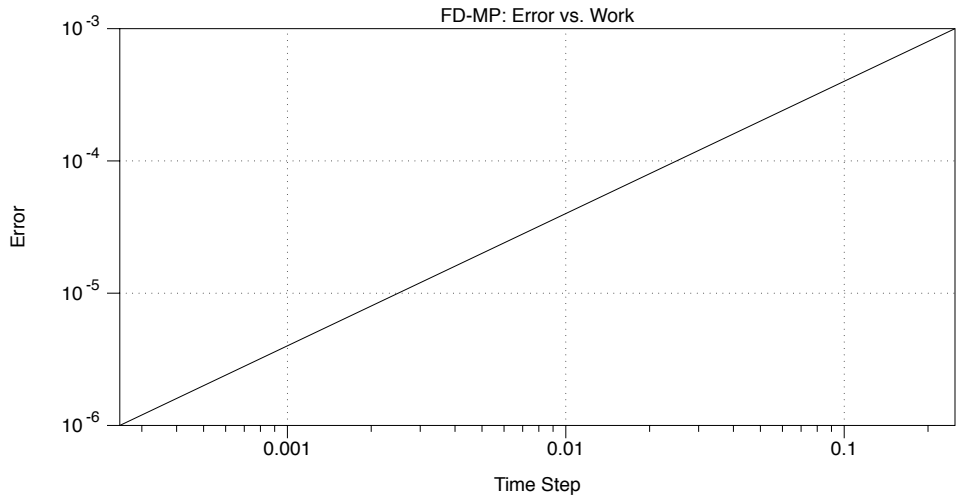

Figure 3.2: DataTank log-log best fit plot of error versus work (time step) for the central difference velocity estimate using the finite difference modified Picard scheme (FD-MP).

Global entropy production (Λ_T):

$$\Lambda_T(t) = \int_0^Z \Lambda(z_i, t)\, \mathrm{d}\Omega = \int_0^Z \frac{1}{\theta} \left(\frac{\epsilon^{\overline{\overline{w}}2}}{\hat{K}^w} \right) \left(v^{\overline{w}} \right)^2 \mathrm{d}z \tag{3.38}$$

Eq. (3.38) can be calculated for each time t, and the value of Λ_T can be examined as the system approaches steady state. The Composite Simpson's rule was used to estimate the solution to Eq. (3.38) for different times t.

Composite Simpson's rule [15]:

$$\int_0^Z \Lambda(z_i, t)\, \mathrm{d}\Omega \approx \frac{\Delta z}{3} \sum_{i=0}^{(n_n-1)/2} \left[\Lambda(z_{2i-2}, t) + 4\Lambda(z_{2i-1}, t) + \Lambda(z_{2i}, t) \right] + \mathcal{O}\left(\Delta z^4\right) \tag{3.39}$$

Steady-states were characterized by the change in volumetric moisture content

θ^w such that

$$\|\theta^{n+1} - \theta^n\|_2 \leq 1 \times 10^{-5} \tag{3.40}$$

The equations discussed in this section, including a 1-D mixed form of Richards' Eq. (3.30), the Darcy velocity estimate Eq. (3.35), and the global entropy production Eq. (3.39) were implemented in `C++`, and simulated under the conditions provided in Table 3.1; the results will be discussed next.

3.3 Results

The results of the numerical simulations for the van Genuchten Mualem model, and the Brooks-Corey Burdine model will be compared and discussed in light of the minimum entropy production rate principle. The MEPRP predicts that the global entropy production rate will be a minimum when the system achieves a steady-state. All plots were created using the dense grid solution $\Delta t = 0.00001$ hours, and $\Delta z = 0.00125$ meters unless otherwise stated.

First, the effective saturation profiles for a time during infiltration and at steady-state are shown for both models in Figure 3.3. The van Genuchten Mualem curves were generated using the parameters in Table 3.1, while the Brooks-Corey Burdine parameters were matched using Eqs. (3.12) and (3.14). The BCB model predicts a larger effective saturation of 0.396 at $z = 0$ meters as compared to the VGM model's prediction of 0.367, while both models predict the same value of 0.029 at $z = 0.3$ meters. The fact that the two models predict different saturation profiles under the chosen simulation conditions should be noted when comparing

the entropy production rate results.

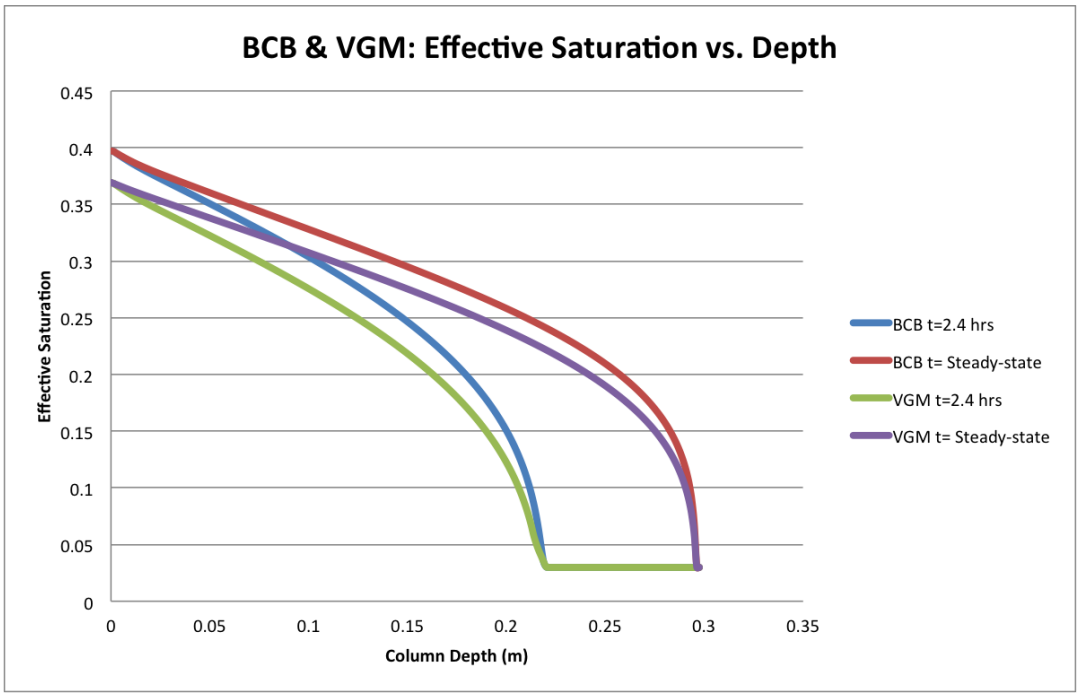

Figure 3.3: Effective saturation profiles versus depth plot for BCB and VGM models

The dense grid solution in time of $\Delta t = 0.00001$ hours was established by plotting the total entropy production rate over time for each model using progressively smaller Δt values, and observing convergence to a common solution; this is shown for the BCB model in Figure 3.4. Similarly, the VGM model also converges by this time step. Figures 3.4 and 3.5 show how the total entropy production rate decreases as the system approaches a steady state. The BCB and VGM models exhibit similar behavior, with the total entropy production rate reaching a minimum at steady state. The VGM model predicts a smaller total entropy production rate over time (1.94×10^{-4} versus 3.83×10^{-4} for the BCB model), but the two model solutions are on the same order of magnitude. If it were necessary

to make the two models match exactly more precise parameter matching between the models could have been used.

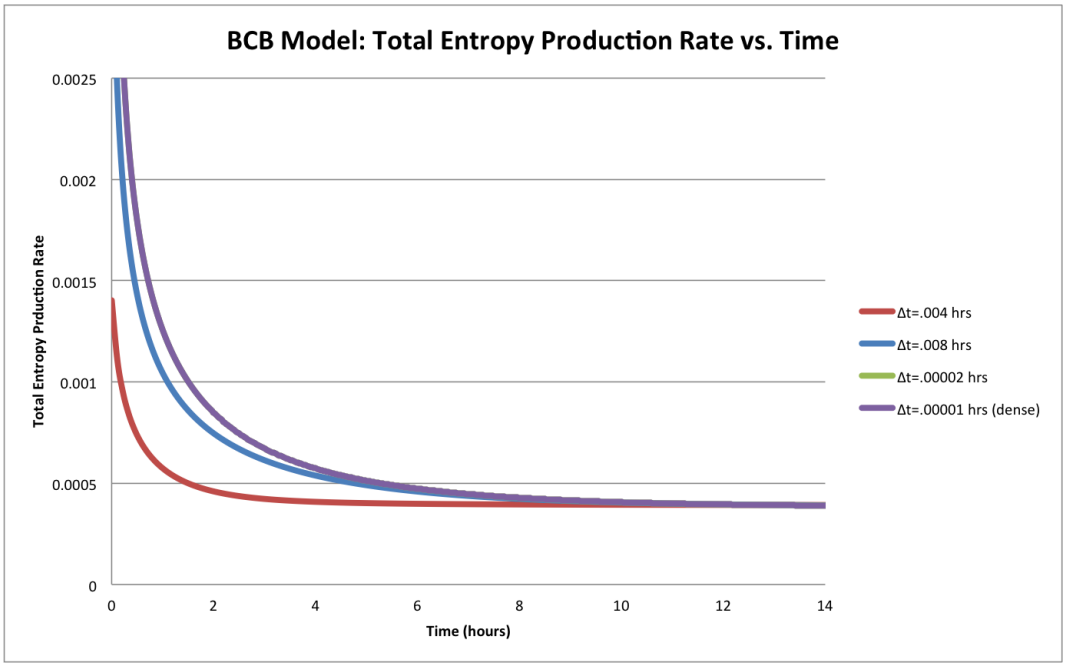

Figure 3.4: The total entropy production versus time plot for the BCB model is shown for different discretizations in time. The solution for $\Delta t = 0.00002$ hours isn't visible, but is included to illustrate that the solution has converged by the dense discretization.

To visualize how the local entropy production along the column contributed to the total entropy production rate over time the entropy production rate (EPR) was plotted for the beginning of the simulation (0-5 minutes) and (0-10 minutes), at an intermediate time (20-30 minutes), and at steady state which was achieved around 20 hours for both models. This was done rather than plotting the different time intervals together because the EPR changes range over two orders of magnitude, so the behavior wasn't clear when the data was plotted together.

The entropy production rate for the first 5 minutes (0.083 hours) is shown

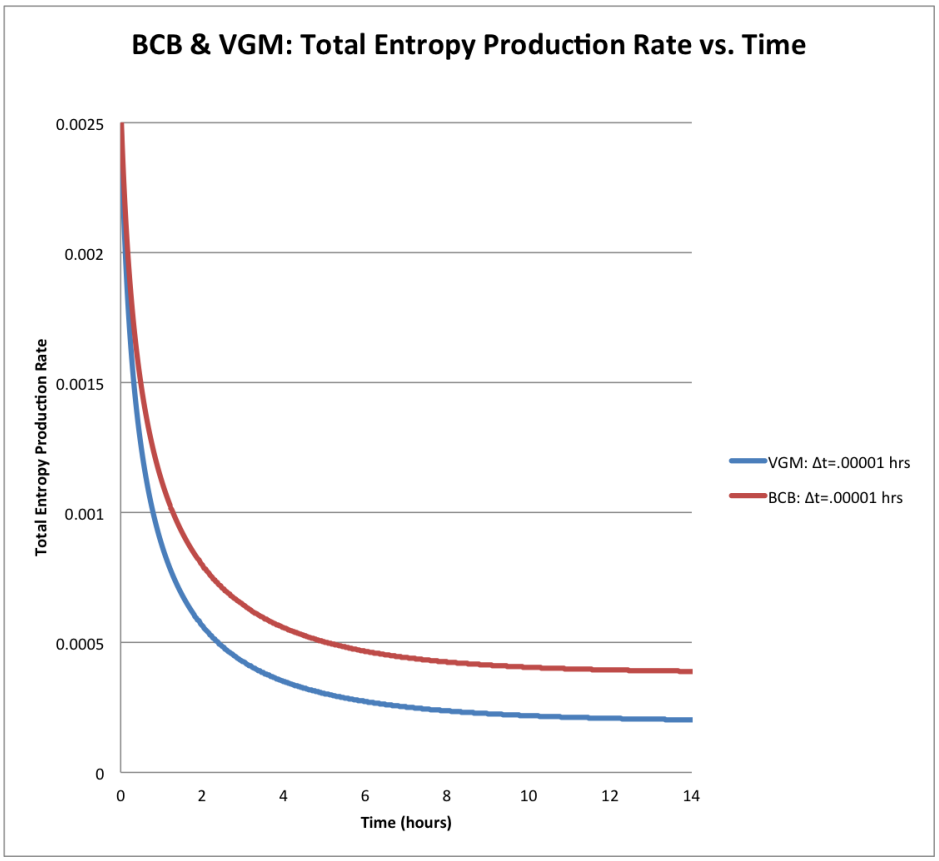

Figure 3.5: The total entropy production versus time comparison plot for BCB and VGM models is shown.

in Figure 3.6 along the column. The pressure front moves through the system quickly at the beginning of the simulation, which contrbutes the moving front shown. The y-axis begins at 2.0×10^{-5} to highlight the plot shape, but the front extends down to zero, as is visible in Figure 3.11. The apparent increase in the entropy production rate at the front in Figures 3.6 and 3.10 is superficial; the discretization in the z-direction is 0.00125 meters, so although the rate decreases monotonically along the column, when the values jump to zero the graph's shape becomes distorted. This point is further illustrated when viewing the transient behavior of the Darcy velocity (Figure 3.9), the saturation (Figure 3.7), and the hydraulic conductivity (Figure 3.8) along the column, as these values dictate the entropy production rate via Eq. (3.38) and no anomalous behavior is visible in either figure.

The last time shown in Figure 3.6 (0.083 hours) is the first time shown in Figure 3.11. After 0.083 hours the entropy production rate plot changes concavity and begins to increase in an exponential fashion, while the effects of the front are still visible as it nears the end of the column at 0.3 meters. The transition for the VGM model exhibits the same behavior, but with a faster moving front, as evidenced by the comparison in Figure 3.10.

From twenty to thirty minutes (0.33 - 0.50 hours) the entropy production rate front has reached the end of the column and approaches an exponential curve, as shown in Figure 3.13. The VGM model reaches steady state more quickly than the BCB model, so the values are smaller. This plot provides an intermediate

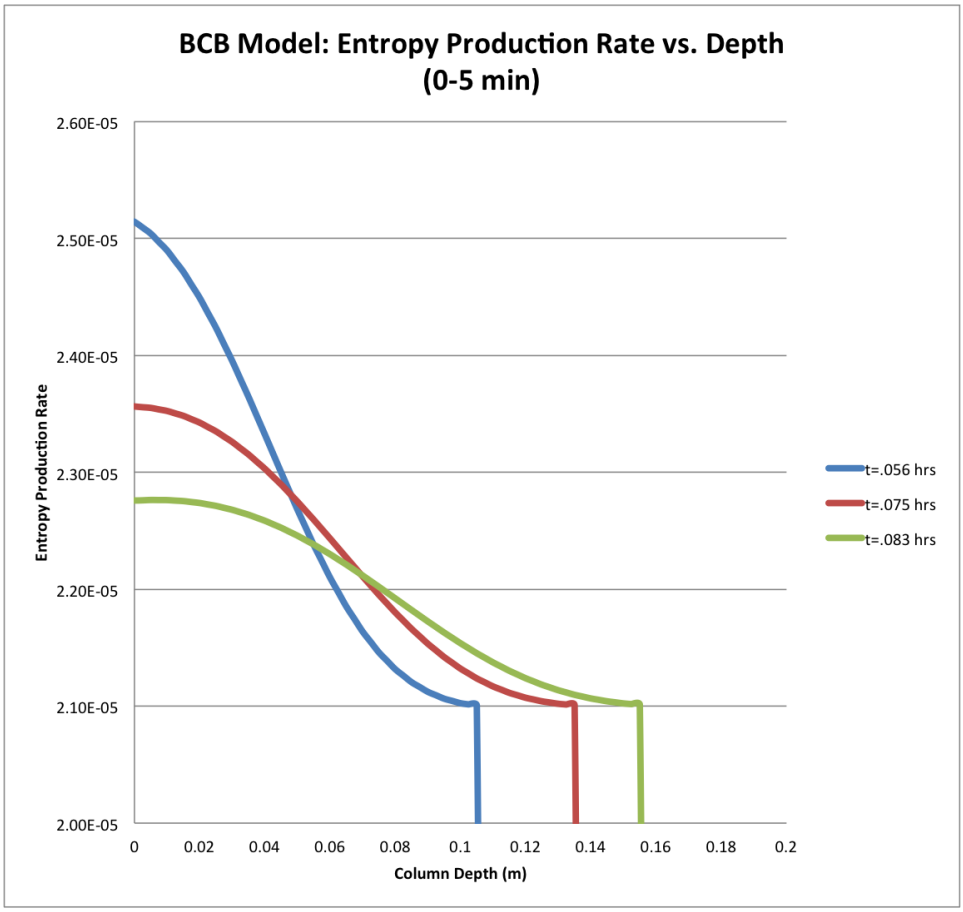

Figure 3.6: The entropy production rate versus depth for plot for the BCB model is shown for the first 5 minutes of the simulation.

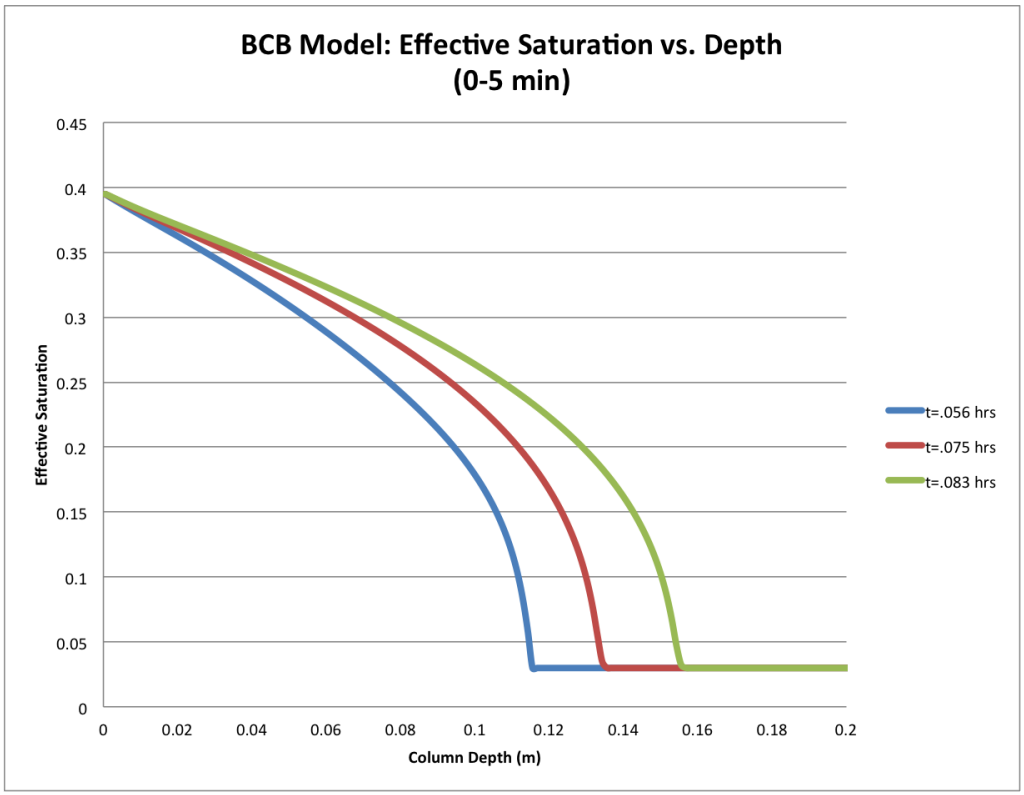

Figure 3.7: The transient behavior of the saturation profile along the column is shown. The column saturation increases above the residual saturation as the infiltration continues, as evidenced by Figure 3.9 which shows the Darcy velocity front.

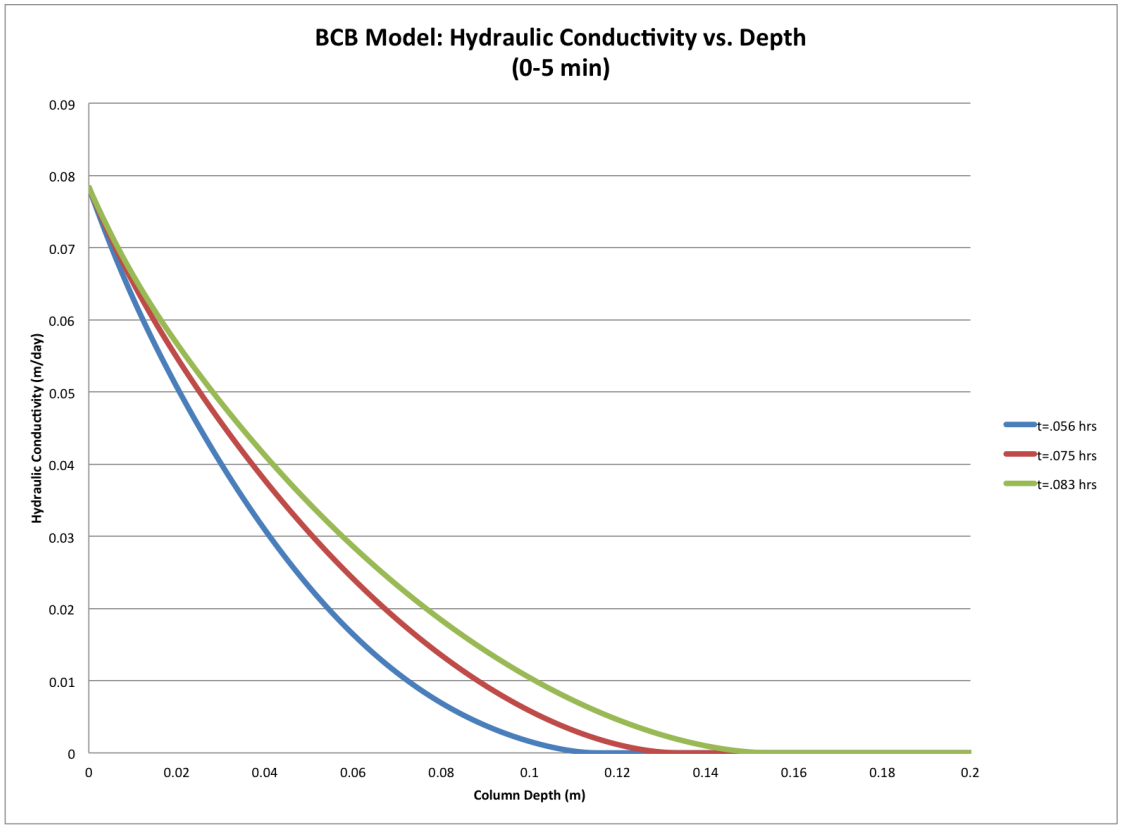

Figure 3.8: The transient behavior of the hydraulic conductivity along the column is shown. This graph, along with Figure 3.9, supports the assertion that the visible increase in the entropy production rate at the front in Figure 3.6 is superficial, as no irregular behavior is present.

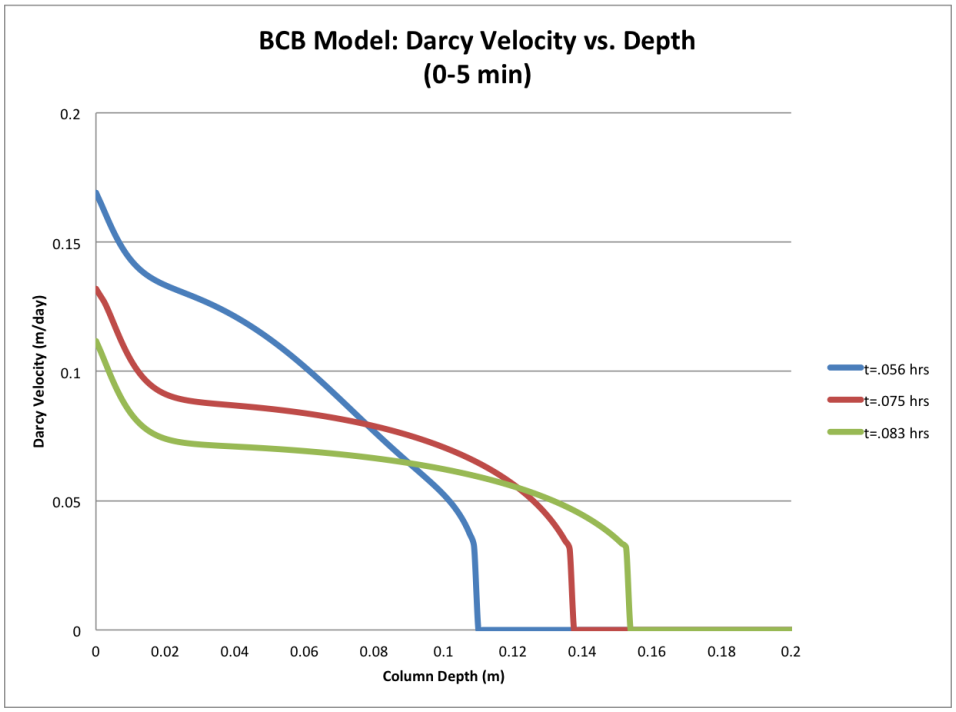

Figure 3.9: The darcy velocity front along the column is shown for the first 5 minutes of the simulation.

comparison between the first five minutes of the simulation in Figure 3.10 and the steady-state behavior shown in Figure 3.13.

The system reached a steady state by 19.2 hours for the VGM model and 22.5 hours for the BCB model, as shown in Figure 3.13; this state was characterized by no further changes in saturation, where the effective saturation profile at steady state is visible in Figure 3.3. The VGM model predicts smaller final values of the entropy production rate which manifests in the lower total entropy production rate for the system which is shown in Figure 3.5.

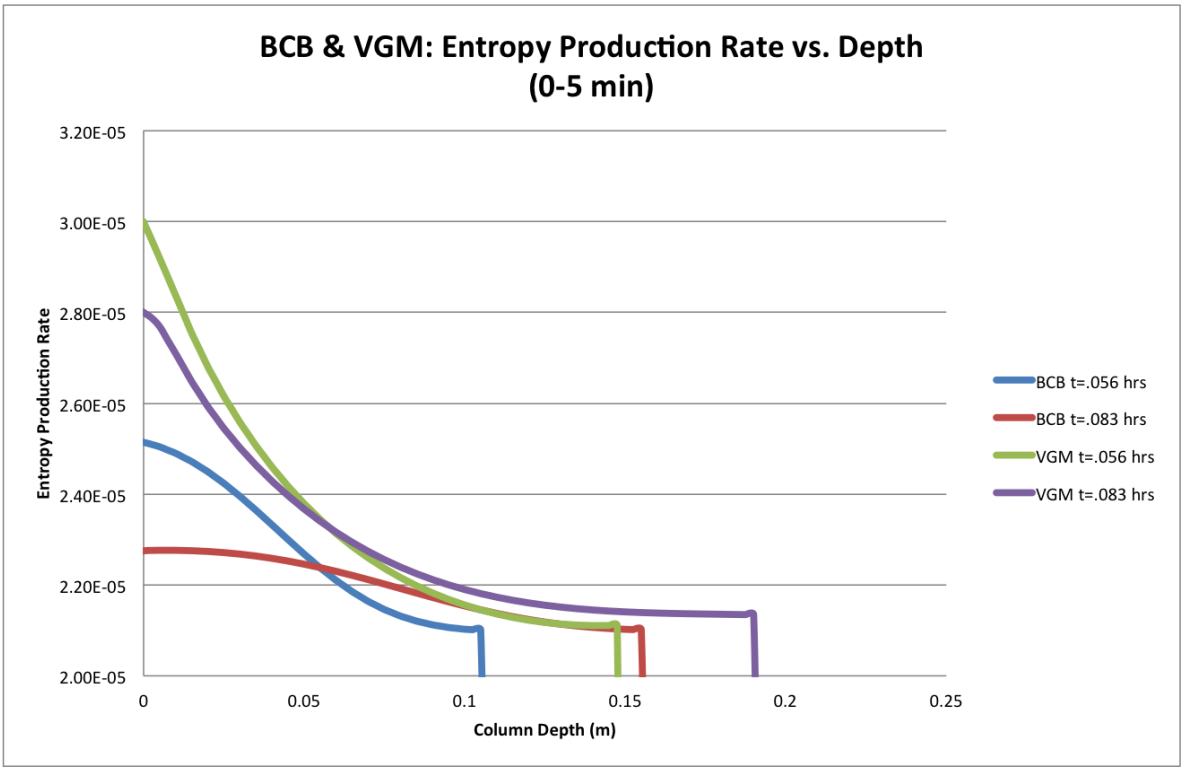

Figure 3.10: The entropy production rate for the first 5 minutes (.083 hours) is shown along the column. This plot provides a comparison between the BCB model (also shown in Figure 3.6) and the VGM model, and illustrates that the VGM model predicts a faster moving front.

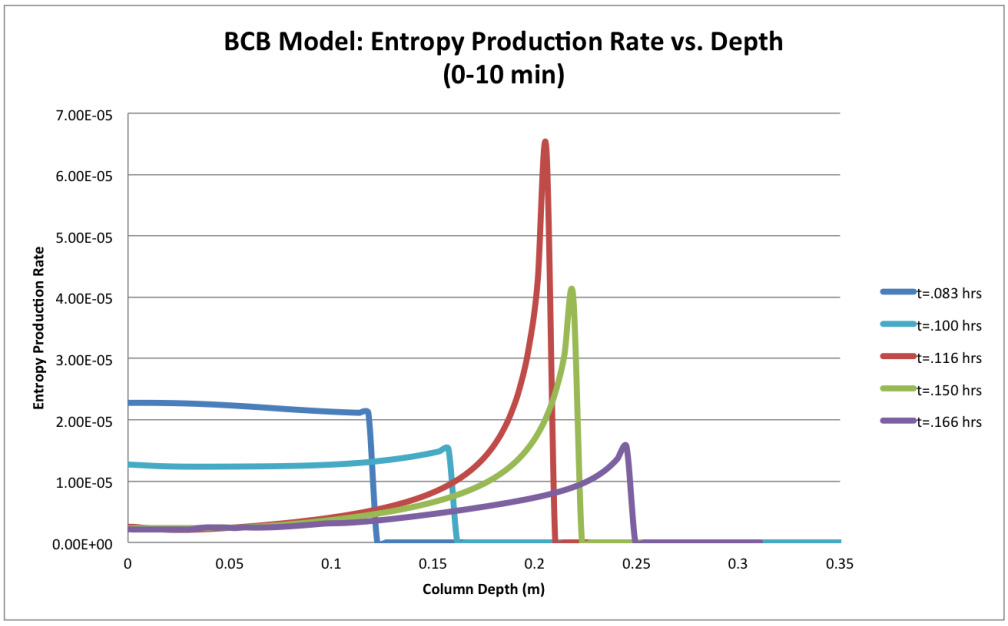

Figure 3.11: The entropy production rate versus depth plot for the first 10 minutes of the simulation using the BCB model is shown.

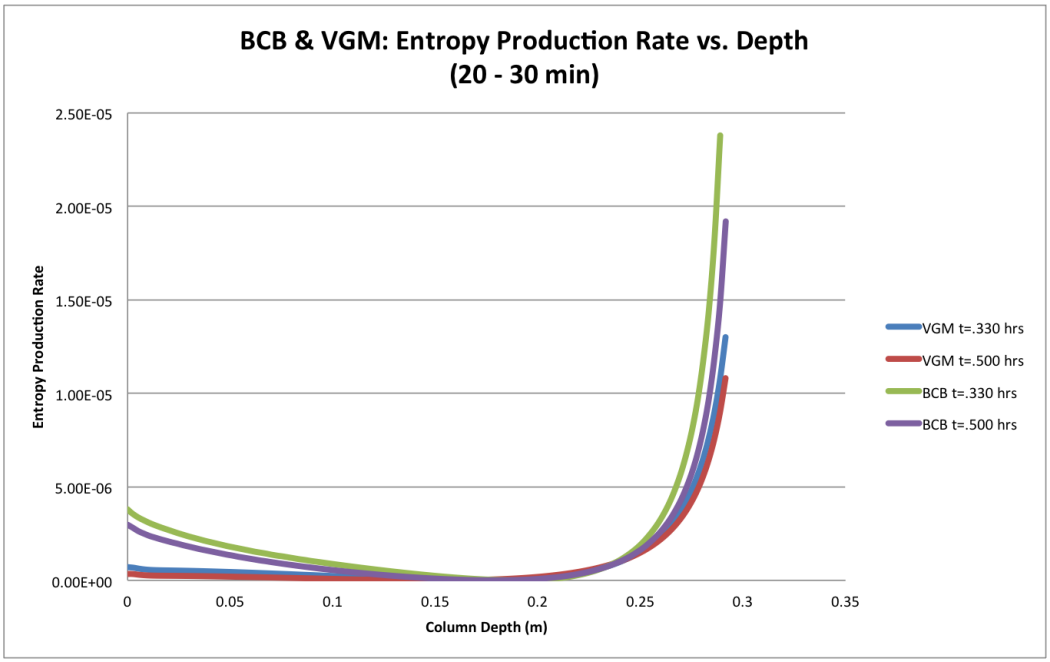

Figure 3.12: The entropy production rate versus depth from 20 to 30 minutes in the simulation is shown for the VGM and BCB models.

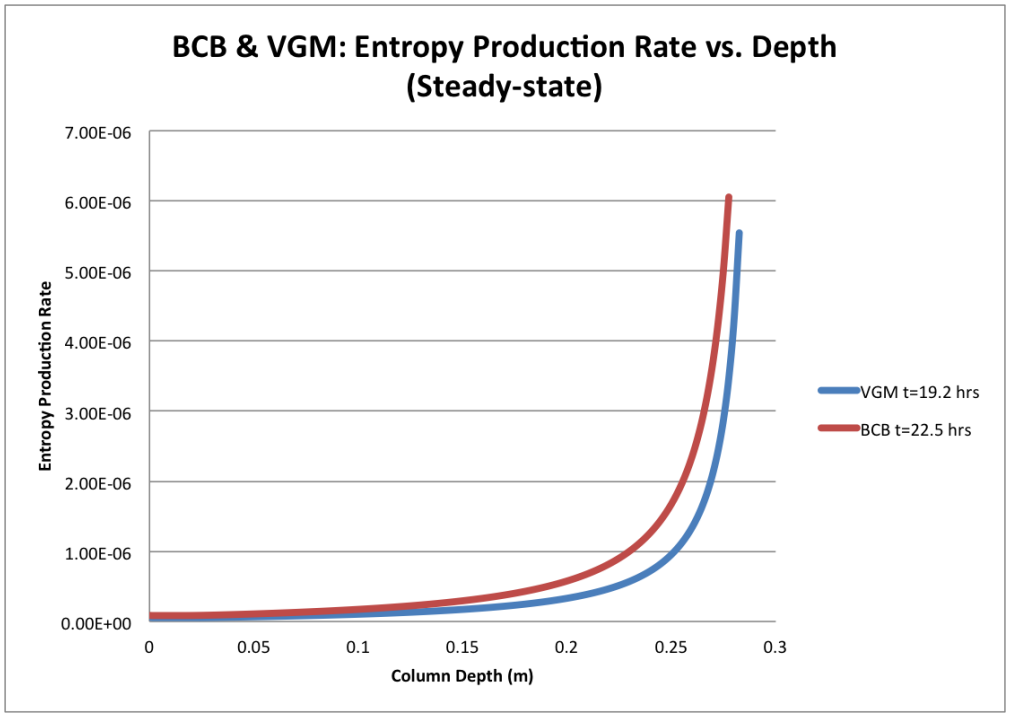

Figure 3.13: The entropy production rate versus depth for the VGM and BCB models is shown at steady-state.

3.4 Discussion

Based on the results of the numerical simulations, both the VGM and BCB pressure-saturation-permeability relations used in conjunction with the one-dimensional mixed form of Richards' equation satisfy the minimum entropy production rate principle. The total entropy production rate for both models decreased monotonically over time, and reached a minimum at steady-state which was verified using Eq. (3.40). All simulations were performed using a set of simulation parameters which model vertical infiltration into a soil column under constant surface ponding; conditions which create a sharp infiltration front. From these results, it seems likely that simpler simulation conditions for which analyt-

ical solutions exist would satisfy the MEPRP as well, although this needs to be verified.

The fact that the MEPRP is satisfied under the current formulation of RE, p-S-K relations, and simulation conditions, is interesting not only because the MEPRP has not been investigated for hydrologic systems, but also because the relationship between pressure, saturation, and permeability is highly nonlinear. Reflecting on the information provided in the first chapter, satisfying the MEPRP requires thermodynamic gradients within a system to be sufficiently small; this stipulation was satisfied for this homogeneous and isothermal model.

It is possible that the empirical p-S-k relations, which are simplified models that exhibit hysteric behavior, contribute to the entropy production rate such that RE satisfies the MEPRP. With that in mind, an interesting extension of this work would be to incorporate a more complete formulation of capillary pressure dynamics into the two-phase flow model, as described in [22], such that a more inclusive pressure-saturation relationship could be simulated and compared to the results predicted by the MEPRP.

This work adds to the body of research which examines the scope of the MEPRP, but further analysis would be useful in determining to what degree multiphase flow systems satisfy this principle. Richards' equation could be examined under different simulation (boundary) conditions, or perhaps more interestingly, a more general two-phase flow model could be developed using the constrained entropy inequality derived in chapter two.

CHAPTER 4

SUMMARY AND CONCLUSIONS

Each of the elements discussed in this work: entropy, the MEPRP, and the TCAT approach to multiphase modeling are nuanced topics which require significant study to master. The goal of this research was to connect each of these topics coherently, rather than provide a comprehensive review of them individually. Using the TCAT framework, a macroscale two-phase flow model was derived for use in a variety of porous medium systems; this model was then simplified to Richards' equation, a standard model for unsaturated flow.

Although this model was reduced to a simplified case, the TCAT approach ensured that the macroscale variables were well-defined averages from microscale precursors, thereby maintaining a connection between scales. Additionally, the rigorous averaging procedure inherent to TCAT was applied to the thermodynamics which ensured a thermodynamically consistent model which was used to track the entropy production rate of the system. The constrained entropy inequality provided in Chapter 2 remains an exact expression for a two-fluid-phase flow model, and can be used to provide theoretical extensions to a hierarchy of closed models incorporating phase, interface, and common curve entity dynamics.

The debated MEPRP was presented, and examined for Richards' equation

using the VGM and BCB pressure-saturation-permeability relations. Under simulation conditions typical of RE, it was determined that RE does satisfy the MEPRP, while further research is needed to verify this assertion using alternative p-S-k relations, and boundary conditions. Using the entropy generation expressions developed from TCAT models, perhaps the MEPRP will be examined for other hydrologic systems to contribute to the dialogue surrounding its position as a true thermodynamic principle.

APPENDIX

Energy Conservation Equation Derivation

The microscale energy conservation equation for a phase can be written as

$$\mathcal{E}_\alpha = \frac{\partial\left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha\right)}{\partial t} + \nabla\cdot\left[\left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha\right)\mathbf{v}_\alpha\right]$$
$$-\nabla\cdot\left(\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha\right) - h_\alpha - \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} = 0 \tag{4.1}$$

Applying an averaging operator to all terms yields

$$\left\langle \frac{\partial\left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha\right)}{\partial t} \right\rangle_{\Omega_\alpha,\Omega}$$
$$+ \left\langle \nabla\cdot\left[\left(E_\alpha + \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha\right)\mathbf{v}_\alpha\right] \right\rangle_{\Omega_\alpha,\Omega}$$
$$- \left\langle \nabla\cdot\left(\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega} - \left\langle h_\alpha \right\rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = 0 \tag{4.2}$$

or, more compactly

$$\left\langle \frac{\partial E_{T\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \nabla\cdot\left(E_{T\alpha}\mathbf{v}_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega} - \left\langle \nabla\cdot\left(\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}$$
$$- \left\langle h_\alpha \right\rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \frac{\partial \psi_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = 0 \tag{4.3}$$

where

$$E_{T\alpha} = \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha + E_\alpha \tag{4.4}$$

Then, applying the transport and divergence theorems eqns (2.5) and (2.6) yields

$$
\begin{aligned}
&\frac{\partial}{\partial t}\langle E_{T\alpha}\rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta E_{T\alpha}\right\rangle_{\Omega_\beta,\Omega} - \langle \mathbf{e}_\alpha \cdot \mathbf{w} E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega} \\
&\quad + \nabla^{\shortparallel} \cdot \langle E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} + \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Omega_\beta,\Omega} + \langle \mathbf{e}_\alpha \cdot E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Gamma_{\alpha M},\Omega} \\
&\quad - \nabla^{\shortparallel} \cdot \langle \mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha\rangle_{\Omega_\alpha,\Omega} - \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot (\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha)\rangle_{\Omega_\beta,\Omega} \\
&\quad - \langle \mathbf{e}_\alpha \cdot (\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega} \\
&\quad - \frac{\partial}{\partial t}\langle \rho_\alpha \psi_\alpha\rangle_{\Omega_\alpha,\Omega} + \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta (\rho_\alpha \psi_\alpha)\right\rangle_{\Omega_\beta,\Omega} \\
&\quad + \langle \mathbf{e}_\alpha \cdot \mathbf{w} (\rho_\alpha \psi_\alpha)\rangle_{\Gamma_{\alpha M},\Omega} - \langle h_\alpha\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}}
\end{aligned}
\tag{4.5}
$$

Working with the first term of equation Eq. (4.5):

$$
\text{Term 1} = \frac{\partial}{\partial t}\left\langle \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha \psi_\alpha + E_\alpha \right\rangle_{\Omega_\alpha,\Omega} \tag{4.6}
$$

Breaking up this term and averaging leaves

$$
\frac{\partial\left(E^{\overline{\overline{\alpha}}} A\right)}{\partial t} = \frac{\partial}{\partial t}\langle E_\alpha\rangle_{\Omega_\alpha,\Omega} \tag{4.7}
$$

$$
\frac{\partial\left(\rho^\alpha \epsilon^{\overline{\overline{\alpha}}} \psi^{\overline{\alpha}} A\right)}{\partial t} = \frac{\partial}{\partial t}\langle \rho_\alpha \psi_\alpha\rangle_{\Omega_\alpha,\Omega} \tag{4.8}
$$

and finally, the kinetic energy portion, which can be manipulated by adding and subtracting $\mathbf{v}^{\overline{\alpha}}$. This is a valid operation because we are adding and subtracting the same quantity, but more importantly, it's a useful operation because mac-

roscale variables don't depend on the microscale variable of integration in the averaging operators, or symbolically

$$\langle f^{\alpha} \rangle_{\Omega_\alpha,\Omega_\alpha} = f^{\alpha} \tag{4.9}$$

This manipulation will help create products of terms that we have already defined which is helpful because we would like to work with a minimum number of uniquely defined quantities, remembering that the end goal is to scale-up microscale equations while retaining the physical meaning of the variables. This way the resulting model can be verified and supplemented with microscale experiments and simulations. Adding and subtracting $\mathbf{v}^{\overline{\alpha}}$ yields

$$\frac{\partial}{\partial t}\left\langle \frac{1}{2}\rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{v}_\alpha \right\rangle_{\Omega_\alpha,\Omega} = \left\langle \frac{1}{2}\rho_\alpha \left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right] \cdot \left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right] \right\rangle_{\Omega_\alpha,\Omega} \tag{4.10}$$

Expanding the right side of Eq. (4.10) gives

$$\begin{aligned}
&\left\langle \frac{1}{2}\rho_\alpha \left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right] \cdot \left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right] \right\rangle_{\Omega_\alpha,\Omega} \\
&= \left\langle \frac{1}{2}\rho_\alpha \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \rho_\alpha \left[\mathbf{v}^{\overline{\alpha}} \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right] \right\rangle_{\Omega_\alpha,\Omega} \\
&+ \left\langle \frac{1}{2}\rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha,\Omega}
\end{aligned} \tag{4.11}$$

Evaluating the averaging operators term by term leaves

$$\left\langle \frac{1}{2}\rho_\alpha \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} \right\rangle_{\Omega_\alpha,\Omega} = \frac{1}{2}\rho^\alpha \epsilon^{\overline{\overline{\alpha}}} \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} A \tag{4.12}$$

$$\left\langle \frac{1}{2}\rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha,\Omega} = \rho^\alpha \epsilon^{\overline{\overline{\alpha}}} K_E^{\overline{\overline{\alpha}}} A \tag{4.13}$$

and

$$\left\langle \rho_\alpha \left[\mathbf{v}^{\overline{\alpha}} \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right] \right\rangle_{\Omega_\alpha,\Omega} = 0 \tag{4.14}$$

Now we have

$$\frac{\partial}{\partial t}\langle E_{T\alpha}\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t}\left[E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \left(\frac{1}{2}\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) \right] \tag{4.15}$$

or

$$\frac{\partial}{\partial t}\langle E_{T\alpha}\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t}\left(E_T^{\overline{\overline{\alpha}}} A \right) \tag{4.16}$$

where

$$E_T^{\overline{\overline{\alpha}}} A = E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \left(\frac{1}{2}\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) \tag{4.17}$$

Moving on to the second line of equation Eq. (4.5) we have the term

$$\text{Term} = \nabla^{\backslash\backslash} \cdot \langle E_{T\alpha} \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} \tag{4.18}$$

which needs to be expanded as we have done before to get products of terms that can be evaluated. In order to get the product $\rho_\alpha \left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right]$ we will add and

subtract $\mathbf{v}^{\overline{\alpha}}$ and divide $E_{T\alpha}$ by ρ_α, which yields

$$\nabla^{\backslash\backslash}\cdot\langle E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} = \left\langle \left(\frac{E_{T\alpha}}{\rho_\alpha}\right)\rho_\alpha\left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right]\right\rangle_{\Omega_\alpha,\Omega} \tag{4.19}$$

Now we can further manipulate the right side of Eq. (4.19) by adding and subtracting $\frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}$ which gives

$$\nabla^{\backslash\backslash}\cdot\langle E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} = \nabla^{\backslash\backslash}\cdot\left\langle \left[\frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \left(\frac{E_{T\alpha}}{\rho_\alpha} - \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\right)\right]\rho_\alpha\left[\mathbf{v}^{\overline{\alpha}} + (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right]\right\rangle_{\Omega_\alpha,\Omega} \tag{4.20}$$

Expanding the products on the right side of Eq. (4.20) leaves

$$\begin{aligned}\nabla^{\backslash\backslash}\cdot\langle E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} &= \nabla^{\backslash\backslash}\cdot\left\langle \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\rho_\alpha\mathbf{v}^{\overline{\alpha}}\right\rangle_{\Omega_\alpha,\Omega} + \nabla^{\backslash\backslash}\cdot\left\langle \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega} \\ &+ \nabla^{\backslash\backslash}\cdot\left\langle \left(\frac{E_{T\alpha}}{\rho_\alpha} - \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\right)\rho_\alpha\mathbf{v}^{\overline{\alpha}}\right\rangle_{\Omega_\alpha,\Omega} \\ &+ \nabla^{\backslash\backslash}\cdot\left\langle \left(\frac{E_{T\alpha}}{\rho_\alpha} - \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\right)\rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega}\end{aligned} \tag{4.21}$$

Now we can evaluate the averaging operators term by term in equation Eq. (4.21) as follows

$$\begin{aligned}\nabla^{\backslash\backslash}\cdot\left\langle \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\rho_\alpha\mathbf{v}^{\overline{\alpha}}\right\rangle_{\Omega_\alpha,\Omega} &= \nabla^{\backslash\backslash}\cdot\left(\frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}A\mathbf{v}^{\overline{\alpha}}\langle\rho_\alpha\rangle_{\Omega_\alpha,\Omega}\right) \\ &= \nabla^{\backslash\backslash}\cdot\left(\frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}A\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}\right) \\ &= \nabla^{\backslash\backslash}\cdot\left(E_T^{\overline{\overline{\alpha}}}\mathbf{v}^{\overline{\alpha}}A\right)\end{aligned} \tag{4.22}$$

The second and third terms in Eq. (4.21) can be evaluated as follows

$$\nabla'' \cdot \left\langle \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha, \Omega} = 0 \tag{4.23}$$

$$\nabla'' \cdot \left\langle \left(\frac{E_{T\alpha}}{\rho_\alpha} - \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} \right) \rho_\alpha \mathbf{v}^{\overline{\alpha}} \right\rangle_{\Omega_\alpha, \Omega} = 0 \tag{4.24}$$

The last term can be expanded by substituting the definitions of $E_T^{\overline{\overline{\alpha}}}$ and $E_{T\alpha}$ into Eq. (4.20) and adding and subtracting $\mathbf{v}^{\overline{\alpha}}$. This yields

$$\begin{aligned}
&\nabla'' \cdot \left\langle \left(\frac{E_{T\alpha}}{\rho_\alpha} - \frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} \right) \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha, \Omega} = \\
&\nabla'' \cdot \left\langle \left(\frac{E_\alpha}{\rho_\alpha} + \frac{1}{2} \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right] \cdot \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right] + \psi_\alpha \right) \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right\rangle_{\Omega_\alpha, \Omega} \\
&- \nabla'' \cdot \left\langle \left(\frac{E^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2} \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha, \Omega}
\end{aligned} \tag{4.25}$$

The first term on the right side of Eq. (4.25) can be expanded as follows

$$\begin{aligned}
&\nabla'' \cdot \left\langle \left(\frac{E_\alpha}{\rho_\alpha} + \frac{1}{2} \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right] \cdot \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right] + \psi_\alpha \right) \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right\rangle_{\Omega_\alpha, \Omega} \\
&\quad = \nabla'' \cdot \Big\langle \left(\frac{E_\alpha}{\rho_\alpha} + \frac{1}{2} \mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + \mathbf{v}^{\overline{\alpha}} \cdot \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \right. \\
&\quad + \left. \frac{1}{2} \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \cdot \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) + \psi_\alpha \right) \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}} \right) \Big\rangle_{\Omega_\alpha, \Omega}
\end{aligned} \tag{4.26}$$

Now, substituting equation Eq. (4.26) into equation Eq. (4.25), and canceling

like terms leaves

$$
\begin{aligned}
&\nabla^{\backslash\backslash}\cdot\left\langle\left(\frac{E_{T\alpha}}{\rho_\alpha}-\frac{E_T^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\right)\rho_\alpha(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega}\\
&=\nabla^{\backslash\backslash}\cdot\Big\langle\left(\frac{E_\alpha}{\rho_\alpha}+\mathbf{v}^{\overline{\alpha}}\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\right.\\
&\left.+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)+\psi_\alpha\right)\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\Big\rangle_{\Omega_\alpha,\Omega}\\
&-\nabla^{\backslash\backslash}\cdot\left\langle\left(\frac{E^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega}
\end{aligned}
\tag{4.27}
$$

The right side of Eq. (4.27) can be combined with the other divergence term from equation Eq. (4.5) to try and get quantities which we have already defined, like the macroscale stress tensor; this will leave only boundary terms to evaluate. The divergence terms are the following

$$
\begin{aligned}
\text{Term 1} = \nabla^{\backslash\backslash}\cdot\Big\langle&\left(\frac{E_\alpha}{\rho_\alpha}+\mathbf{v}^{\overline{\alpha}}\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\right.\\
&\left.+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)+\psi_\alpha\right)\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\Big\rangle_{\Omega_\alpha,\Omega}
\end{aligned}
\tag{4.28}
$$

$$
\text{Term 2} = -\nabla^{\backslash\backslash}\cdot\left\langle\left(\frac{E^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega}
\tag{4.29}
$$

and

$$
\text{Term 3} = -\nabla^{\backslash\backslash}\cdot\langle\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\rangle_{\Omega_\alpha,\Omega}+\nabla^{\backslash\backslash}\cdot\left(E_T^{\overline{\overline{\alpha}}}\mathbf{v}^{\overline{\alpha}}A\right)
\tag{4.30}
$$

The stress tensor/heat flux term can be rearranged as follows

$$
\nabla^{\backslash\backslash}\cdot\langle\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\rangle_{\Omega_\alpha,\Omega}=\nabla^{\backslash\backslash}\cdot\left\langle\mathbf{q}_\alpha+\mathbf{t}_\alpha\cdot\left[\mathbf{v}^{\overline{\alpha}}+\left(\mathbf{v}_\alpha+\mathbf{v}^{\overline{\alpha}}\right)\right]\right\rangle_{\Omega_\alpha,\Omega}
$$

$$= \nabla^{\backslash\backslash}\cdot\left\langle \mathbf{q}_\alpha + \mathbf{t}_\alpha\cdot\mathbf{v}^{\overline{\alpha}} + \mathbf{t}_\alpha\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \tag{4.31}$$

We can combine equation Eq. (4.31) and the remaining divergence term $\nabla^{\backslash\backslash}\cdot\left(E_T^{\overline{\overline{\alpha}}}\mathbf{v}^{\overline{\alpha}}\right)$ which will be expanded to leave

$$\begin{aligned}
&\nabla^{\backslash\backslash}\cdot\langle E_{T\alpha}\mathbf{v}_\alpha - \mathbf{q}_\alpha - \mathbf{t}_\alpha\cdot\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} \\
&\quad = \nabla^{\backslash\backslash}\cdot\left\langle\left(-K_E^{\overline{\overline{\alpha}}} + \psi_\alpha - \psi^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) + \mathbf{t}_\alpha\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad - \nabla^{\backslash\backslash}\cdot\left\langle \mathbf{q}_\alpha + \left(\frac{E_\alpha}{\rho_\alpha} - \frac{E^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right)\rho_\alpha\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad - \nabla^{\backslash\backslash}\cdot\left\langle\left[\mathbf{t}_\alpha - \rho_\alpha\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right]\cdot\mathbf{v}^{\overline{\alpha}}\right\rangle_{\Omega_\alpha,\Omega} + \nabla^{\backslash\backslash}\cdot\left(E_T^{\overline{\overline{\alpha}}}\mathbf{v}^{\overline{\alpha}}A\right)
\end{aligned} \tag{4.32}$$

Now, we can see the definition for the macroscale stress tensor (Eq. (2.26)) which we defined in forming the macroscale momentum equation. The remaining terms will be used to define the macroscale heat flux vector as

$$\begin{aligned}
&\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}A \\
&= \nabla^{\backslash\backslash}\cdot\left\langle \mathbf{q}_\alpha + \left(\frac{E_\alpha}{\rho_\alpha} - \frac{E^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right)\rho_\alpha\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \\
&+ \nabla^{\backslash\backslash}\cdot\left\langle\left(-K_E^{\overline{\overline{\alpha}}} + \psi_\alpha - \psi^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}) + \mathbf{t}_\alpha\cdot\left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}
\end{aligned} \tag{4.33}$$

All of the divergence terms are now defined, so pulling all of the definitions to-

gether leaves the macroscale terms

$$
\begin{aligned}
&\nabla^{\backslash\backslash}\cdot\langle E_{T\alpha}\mathbf{v}_\alpha - \mathbf{q}_\alpha - \mathbf{t}_\alpha\cdot\mathbf{v}_\alpha\rangle_{\Omega_\alpha,\Omega} \\
&= \nabla^{\backslash\backslash}\cdot\left[\left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right)\mathbf{v}^{\overline{\alpha}} - A\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}} - A\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right]
\end{aligned}
\tag{4.34}
$$

Combining equation Eq. (4.34) with the boundary terms from equation Eq. (4.5) and all of the previously defined quantities leaves

$$
\begin{aligned}
\langle\mathcal{E}_\alpha\rangle_{\Omega_\alpha,\Omega} = &\frac{\partial\left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right)}{\partial t} \\
&+ \nabla^{\backslash\backslash}\cdot\left[\left(E^{\overline{\overline{\alpha}}}A + \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha A\left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right)\mathbf{v}^{\overline{\alpha}} - A\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}} - A\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right] \\
&- \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta E_{T\alpha}\right\rangle_{\Omega_\beta,\Omega} - \langle\mathbf{e}_\alpha\cdot\mathbf{w}E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle\mathbf{n}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Omega_\beta,\Omega} + \langle\mathbf{e}_\alpha\cdot E_{T\alpha}\mathbf{v}_\alpha\rangle_{\Gamma_{\alpha M},\Omega} \\
&- \sum_{\beta\in\mathcal{J}_{c\alpha}} \langle\mathbf{n}_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha + \mathbf{q}_\alpha\right)\rangle_{\Omega_\beta,\Omega} - \langle\mathbf{e}_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha + \mathbf{q}_\alpha\right)\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \sum_{\beta\in\mathcal{J}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left(\rho_\alpha\psi_\alpha\right)\right\rangle_{\Omega_\beta,\Omega} \\
&+ \langle\mathbf{e}_\alpha\cdot\mathbf{w}\left(\rho_\alpha\psi_\alpha\right)\rangle_{\Gamma_{\alpha M},\Omega} - \langle h_\alpha\rangle_{\Omega_\alpha,\Omega} \\
&- \frac{\partial}{\partial t}\langle\rho_\alpha\psi_\alpha\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha\in\mathcal{J}_{\mathrm{P}}
\end{aligned}
\tag{4.35}
$$

Working with the unit normal vector terms yields

$$\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\alpha E_{T\alpha}\rangle_{\Omega_\beta,\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \mathbf{n}_\alpha \cdot \mathbf{v}_\beta E_{T\alpha}\right\rangle_{\Omega_\beta,\Omega}$$
$$= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle E_{T\alpha}\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \tag{4.36}$$

Substituting the definition for $E_{T\alpha}$ and adding and subtracting $E_{T\alpha}^{\overline{\overline{\beta}}}$ yields

$$-\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle E_{T\alpha}\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}$$
$$= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left[\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_\alpha^{\overline{\beta}}\right) + \left(\left(\frac{E_\alpha}{\rho_\alpha} + \frac{1}{2}\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha + \psi_\alpha\right)\right.\right.$$
$$\left.\left. - \left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_\alpha^{\overline{\beta}}\right)\right)\right] \rho_\alpha\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \tag{4.37}$$

which simplifies to

$$-\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle E_{T\alpha}\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}$$
$$= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_\alpha^{\overline{\beta}}\right) A^{\beta\to\alpha} M$$
$$- \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left[\left(\frac{E_\alpha}{\rho_\alpha} + \frac{1}{2}\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha + \psi_\alpha\right)\right.\right.$$
$$\left.\left. - \left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_\alpha^{\overline{\beta}}\right)\right] \rho_\alpha\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \tag{4.38}$$

The last term in equation Eq. (4.38) includes the dot product of the microscale

phase velocity which can be expanded as follows

$$
\begin{aligned}
&-\sum_{\beta\in\mathcal{I}_{c\alpha}} \Big\langle \Bigg[\left(\frac{E_\alpha}{\rho_\alpha}+\frac{1}{2}\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha+\psi_\alpha\right)\\
&-\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)\Bigg]\rho_\alpha\left(\mathbf{v}_\beta-\mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\Big\rangle_{\Omega_\beta,\Omega}\\
&=-\sum_{\beta\in\mathcal{I}_{c\alpha}} \Big\langle \Bigg(\frac{E_\alpha}{\rho_\alpha}+\frac{1}{2}\left[\mathbf{v}_\alpha^{\overline{\beta}}+\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)\right]\cdot\left[\mathbf{v}_\alpha^{\overline{\beta}}+\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)\right]\\
&+\psi_\alpha\Bigg)\rho_\alpha\left(\mathbf{v}_\beta-\mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\Big\rangle_{\Omega_\beta,\Omega}\\
&+\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)\rho_\alpha(\mathbf{v}_\beta-\mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&=-\sum_{\beta\in\mathcal{I}_{c\alpha}} \Big\langle \Bigg(\frac{E_\alpha}{\rho_\alpha}+\mathbf{v}_\alpha^{\overline{\beta}}\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)\\
&+\psi_\alpha\Bigg)\rho_\alpha\left(\mathbf{v}_\beta-\mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\Big\rangle_{\Omega_\beta,\Omega}\\
&+\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)\rho_\alpha(\mathbf{v}_\beta-\mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}
\end{aligned}
\tag{4.39}
$$

Substituting equation Eq. (4.39) into equation Eq. (4.38) and adding and expanding the stress tensor term $\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle\mathbf{n}_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\right)\rangle_{\Omega_\beta,\Omega}$ and $\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left(\rho_\alpha\psi_\alpha\right)\right\rangle_{\Omega_\beta,\Omega}$ leaves

$$
\begin{aligned}
&\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle\mathbf{n}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Omega_\beta,\Omega}-\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta E_{T\alpha}\right\rangle_{\Omega_\beta,\Omega}\\
&\quad-\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle\mathbf{n}_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\right)\rangle_{\Omega_\beta,\Omega}\\
&\quad=-\sum_{\beta\in\mathcal{I}_{c\alpha}} \Big\langle \Bigg(\frac{E_\alpha}{\rho_\alpha}+\mathbf{v}_\alpha^{\overline{\beta}}\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)
\end{aligned}
$$

$$
\begin{aligned}
&+\psi_\alpha)\,\rho_\alpha\left(\mathbf{v}_\beta-\mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\Big\rangle_{\Omega_\beta,\Omega}\\
&+\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)\rho_\alpha(\mathbf{v}_\beta-\mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)A\overset{\beta\to\alpha}{M}\\
&-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\mathbf{t}_\alpha\cdot\left[\mathbf{v}_\alpha^{\overline{\beta}}+\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)+\mathbf{q}_\alpha\right]\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&+\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left(\rho_\alpha\psi_\alpha\right)\right\rangle_{\Omega_\beta,\Omega}
\end{aligned}
\tag{4.40}
$$

Grouping terms to get the momentum transfer term defined in Eq. (2.27) yields

$$
\begin{aligned}
&\sum_{\beta\in\mathcal{I}_{c\alpha}}\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Omega_\beta,\Omega}-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta E_{T\alpha}\right\rangle_{\Omega_\beta,\Omega}\\
&\quad-\sum_{\beta\in\mathcal{I}_{c\alpha}}\langle\mathbf{n}_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\right)\rangle_{\Omega_\beta,\Omega}\\
&=-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\frac{E_\alpha}{\rho_\alpha}+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)+\psi_\alpha\right)\rho_\alpha\left(\mathbf{v}_\beta-\mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&\quad+\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)\rho_\alpha(\mathbf{v}_\beta-\mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&\quad-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left(\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}}+K_{E\alpha}^{\overline{\overline{\beta}}}+\psi_\alpha^{\overline{\beta}}\right)A\overset{\beta\to\alpha}{M}\\
&\quad-\sum_{\beta\in\mathcal{I}_{c\alpha}}A\overset{\beta\to\alpha}{\mathbf{T}}\cdot\mathbf{v}_\alpha^{\overline{\beta}}-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left[\mathbf{t}_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_\alpha^{\overline{\beta}}\right)+\mathbf{q}_\alpha\right]\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega}\\
&\quad+\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left(\rho_\alpha\psi_\alpha\right)\right\rangle_{\Omega_\beta,\Omega}
\end{aligned}
\tag{4.41}
$$

The terms inEq. (4.41) can be regrouped to define a heat transfer term

$$
\begin{aligned}
\overset{\beta\to\alpha}{A\,Q} = &\sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \mathbf{n}_\alpha\cdot\mathbf{q}_\alpha + \mathbf{n}_\alpha\cdot\mathbf{t}_\alpha\cdot\left(\mathbf{v}_\alpha - \mathbf{v}_\alpha^{\overline{\beta}}\right)\right\rangle_{\Omega_\beta,\Omega} \\
&+ \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left(\frac{E_\alpha}{\rho_\alpha} - \frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}\right)\rho_\alpha\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \\
&+ \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \frac{1}{2}\left(\mathbf{v}_\alpha - \mathbf{v}_\alpha^{\overline{\beta}}\right)\cdot\left(\mathbf{v}_\alpha - \mathbf{v}_\alpha^{\overline{\beta}}\right)\rho_\alpha\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \\
&+ \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \left(\psi_\alpha - \psi_\alpha^{\overline{\beta}} - K_{E\alpha}^{\overline{\overline{\beta}}}\right)\rho_\alpha\left(\mathbf{v}_\beta - \mathbf{v}_\alpha\right)\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\beta,\Omega} \\
&+ \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left(\rho_\alpha\psi_\alpha\right)\right\rangle_{\Omega_\beta,\Omega}
\end{aligned}
\tag{4.42}
$$

Now equation Eq. (4.41) reduces to

$$
\begin{aligned}
&\sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Omega_\beta,\Omega} - \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \mathbf{n}_\alpha\cdot\mathbf{v}_\beta E_{T\alpha}\right\rangle_{\Omega_\beta,\Omega} \\
&- \sum_{\beta\in\mathcal{I}_{c\alpha}} \langle \mathbf{n}_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha + \mathbf{q}_\alpha\right)\rangle_{\Omega_\beta,\Omega} + \sum_{\beta\in\mathcal{I}_{c\alpha}} \left\langle \mathbf{n}_\alpha\cdot\mathbf{v}_\beta\left(\rho_\alpha\psi_\alpha\right)\right\rangle_{\Omega_\beta,\Omega} \\
&= -\sum_{\beta\in\mathcal{I}_{c\alpha}} \left(\left[\frac{E_\alpha^{\overline{\overline{\beta}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\mathbf{v}_\alpha^{\overline{\beta}}\cdot\mathbf{v}_\alpha^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_\alpha^{\overline{\beta}}\right]\overset{\beta\to\alpha}{A\,M} + \overset{\beta\to\alpha}{A\,\mathbf{T}}\cdot\mathbf{v}_\alpha^{\overline{\beta}} + \overset{\beta\to\alpha}{A\,Q}\right)
\end{aligned}
\tag{4.43}
$$

Grouping the unit tangent vector terms from equation Eq. (4.35) yields

$$
\begin{aligned}
&\langle \mathbf{e}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega} - \langle \mathbf{e}_\alpha\cdot\mathbf{w} E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega} \\
&\qquad = -\langle E_{T\alpha}\left(\mathbf{w} - \mathbf{v}_\alpha\right)\cdot\mathbf{e}_\alpha\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned}
\tag{4.44}
$$

Substituting the definition for $E_{T\alpha}$ and adding and subtracting $E_{TM}^{\overline{\overline{\alpha}}}$ yields

$$
\begin{aligned}
&-\langle E_{T\alpha}\left(\mathbf{w}-\mathbf{v}_{\alpha}\right)\cdot\mathbf{e}_{\alpha}\rangle_{\Gamma_{\alpha M},\Omega} \\
&=-\left\langle\left[\left(\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha}\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_{M}^{\overline{\alpha}}\cdot\mathbf{v}_{M}^{\overline{\alpha}}+K_{E_{M}}^{\overline{\overline{\alpha}}}+\psi_{M}^{\overline{\alpha}}\right)+\left(\left(\frac{E_{\alpha}}{\rho_{\alpha}}+\frac{1}{2}\mathbf{v}_{\alpha}\cdot\mathbf{v}_{\alpha}+\psi_{\alpha}\right)\right.\right.\right. \\
&\quad\left.\left.\left.-\left(\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha}\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_{M}^{\overline{\alpha}}\cdot\mathbf{v}_{M}^{\overline{\alpha}}+K_{E_{M}}^{\overline{\overline{\alpha}}}+\psi_{M}^{\overline{\alpha}}\right)\right)\right]\rho_{\alpha}\left(\mathbf{w}-\mathbf{v}_{\alpha}\right)\cdot\mathbf{e}_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega} \\
&=-\left(\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha}\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_{M}^{\overline{\alpha}}\cdot\mathbf{v}_{M}^{\overline{\alpha}}+K_{E_{M}}^{\overline{\overline{\alpha}}}+\psi_{M}^{\overline{\alpha}}\right)A\overset{\alpha\rightarrow}{M}_{M} \\
&\quad-\left\langle\left[\left(\frac{E_{\alpha}}{\rho_{\alpha}}+\frac{1}{2}\mathbf{v}_{\alpha}\cdot\mathbf{v}_{\alpha}+\psi_{\alpha}\right)\right.\right. \\
&\quad\left.\left.-\left(\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha}\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_{M}^{\overline{\alpha}}\cdot\mathbf{v}_{M}^{\overline{\alpha}}+K_{E_{M}}^{\overline{\overline{\alpha}}}+\psi_{M}^{\overline{\alpha}}\right)\right]\rho_{\alpha}\left(\mathbf{w}-\mathbf{v}_{\alpha}\right)\cdot\mathbf{e}_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned}
\tag{4.45}
$$

The dot product of the microscale phase velocity in the last term in equation Eq. (4.45) can be expanded as follows

$$
\begin{aligned}
&-\left\langle\left[\left(\frac{E_{\alpha}}{\rho_{\alpha}}+\frac{1}{2}\mathbf{v}_{\alpha}\cdot\mathbf{v}_{\alpha}+\psi_{\alpha}\right)\right.\right. \\
&\left.\left.-\left(\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha}\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_{M}^{\overline{\alpha}}\cdot\mathbf{v}_{M}^{\overline{\alpha}}+K_{E_{M}}^{\overline{\overline{\alpha}}}+\psi_{M}^{\overline{\alpha}}\right)\right]\rho_{\alpha}\left(\mathbf{w}-\mathbf{v}_{\alpha}\right)\cdot\mathbf{e}_{\alpha}\right\rangle_{\Gamma_{\alpha M},\Omega} \\
&=-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\frac{E_{\alpha}}{\rho_{\alpha}}+\frac{1}{2}\left[\mathbf{v}_{M}^{\overline{\alpha}}+\left(\mathbf{v}_{\alpha}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\right]\cdot\left[\mathbf{v}_{M}^{\overline{\alpha}}+\left(\mathbf{v}_{\alpha}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\right]\right.\right. \\
&\left.\left.+\psi_{\alpha}\right)\rho_{\alpha}\left(\mathbf{w}-\mathbf{v}_{\alpha}\right)\cdot\mathbf{e}_{\alpha}\right\rangle_{\Omega_{\beta},\Omega} \\
&+\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha}\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_{M}^{\overline{\alpha}}\cdot\mathbf{v}_{M}^{\overline{\alpha}}+K_{E_{M}}^{\overline{\overline{\alpha}}}+\psi_{M}^{\overline{\alpha}}\right)\rho_{\alpha}(\mathbf{w}-\mathbf{v}_{\alpha})\cdot\mathbf{e}_{\alpha}\right\rangle_{\Omega_{\beta},\Omega} \\
&=-\sum_{\beta\in\mathcal{I}_{c\alpha}}\left\langle\left(\frac{E_{\alpha}}{\rho_{\alpha}}+\mathbf{v}_{M}^{\overline{\alpha}}\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}_{M}^{\overline{\alpha}}\right)+\frac{1}{2}\left(\mathbf{v}_{\alpha}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}_{M}^{\overline{\alpha}}\right)\right.\right. \\
&\left.\left.+\psi_{\alpha}\right)\rho_{\alpha}\left(\mathbf{w}-\mathbf{v}_{\alpha}\right)\cdot\mathbf{e}_{\alpha}\right\rangle_{\Omega_{\beta},\Omega}
\end{aligned}
$$

$$+\left\langle\left(\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_{E_M}^{\overline{\overline{\alpha}}}+\psi_M^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{w}-\mathbf{v}_\alpha)\cdot\mathbf{e}_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega} \tag{4.46}$$

Substituting equation Eq. (4.46) into equation Eq. (4.45), and adding and expanding the stress tensor term $\langle\mathbf{e}_\alpha\cdot(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}$ and $\langle\mathbf{e}_\alpha\cdot\mathbf{w}\,(\rho_\alpha\psi_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}$ leaves

$$\begin{aligned}
&\langle\mathbf{e}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega}-\langle\mathbf{e}_\alpha\cdot\mathbf{w}E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega}-\langle\mathbf{e}_\alpha\cdot(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}\\
&=-\Big\langle\Big(\frac{E_\alpha}{\rho_\alpha}+\mathbf{v}_M^{\overline{\alpha}}\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)\\
&+\psi_\alpha\Big)\rho_\alpha\left(\mathbf{w}-\mathbf{v}_\alpha\right)\cdot\mathbf{e}_\alpha\Big\rangle_{\Gamma_{\alpha M},\Omega}\\
&+\left\langle\left(\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_{E_M}^{\overline{\overline{\alpha}}}+\psi_M^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{w}-\mathbf{v}_\alpha)\cdot\mathbf{e}_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}\\
&-\left(\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_M^{\overline{\alpha}}\cdot\mathbf{v}_M^{\overline{\alpha}}+K_{E_M}^{\overline{\overline{\alpha}}}+\psi_M^{\overline{\alpha}}\right)A\overset{\alpha\rightarrow}{M}_M\\
&-\left\langle\left(\mathbf{t}_\alpha\cdot\left[\mathbf{v}_M^{\overline{\alpha}}+\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)+\mathbf{q}_\alpha\right]\right)\cdot\mathbf{e}_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}+\langle\mathbf{e}_\alpha\cdot\mathbf{w}\,(\rho_\alpha\psi_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned} \tag{4.47}$$

Grouping terms to get the momentum transfer term yields

$$\begin{aligned}
&\langle\mathbf{e}_\alpha\cdot\mathbf{v}_\alpha E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega}-\langle\mathbf{e}_\alpha\cdot\mathbf{w}E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega}-\langle\mathbf{e}_\alpha\cdot(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}\\
&=-\left\langle\left(\frac{E_\alpha}{\rho_\alpha}+\frac{1}{2}\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)+\psi_\alpha\right)\rho_\alpha\left(\mathbf{w}-\mathbf{v}_\alpha\right)\cdot\mathbf{e}_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}\\
&+\left\langle\left(\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+K_{E_M}^{\overline{\overline{\alpha}}}+\psi_M^{\overline{\alpha}}\right)\rho_\alpha(\mathbf{w}-\mathbf{v}_\alpha)\cdot\mathbf{e}_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}\\
&-\left(\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha\epsilon^{\overline{\overline{\alpha}}}}+\frac{1}{2}\mathbf{v}_M^{\overline{\alpha}}\cdot\mathbf{v}_M^{\overline{\alpha}}+K_{E_M}^{\overline{\overline{\alpha}}}+\psi_M^{\overline{\alpha}}\right)A\overset{\alpha\rightarrow}{M}_M\\
&-A\overset{\alpha\rightarrow}{T}_M\cdot\mathbf{v}_M^{\overline{\alpha}}-\left\langle\left[\mathbf{t}_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}_M^{\overline{\alpha}}\right)+\mathbf{q}_\alpha\right]\cdot\mathbf{e}_\alpha\right\rangle_{\Gamma_{\alpha M},\Omega}+\langle\mathbf{e}_\alpha\cdot\mathbf{w}\,(\rho_\alpha\psi_\alpha)\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned} \tag{4.48}$$

The remaining terms in Eq. (4.48) can be regrouped to define a heat transfer term

$$
\begin{aligned}
A\overset{\alpha\rightarrow}{Q}_M =& \left\langle \mathbf{e}_\alpha \cdot \mathbf{q}_\alpha + \mathbf{n}_\alpha \cdot \mathbf{t}_\alpha \cdot \left(\mathbf{v}_\alpha - \mathbf{v}_M^{\overline{\alpha}}\right)\right\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \left\langle \left(\frac{E_\alpha}{\rho_\alpha} - \frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}}\right) \rho_\alpha \left(\mathbf{w} - \mathbf{v}_\alpha\right) \cdot \mathbf{e}_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \left\langle \frac{1}{2}\left(\mathbf{v}_\alpha - \mathbf{v}_M^{\overline{\alpha}}\right) \cdot \left(\mathbf{v}_\alpha - \mathbf{v}_M^{\overline{\alpha}}\right) \rho_\alpha \left(\mathbf{w} - \mathbf{v}_\alpha\right) \cdot \mathbf{e}_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \left\langle \left(\psi_\alpha - \psi_M^{\overline{\alpha}} - K_{E_M}^{\overline{\overline{\alpha}}}\right) \rho_\alpha \left(\mathbf{w} - \mathbf{v}_\alpha\right) \cdot \mathbf{e}_\alpha \right\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \left\langle \mathbf{e}_\alpha \cdot \mathbf{w} \left(\rho_\alpha \psi_\alpha\right)\right\rangle_{\Gamma_{\alpha M},\Omega}
\end{aligned}
\tag{4.49}
$$

Now equation Eq. (4.48) reduces to

$$
\begin{aligned}
&\langle \mathbf{e}_\alpha \cdot \mathbf{v}_\alpha E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega} - \langle \mathbf{e}_\alpha \cdot \mathbf{w} E_{T\alpha}\rangle_{\Gamma_{\alpha M},\Omega} - \langle \mathbf{e}_\alpha \cdot \left(\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha\right)\rangle_{\Gamma_{\alpha M},\Omega} \\
&+ \langle \mathbf{e}_\alpha \cdot \mathbf{w} \left(\rho_\alpha \psi_\alpha\right)\rangle_{\Gamma_{\alpha M},\Omega} \\
&= -\left(\left[\frac{E_M^{\overline{\overline{\alpha}}}}{\rho^\alpha \epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2}\mathbf{v}_M^{\overline{\alpha}} \cdot \mathbf{v}_M^{\overline{\alpha}} + K_{E_M}^{\overline{\overline{\alpha}}} + \psi_M^{\overline{\alpha}}\right] A\overset{\alpha\rightarrow}{M}_M + A\overset{\alpha\rightarrow}{T}_M \cdot \mathbf{v}_M^{\overline{\alpha}} + A\overset{\alpha\rightarrow}{Q}_M\right)
\end{aligned}
\tag{4.50}
$$

We have now dealt with the boundary terms, so equations Eq. (4.6) and Eq. (4.50) can be combined with the rotation of the defined macroscale terms in Eq. (4.35). The macroscale energy equation can finally be written as

$$
\begin{aligned}
A\mathcal{E}^{\overline{\overline{\alpha}}} =& \frac{\partial\left(E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right)}{\partial t} \\
&+ \nabla^{\backslash\backslash} \cdot \left[\left(E^{\overline{\overline{\alpha}}} A + \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha A \left[\frac{1}{2}\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right]\right) \mathbf{v}^{\overline{\alpha}} - A\epsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} - A\epsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} \cdot \mathbf{v}^{\overline{\alpha}}\right]
\end{aligned}
$$

$$
\begin{aligned}
&- \sum_{\beta \in \mathcal{I}_{c\alpha}} \left(\left[\frac{E_{\alpha}^{\overline{\overline{\beta}}}}{\rho^{\alpha} \epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2} \mathbf{v}_{\alpha}^{\overline{\beta}} \cdot \mathbf{v}_{\alpha}^{\overline{\beta}} + K_{E\alpha}^{\overline{\overline{\beta}}} + \psi_{\alpha}^{\overline{\beta}} \right] A \overset{\beta \to \alpha}{M} + A \overset{\beta \to \alpha}{\mathbf{T}} \cdot \mathbf{v}_{\alpha}^{\overline{\beta}} + A \overset{\beta \to \alpha}{Q} \right) \\
&- \left(\left[\frac{E_{M}^{\overline{\overline{\alpha}}}}{\rho^{\alpha} \epsilon^{\overline{\overline{\alpha}}}} + \frac{1}{2} \mathbf{v}_{M}^{\overline{\alpha}} \cdot \mathbf{v}_{M}^{\overline{\alpha}} + K_{E_M}^{\overline{\overline{\alpha}}} + \psi_{M}^{\overline{\alpha}} \right] A \overset{\alpha \to}{M}_{M} + A \overset{\alpha \to}{T}_{M} \cdot \mathbf{v}_{M}^{\overline{\alpha}} + A \overset{\alpha \to}{Q}_{M} \right) \\
&- \epsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{\alpha}}} A - \left\langle \rho_{\alpha} \frac{\partial \psi_{\alpha}}{\partial t} \right\rangle_{\Omega_{\alpha}, \Omega} = 0 \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{P}}
\end{aligned}
\tag{4.51}
$$

BIBLIOGRAPHY

[1] L. M. Abriola and K. Rathfelder. Mass balance errors in modeling two-phase immiscible flows: Causes and remedies. *Advances in Water Resources*, 16:223–239, 1993.

[2] P. M. Adler. *Porous Media: Geometry and Transports*. Butterworth-Heinemann, Boston, 1992.

[3] J. Bear. *Dynamics of Fluids in Porous Media*. Elsevier, New York, 1972.

[4] V. Bertola and E. Cafaro. A critical analysis of the minimum entropy production theorem and its application to heat and fluid flow. *International Journal of Heat and Mass Transfer*, 51:1907–1912, 2008.

[5] S. A. Bradford, L. M. Abriola, and F. J. Leij. Wettability effects on two- and three-fluid relative permeabilities. *Journal of Contaminant Hydrology*, 28(1-2):171–191, 1997.

[6] S. A. Bradford and F. J. Leij. Predicting two- and three-fluid capillary pressure saturation relationships of porous media with fractional wettability. *Water Resources Research*, 32(2):251–259, 1996.

[7] R. H. Brooks and A. T. Corey. Properties of porous media affecting fluid flow. *Journal of the Irrigation and Drainage Division, Proceedings of the American Society of Civil Engineers*, IR2:61–88, 1966.

[8] H.-J. Butt, K. Graf, and M. Kappl. *Physics and Chemistry of Interfaces*. Wiley–VCH, 2003.

[9] H. B. Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, New York, 1985.

[10] M. A. Celia and P. Binning. A mass conservative numerical solution for two-phase flow in porous media with application to unsaturated flow. *Water Resources Research*, 28(10):2819–2828, 1992.

[11] M. A. Celia, E. T. Bouloutas, and R. L. Zarba. A general mass-conservative numerical solution for the unsaturated flow equation. *Water Resources Research*, 26(7):1483–1496, 1990.

[12] I. Danielewicz-Ferchmin and A. R. Ferchmin. A check of prigogine's theorem of minimum entropy production in a rod in a nonequilibrium stationary state. *American Journal of Physics*, 68(10):962–965, 2000.

[13] K. G. Denbigh. *The Principles of Chemical Equilibrium*. Cambridge Univer-

sity Press, Cambridge, 1981.

[14] P. Glansdorff and I. Prigogine. *Thermodynamic Theory and Structure, Stability and Fluctuations*. John Wiley & Sons, Inc., New York, 1971.

[15] G. Golub and C. F. van Loan. *Matrix Computations*. The Johns Hopkins University Press, Baltimore and London, 1989.

[16] W. G. Gray, A. Leijnse, R. L. Kolar, and C. A. Blain. *Mathematical Tools for Changing Spatial Scales in the Analysis of Physical Systems*. CRC Press, Boca Raton, 1993.

[17] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 1. motivation and overview. *Advances in Water Resources*, 28(2):161–180, 2005.

[18] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 3. single-fluid-phase flow. *Advances in water resources*, 29(11):1745–1765, 2006.

[19] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 7. single-phase megascale flow models. *Advances in water resources*, 32(8):1121–1142, 2009.

[20] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 8. interface and common curve dynamics. *Advances in water resources*, 33(12):1427–1443, 2010.

[21] W. G. Gray and C. T. Miller. On the algebraic and differential forms of Darcy's equation. *Journal of Porous Media*, 14(1):33–50, 2011.

[22] W. G. Gray and C. T. Miller. TCAT analysis of capillary pressure in non-equilibrium, two-fluid-phase, porous medium systems. *Advances in Water Research*, 34(6):770–778, 2011.

[23] W. G. Gray and C. T. Miller. *Introduction to the Thermodynamically Constrained Averaging Theory for Porous Medium Systems*. Advances in Geophysical and Environmental Mechanics and Mathematics. Springer, 2014 edition, 2014.

[24] A. W. Harbaugh, E. R. Banta, M. C. Hill, and M. G. McDonald.

MODFLOW-2000, the U. S. Geological Survey modular ground-water model: User guide to modularization concepts and the ground-water flow process. Technical Report U.S. Geological Survey Open-File Report 00-92, U.S. Geological Survey, 2000.

[25] R. Haverkamp, M. Vauclin, P. Touma, P. J. Wierenga, and G. Vachaud. A comparison of numerical simulation models for one-dimensional infiltration. *Soil Sci. Soc. Am. J.*, 14:285–294., 1997.

[26] W. G. Hoover. Note on "comment on 'a check of prigogine's theorem of minimum entropy production in a rod in a nonequilibrium stationary state,' by irena danielewicz-ferchmin and a. ryszard ferchmin" [am. j. phys. 68 (10), 962–965 (2000)], by peter palffy-muhoray [am. j. phys. 69 (7), 825–826 (2001)]. *American Journal of Physics*, 70(4):452–454, 2002.

[27] A. B. S. Jackson. *Multiscale Modeling of Multiphase Flow in Porous Medium Systems Using the Thermodynamically Constrained Averaging Theory Approach*. PhD thesis, University of North Carolina at Chapel Hill, Doctoral Dissertation, Chapel Hill, North Carolina, 2011.

[28] A. S. Jackson, C. T. Miller, and W. G. Gray. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 6. two-fluid-phase flow. *Advances in Water Resources*, 32(6):779 – 795, 2009.

[29] E. T. Jaynes. Information theory and statistical mechanics. *Phys. Rev.*, 106:620–630, May 1957.

[30] E. T. Jaynes. Information theory and statistical mechanics. ii. *Phys. Rev.*, 108:171–190, Oct 1957.

[31] E. T. Jaynes. Violation of boltzmann's h theorem in real gases. *Phys. Rev. A*, 4:747–750, Aug 1971.

[32] E. T. Jaynes. The minimum entropy production principle. *Annual Review of Physical Chemistry*, 31(1):579–601, 1980.

[33] R. J. J. Jongschaap and H. C. Öttinger. Nonequilibrium thermodynamics and complex fluids. *Journal of Non-Newtonian Fluid Mechanics*, 96(1-2):1–3, 2001.

[34] M. J. Klein and P. H. E. Meijer. Principle of minimum entropy production. *Phys. Rev.*, 96:250–255, Oct 1954.

[35] Z. Kolenda, J. Donizak, and J. Hubert. On the minimum entropy production

in steady state heat conduction processes. *Energy*, 29(12–15):2441 – 2460, 2004. Efficiency, Costs, Optimization, Simulation and Environmental Impact of Energy Systems.

[36] D. Kondepudi and I. Prigogine. *Modern Thermodynamics*. Wiley, Chichester, 1998.

[37] F. L. Lambert. Disorder - a cracked crutch for supporting entropy discussions. *Journal of Chemical Education*, 79(2):187, 2002.

[38] R. Landauer. Inadequacy of entropy and entropy derivatives in characterizing the steady state. *Physical Review A*, 1975.

[39] R. Landauer. Stability and entropy production in electrical circuits. *Journal of Statistical Physics*, 13(1):1–16, 1975.

[40] C. W. Li. A simplified Newton iteration method with linear finite elements for transient unsaturated flow. *Water Resources Research*, 29(4):965–971, 1993.

[41] J. E. McClure. *Microscale Modeling of Fluid Flow in Porous Medium Systems*. PhD thesis, University of North Carolina at Chapel Hill, Doctoral Dissertation, Chapel Hill, North Carolina, 2011.

[42] C. T. Miller, G. Christakos, P. T. Imhoff, J. F. McBride, J. A. Pedit, and J. A. Trangenstein. Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches. *Advances in Water Resources*, 21(2):77–120, 1998.

[43] C. T. Miller, S. N. Gleyzer, P. T. Imhoff, J. F. McBride, J. A. Pedit, and V. R. Raghu. Multiphase model formulation: Issues and approaches. In *Advanced Simulation of Subsurface Flow and Contaminant Transport*, Research Triangle Park, NC, 1996. Cray Research, Inc. and the North Carolina Supercomputing Center.

[44] C. T. Miller and W. G. Gray. Hydrogeological research: Just getting started. *Ground Water*, 40(3):224–231, 2002.

[45] C. T. Miller and W. G. Gray. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 2. foundation. *Advances in Water Resources*, 28(2):181–202, 2005.

[46] C. T. Miller and P. T. Imhoff. Formulating models for multiphase flow and transport in heterogeneous porous media: Challenges and approaches. *CMR News*, 2(2):1–6, 1996.

[47] P. C. D. Milly. A mass-conservative procedure for time-stepping in models of unsaturated flow. *Advances in Water Resources*, 8(3):32–36, 1985.

[48] J. M. Nordbotten, M. A. Celia, H. K. Dahle, and S. M. Hassanizadeh. Interpretation of macroscale variables in Darcy's law. *Water Resources Research*, 43:10.1029/2006WR005018, 2007.

[49] L. Onsager. Reciprocal relations in irreversible processes: I. *Physical Review*, 37:405–426, 1931.

[50] C. Paniconi, A. A. Aldama, and E. F. Wood. Numerical evaluation of interative and noniterative methods for the solution of the nonlinear Richards equation. *Water Resources Research*, 27(6):1147–1163, 1991.

[51] G. F. Pinder and W. G. Gray. *Essentials of multiphase flow in porous media*. John Wiley & Sons, 2008.

[52] I. Prigogine. *Introduction to Thermodynamics of Irreversible Processes*. Interscience, New York, 1961.

[53] I. Prigogine. Time, structure and fluctuations. In *Nobel Lectures*, volume Chemistry 1971–1980, pages 263–285. World Scientific Publishing, Co., Singapore, 1983.

[54] K. Rathfelder and L. M. Abriola. Mass conservative numerical solutions of the head-based Richards equation. *Water Resources Research*, 30(9):2579–2586, 1994.

[55] P. J. Ross. Efficient numerical methods for infiltration using Richards' equation. *Water Resources Research*, 26(2):279–290, 1990.

[56] E. D. Schneider and D. Sagan. *Into the cool : energy flow, thermodynamics, and life*. University of Chicago Press Chicago, 2005.

[57] J. M. Stankovich and D. A. Lockington. Brooks-Corey and van Genuchten soil retention models. *Journal of Irrigation and Drainage*, 121:1–7, 1995.

[58] M. D. Tocci, C. T. Kelley, and C. T. Miller. Accurate solution of the pressure head for of richards' equation by the method of lines. In *1995 SIAM Annual Meeting*, Charlotte, NC, 1995.

[59] M. D. Tocci, C. T. Kelley, and C. T. Miller. Accurate and economical solution of the pressure-head form of Richards' equation by the method of lines. *Advances in Water Resources*, 20(1):1–14, 1997.

[60] M. T. van Genuchten. A closed-form equation for predicting the hydraulic

conductivity of unsaturated soils. *Soil Science Society of America Journal*, 44:892–898, 1980.

[61] G. A. Williams, C. T. Miller, C. T. Kelley, and M. D. Tocci. Approaches to modeling Richards' equation. *CMR News*, 2(2):18–26, 1996.

[62] R. L. Zarba. A numerical investigation of unsaturated flow. Master's thesis, M.I.T, 1988.