A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Applied Physical Sciences

Chapel Hill
2015

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ABSTRACT

Shaun Morgan Gidcumb: Characterization of Methane Storage in Gas Shales Using NMR
(Under the direction of Yue Wu)

Over the last twenty years technological innovations in the oil industry such as horizontal drilling and hydraulic fracturing have led to the so called 'shale revolution’, where gas shale has become one of the most important unconventional hydrocarbon reservoirs on the planet. Gas shale is a porous sedimentary rock composed primarily of compacted fine-grained clay particles which typically has porosities less than 10%, pore diameters of a few nanometers, and the majority of the porosity is found in the organic matter of the shale. A current topic of debate and focus of research into gas shale reservoirs is how to accurately estimate the gas in-place of gas shale reservoirs, and what role if any does the organic carbon play in the storage potential of the gas shale.

Gas shale samples with high and low organic carbon contents show evidence of absorption in the gas shale’s organic content and cooperative adsorption of methane due to confinement in gas shale nanopores respectively through an in situ proton nuclear magnetic resonance study of high pressure methane sorption isotherms on crushed gas shale samples. Currently, a combination of the estimated free gas and adsorbed gas that is contained in the prospective area is used to calculate the gas in-place, taking into account the formation’s pore size and formation pressure. Cooperative adsorption of methane due to confinement in nanopores provides evidence that there are effective pressures inside the nanopores higher than the pressure typically considered to be that of the shale formation. This mechanism allows for greater than expected densities of methane to be present at lower formation pressures, therefore understanding how this mechanism works in gas shales would allow for better gas in-place estimations, and hopefully increase the amount of natural gas that is
technically recoverable.
To my best friend and wife Emily, for the love and support you’ve shown me.
ACKNOWLEDGEMENTS

Many people have contributed to this dissertation in many different ways. First and foremost I would like to thank my advisor, Dr. Yue Wu. His enthusiasm for scientific research and discovery has been enormously helpful, conversations covering a broad number of topics have been stimulating, and his guidance has kept me on track. I truly appreciate everything I have learned from him, and that he has done for me.

Second, I would like to thank my co-advisor, Dr. Alfred Kleinhammes, who not only provided valuable insight into my research, but more importantly he shared with me his knowledge of experimental science. Without being able to work with Alfred during my graduate research I would not have the confidence and knowledge I do working with hardware, and I am forever grateful to him for this.

Third, I would like to thank Boqin Sun and Li Ling from Chevron Energy Technology Company for many helpful discussions in relation to gas shales and their measurements. I especially would like to thank Boqin Sun for the guidance he gave during my internship with Chevron Energy Technology Company, and with the knowledge he shared of all aspects of NMR.

Finally, I would like to thank the many people over the years who I have met through my research group at UNC who have had played a role in one way or another, some of whom I am bound to forget here. To Horst Kessemeir, I thoroughly enjoyed every single one of your old stories on the history of NMR, and it put a new spin on a field of study that I love. To Pabitra Sen, I appreciated your insight into the business aspects of scientific research that you shared with me, and the encouragement you gave me on my work. To Jacob Forstater, having you in the research group was a blast, and kept me sane. To everyone else from the Wu group, I really enjoyed the time I was able to spend with you, and I thank you for all of
your various contributions you have made to getting me where I am today.
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\( \beta \) flip angle
\( \chi \) magnetic susceptibility
\( \delta \) chemical shift
\( \gamma \) gyromagnetic ratio of the nucleus
\( \hat{n} \) unit vector normal to a surface
\( \hbar \) reduced Planck constant \([1.0546 \times 10^{-34} \text{ (J} \cdot \text{s)}]\)
\( \nu_0 \) prefactor of the desorption rate constant \((\text{s}^{-1})\)
\( \omega_{RF} \) frequency of radio frequency time varying magnetic field
\( \phi \) porosity
\( \rho \) surface relaxivity
\( \sigma \) cross sectional area of a molecule
\( \sigma \) nuclear shielding constant
\( \tau \) delay time after pulse
\( \varnothing \) pore diameter
CPMG Carr-Purcell-Meiboom-Gill
CVX Chevron Energy Technology Company
EPR Electron Paramagnetic Resonance
FID Free Induction Decay
NMR Nuclear Magnetic Resonance
PAS Primary Adsorption Sites
PEEK PolyEtherEther Ketone
ppm part per million \((10^{-6})\)
psi pounds per square inch \([1 \text{ psi} = 6,894.76 \text{ Pascals (Pa)}]\)
RDS Royal Dutch Shell
RD Recycle Delay
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SA</td>
<td>Simulated Annealing</td>
</tr>
<tr>
<td>SVD</td>
<td>Singular Value Decomposition</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>ZTA</td>
<td>Alumina-toughened Zirconia Oxide</td>
</tr>
<tr>
<td>$\vec{\mu}$</td>
<td>nuclear magnetic moment</td>
</tr>
<tr>
<td>$\vec{a}_0$</td>
<td>angular frequency of precession</td>
</tr>
<tr>
<td>$\vec{\tau}$</td>
<td>torque</td>
</tr>
<tr>
<td>$\vec{B}_0$</td>
<td>static magnetic field</td>
</tr>
<tr>
<td>$\vec{I}$</td>
<td>nuclear spin</td>
</tr>
<tr>
<td>$\vec{J}$</td>
<td>angular momentum</td>
</tr>
<tr>
<td>$\vec{M}$</td>
<td>bulk magnetization vector</td>
</tr>
<tr>
<td>$B(T)$</td>
<td>second Virial coefficient</td>
</tr>
<tr>
<td>$C(T)$</td>
<td>third Virial coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)</td>
</tr>
<tr>
<td>$d_i$</td>
<td>inner diameter</td>
</tr>
<tr>
<td>$d_o$</td>
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</tr>
<tr>
<td>$E$</td>
<td>energy</td>
</tr>
<tr>
<td>$E_d$</td>
<td>activation energy of desorption</td>
</tr>
<tr>
<td>$f(T_2)$</td>
<td>$T_2$ distribution</td>
</tr>
<tr>
<td>$f_L$</td>
<td>Larmor frequency of precession</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant $[1.3806 \times 10^{-23} \text{ (kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{K}^1\text{)]}$</td>
</tr>
<tr>
<td>$l_\rho$</td>
<td>relaxation length</td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass ($\text{kg} \cdot \text{mol}^{-1}$)</td>
</tr>
<tr>
<td>$m$</td>
<td>allowed nuclear moment orientations</td>
</tr>
<tr>
<td>$m$</td>
<td>mass</td>
</tr>
<tr>
<td>$M_0$</td>
<td>equilibrium longitudinal magnetization</td>
</tr>
</tbody>
</table>
$N$  number of molecules

$N_i$  number of spins in a state $i$

$N_A$  Avagadro’s number $[6.0221 \times 10^{23} \text{ (mol}^{-1})]$  

$P$  gas pressure  

$T$  temperature  

$T_1$  spin-lattice relaxation time  

$T_2$  spin-spin relaxation time  

$T_2^*$  effective spin-spin relaxation time  

$t_E$  time between $180^\circ$ pulses in CPMG pulse sequence  

$t_{RF}$  duration of the radio frequency pulse  

$V$  volume  

$Z$  gas compressibility factor
CHAPTER 1
INTRODUCTION

The late 18th century saw the rise of the industrial revolution in England, but along with the revolution in manufacturing technology came a revolution in how humans source and use energy. Before the industrial revolution, we mostly relied on the muscle power of humans and animals, or biomass such as wood as the sources for all of our energy needs. During the period of the industrial revolution we transitioned to coal as the main primary energy source, mainly used for powering steam engines.

Since the industrial revolution began, the sourcing of energy has remained one of the biggest concerns for modern, industrialized economies. Over time energy consumption patterns have changed not only with need, but also as new technology and sources of energy are discovered and developed. For example, in the United States coal was the main source of energy in the early part of the 20th century, until it was overtaken by petroleum in the 1950’s.

1.1 America’s Energy Landscape

The current energy landscape of the United States is very diverse coming from many different sources, as can be seen in Figure 1.1, including oil and gas, coal, nuclear, and renewables such as solar and wind. Natural gas is currently the second largest primary energy source in the United States, supplying about 26% of the primary energy, and is expected to grow to to 30% in the next 30 years.
Demand for energy from natural gas over the last fifteen years has been primarily driven by industry and electrical power plants (Figure 1.2a). Growth in the consumption of natural gas used to generate electricity has been very steady, until the late 1990’s when industry’s consumption slowed for a decade. However, in 2009 the trend in industry’s consumption turned around, coinciding with the beginning of the drastic increase in production of natural gas from shale (Figure 1.2b).
Figure 1.2  Historic and projected natural gas consumption and production in the United States. (a) Natural gas consumption by sector given in trillions of cubic feet\(^3\); (b) Natural gas production by source given in trillions of cubic feet\(^4\).
1.2 Natural Gas and the Shale Gas Boom

Despite the growing demand for natural gas, production from conventional sources has been declining over the last fifteen years (Figure 1.2b). To make up the difference, there has been an increase in production from unconventional sources, such as shale gas reservoirs, to meet the increased demand. Unconventional reservoirs differ from conventional reservoirs in that they are characterized by their low permeability, low porosity, and high organic carbon content of the reservoir rock containing the natural gas.

Recent technology development over the last decade has made these unconventional reservoirs economically viable for production. Before the arrival of these new technologies unconventional reservoirs weren’t economically viable for production due to the reservoir rock’s low permeability and porosity. The two major developments making this possible are horizontal drilling and hydraulic fracturing. Figure 1.3 shows a schematic of a horizontally drilled well into a shale formation that has been hydraulically fractured. Horizontal drilling allows access to more surface area of the formation than vertical drilling, which increases the rate at which natural gas will flow into the well. Hydraulically fracturing the shale formation introduces small fractures in the formation. The induced fractures provide a highly permeable path for the gas to travel to the well in the typically low permeable shale, which increases the rate at which gas flows into the well. Both horizontal drilling and hydraulic fracturing have allowed extraction of natural gas from shale to be economically viable.
Horizontal drilling and hydraulic fracturing allow more natural gas to be recovered from shale formations than using traditional drilling techniques. Horizontal drilling allows access to more of the shale formation containing the natural gas than vertical drilling, and hydraulic fracturing creates small fissures in the formation that the natural gas can flow through.

There are several major shale formations in the United States including the Marcellus, Eagle Ford, Haynesville, Woodford, Barnett, and Bakken formations (Figure 1.4). These gas shale formations are projected to produce around 16 trillion cubic feet of natural gas by 2040, supplying approximately 50% of the natural gas produced in the United States at the time. If these projections hold true, it would mean that natural gas produced from shale would be responsible for a significant percentage of the total energy used in the United States, surpassing both nuclear and renewable energy sources.
Figure 1.4  Shale gas plays in the lower 48 states\textsuperscript{8}.  

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{shale_gas_map}
\caption{Shale gas plays in the lower 48 states.}
\end{figure}
1.3 Nuclear Magnetic Resonance in Oil Exploration

After first being observed independently in 1945 by scientists at Stanford\(^9\) and Harvard\(^{10}\), nuclear magnetic resonance (NMR) quickly grew, and found many applications in physics and chemistry. One of the first industries to use NMR was the petroleum industry, with scientists at oil companies such as Chevron, Shell, Mobil, Exxon, and Texaco being early pioneers in the field of NMR\(^{11}\). This early work mainly was investigating the composition of petroleum and petroleum fractions, and later included petrophysical analysis of rock core samples saturated with different types of fluids, such as brine or kerosene.

In 1952 Russel Varian filed a patent for an Earth’s field NMR well logging tool, which was the first hint that NMR might be a useful tool in oil exploration. Well logging is the means by which physical properties of subsurface earth formations are measured \textit{in situ}\(^{12}\). The first commercial NMR logging tool was built by Chevron Research Lab in 1960. During the 1960’s many other oil companies developed their own logging tools such as Pan Geo Atlas and Schlumberger, and many improvements to these tools have been implemented. NMR along with resistivity, induction, acoustic, neutron, and \(\gamma\) ray measurements form the fundamental well logging measurements that are used all over the world for oil exploration\(^{13}\).

1.4 Dissertation Outline

Even though NMR has a long history of use in measuring the petrophysical properties of rocks in both the laboratory and \textit{in situ}, these measurements have mostly been focused on conventional reservoir rocks, such as sandstones and carbonates. With the recent ‘shale revolution’ a current topic of debate and research into gas shale reservoirs is how to accurately estimate the gas in-place of the reservoir\(^{14,15}\). This requires well logging data from test wells along with laboratory measurements of gas shales\(^{15}\). Currently, a combination of the estimated free gas and adsorbed gas that is contained in the prospective area is used to calculate the gas in-place, taking into account the formation’s pore size and formation
pressure. This dissertation establishes a methodology to analyze crushed gas shale samples using NMR to measure their methane storage properties, and to investigate the role of the gas shale’s organic carbon content in its storage potential.

Chapter 2 discusses the basic theory of nuclear magnetic resonance (NMR). Included is a brief discussion of spin-lattice and spin-spin relaxation, along with the experimental techniques used to measure both. Chapter 3 introduces the physical properties of porous media, and NMR relaxation mechanisms in porous media. Chapter 4 introduces the theory behind the inverse Laplace transform. The ill-posed nature of the inverse Laplace transform, commonly used inversion methods found in literature, and a model based inversion method developed to analyze the data in this dissertation will be presented. Chapter 5 describes the experimental setup used to collect the experimental data in this dissertation in detail. Chapter 6 presents the results for experiments conducted to identify the NMR signal for the methane gas in the gas shale’s organic content nanopores. Chapter 7 presents the results for high pressure methane adsorption isotherm measurements made on crushed shale samples. Also presented will be results for experiments performed to determine the relationship between methane storage capacity and the total organic content of gas shales. Chapter 8 will discuss the conclusions reached, and present future work that is possible based on the results from the work in this dissertation.
CHAPTER 2
NUCLEAR MAGNETIC RESONANCE

In 1945 the phenomenon of nuclear magnetic resonance (NMR) was discovered independently by research groups led by Felix Bloch\(^9\) and Edward Purcell\(^10\). The two groups observed that certain nuclei placed in a magnetic field could absorb electromagnetic radiation at a given frequency, and then would later re-emit the electromagnetic radiation at the same frequency. Since the initial discovery of NMR there have been significant advances in the field. The first advance is the discovery of the chemical shift\(^17\), that the chemical environment influences the precession rate of spins in molecules. The second advance was the discovery of the spin echo by Erwin Hahn\(^18\). Other major advancements include the development of Fourier transform NMR by Richard Ernst, Weston Anderson, and Russel Varian\(^19\); and magnetic resonance imaging by Paul Lauterbur and Peter Mansfield\(^20\). These advancements, along with others, have made NMR one of the most powerful tools for investigating materials available today.

For the purposes of this dissertation, it is important to have a basic understanding of the theoretical foundations of NMR, and how NMR can be applied to study porous media. In this chapter the basic theory of NMR will be presented using a classical and quantum mechanical approach. The following chapter will present applications of NMR in the study of porous media. There are many resources\(^21–24\) to consult for a more in depth treatment of the theory and applications of NMR.
2.1 Nuclear Spin and Magnetic Moment

NMR is observed in systems where the nuclei that make up the system have a nuclear magnetic moment $\vec{\mu}$. All nuclei are made up of protons and neutrons, both of which have an intrinsic spin with a magnitude of $\frac{1}{2}$. For NMR to be observed, the nuclei being observed must have unpaired protons or neutrons, which will give them a non-zero nuclear spin and a nuclear moment.

Consider a nucleus that has an angular momentum $\vec{J}$ and nuclear moment $\vec{\mu}$, and is placed in a static magnetic field $\vec{B}_0$. The nuclear moment $\vec{\mu}$ is related to the angular momentum $\vec{J}$ by

$$\vec{\mu} = \gamma \vec{J}$$

(2.1)

where $\gamma$ is the gyromagnetic ratio of the nucleus, and is a unique constant for each specific nucleus. As an example, for a $^1\text{H}$ nuclei $\frac{\gamma}{2\pi} = 42.58 \text{ MHz} \cdot \text{T}^{-1}$.

Table 2.1 Gyromagnetic ratios and other important properties of nuclei commonly used in NMR experiments, and the electron which is used in electron paramagnetic resonance (EPR) experiments$^{24}$.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Spin</th>
<th>Abundance (%)</th>
<th>$\gamma \left(10^6 \text{ rad} \cdot \text{s}^{-1} \cdot \text{T}^{-1}\right)$</th>
<th>$\frac{\gamma}{2\pi} \left(\text{MHz} \cdot \text{T}^{-1}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{H}$</td>
<td>$\frac{1}{2}$</td>
<td>99.9885</td>
<td>267.513</td>
<td>42.576</td>
</tr>
<tr>
<td>$^3\text{He}$</td>
<td>$\frac{1}{2}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>41.065</td>
<td>6.536</td>
</tr>
<tr>
<td>$^7\text{Li}$</td>
<td>$\frac{3}{2}$</td>
<td>92.410</td>
<td>103.962</td>
<td>16.546</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>$\frac{1}{2}$</td>
<td>1.07</td>
<td>67.262</td>
<td>10.705</td>
</tr>
<tr>
<td>$^{19}\text{F}$</td>
<td>$\frac{1}{2}$</td>
<td>100.00</td>
<td>251.662</td>
<td>40.053</td>
</tr>
<tr>
<td>$^{129}\text{Xe}$</td>
<td>$\frac{3}{2}$</td>
<td>21.180</td>
<td>$-73.997$</td>
<td>$-11.777$</td>
</tr>
<tr>
<td>$e^-$</td>
<td>$\frac{1}{2}$</td>
<td>100.00</td>
<td>$-1.76 \times 10^5$</td>
<td>$-2.8 \times 10^4$</td>
</tr>
</tbody>
</table>

The magnetic field will exert a torque $\vec{\tau}$ on the nuclear moment, causing it to precess around the direction of the static magnetic field. The exerted torque is the rate of change of
angular momentum for the nucleus, and is given by

\[ \vec{\tau} = \frac{d\vec{J}}{dt} \]  

(2.2a)

\[ = \vec{\mu} \times \vec{B}_0 \]  

(2.2b)

\[ = \gamma \vec{J} \times \vec{B}_0 \]  

(2.2c)

\[ = \gamma JB_0 \sin \theta \hat{\phi} \]  

(2.2d)

where \( \theta \) is the angle that \( \vec{\mu} \) makes with respect to \( \vec{B}_0 \). We know that \( d\vec{J} \) is

\[ d\vec{J} = J \sin \theta \ d\hat{\phi} \]  

(2.3)

Therefore, the angular frequency of precession \( \vec{\omega}_0 \) is given by

\[ \vec{\omega}_0 = \frac{d\hat{\phi}}{dt} \]  

(2.4a)

\[ = -\frac{d\phi}{d\vec{J}} \cdot \frac{d\vec{J}}{dt} \]  

(2.4b)

\[ = \frac{1}{J \sin \theta} \cdot \gamma JB_0 \sin \theta \hat{\phi} \]  

(2.4c)

\[ = \gamma B_0 \hat{\phi} \]  

(2.4d)

**Figure 2.1** A spin placed in a magnetic field \( B_0 \) will precess around the direction of the static magnetic field at the Larmor frequency.

If we let the Larmor frequency \( f_L = \omega_0 / 2\pi \), then the frequency of precession is

\[ f_L = \frac{\omega_0}{2\pi} \]  

(2.5a)

\[ = \frac{\gamma}{2\pi} B_0 \]  

(2.5b)
2.2 The Zeeman Interaction and Magnetic Resonance

Quantum mechanics requires that the angular momentum, and therefore the orientation of the nuclear moment with respect to the magnetic field, be quantized. The angular momentum \( \vec{J} \) of the nucleus is quantized in units of \( \hbar \) with relation to the nuclear spin \( \vec{I} \) as

\[
\vec{J} = h\vec{I}
\]  
(2.6)

The number of allowed orientations of the nuclear moment is \( 2I + 1 \), and the allowed orientations \( m \) are quantized such that

\[
m = -I, -(I-1), \ldots, 0, (I-1), I
\]  
(2.7)

Classically, in a static magnetic field the nucleus will have an energy \( E \) given by

\[
E = -\vec{\mu} \cdot \vec{B}_0
\]  
(2.8a)
\[
= -\gamma\vec{J} \cdot \vec{B}_0
\]  
(2.8b)
\[
= -\gamma h\vec{I} \cdot \vec{B}_0
\]  
(2.8c)

Assuming the magnetic field is in the \( \hat{z} \)-direction, the energy of the nucleus will be

\[
E = -\gamma hI_zB_0,
\]  
(2.9)
while the energy of the spin states are

\[
E_m = -\gamma h m_I B_0,
\]  
(2.10)

For spin \( \frac{1}{2} \) nuclei, there are two spin states allowed. One of the states is with the spin parallel to the magnetic field, \( m = +\frac{1}{2} \), and is called the spin up state. The other state is anti-parallel to the magnetic field, \( m = -\frac{1}{2} \), and is called the spin down state. The energy difference between the two states \( \Delta E \) using the proton as our nucleus is

\[
\Delta E = \gamma h \left( \frac{1}{2} - -\frac{1}{2} \right) B_0
\]  
(2.11a)
\[
\Delta E = \gamma hB_0
\]  
(2.11b)
A spin can transition into a different energy state by absorbing or emitting a certain amount of energy in the form of a photon. This energy required to cause a transition is quantized, and from Planck’s law is equal to $\hbar \omega$. From the previous section we defined $\omega_0 = \gamma B_0$, therefore

$$\Delta E = \gamma \hbar B_0$$

(2.12a)

$$= \hbar \omega_0$$

(2.12b)

Therefore to cause a transition between energy states the nuclear moment must be exposed to radiation with precisely the Larmor frequency, or else no transition will occur. This is what is meant by the word resonance in nuclear magnetic resonance.

\[\begin{array}{c}
\text{Figure 2.2} \quad \text{Energy level diagram for nuclei with spins } I = \frac{1}{2} \text{ (left) and } I = 1 \text{ (right) before and after a magnetic field of magnitude } B_0 \text{ is turned on. The difference in energy levels is } \Delta E = \gamma \hbar B_0
\end{array}\]

2.3 Chemical Shifts

The NMR frequency of a nucleus in a molecule is determined principally by its gyromagnetic ratio $\gamma$ and the strength of the magnetic field it is in $B_0$ (Equation 2.4). However, not all nuclei in a macroscopic sample experience the same magnetic field, and often experience different local magnetic fields $B_{loc}$. The presence of differing local magnetic fields for different nuclei in macroscopic samples leads to a phenomenon called the chemical shift $\delta$, and is responsible for NMR being one of the most widely used experimental techniques in the world to identify chemical compounds.
2.3.1 Nuclear Shielding

The chemical shift $\delta$ is a measure of the amount of screening the electrons surrounding a nuclei provide from an external magnetic field $B_0$. For this reason the chemical shift is often related to a nuclear screening constant $\sigma$ as

$$\sigma = -\delta \quad (2.13)$$

The motion of the electrons present in the atom or molecule creates a small electrical current, which generates a small magnetic field $B_{\text{ext}}$ in the opposite direction of $B_0$. This additional magnetic field from the electrons shields the nucleus from the external field, and the local magnetic field at the nucleus $B_{\text{loc}}$ can be written as

$$B_{\text{loc}} = B_0 - B_{\text{ext}} = B_0 (1 - \sigma) \quad (2.14)$$

As a result of nuclear shielding, the resonance condition (Equation 2.4) now becomes

$$\omega = \gamma B_0 (1 - \sigma) \quad (2.15)$$

From Equation 2.15 we see that the resonance frequency of a nucleus in an atom is slightly lower than that of just the nucleus. In molecules the induced fields can either be parallel or anti-parallel to the external field, so the induced magnetic field affects the resonance frequency by making it lower or higher depending on the direction of the induced field.

The nuclear shielding constant $\sigma$ is actually a sum of three possible contributing mechanisms: $(\sigma^{\text{dia}})$ diamagnetic contributions from the motion of unperturbed spherical electrons, $(\sigma^{\text{para}})$ paramagnetic contributions from perturbed non-spherical electrons, and other contributions $(\sigma^*)$ caused by magnetic anisotropy of neighboring groups$^{25}$. These three different contributions may add to give very large variations in chemical shifts for different nuclei depending on their chemical environment.

Chemical shifts in NMR experiments are defined as the difference in resonance frequencies between the nucleus of interest $\omega$ and a reference nucleus $\omega_{\text{ref}}$ by means of a
dimensionless parameter $\delta$

$$\delta = 10^6 \frac{\omega - \omega_{ref}}{\omega_{ref}}$$

(2.16)

By dividing $\omega - \omega_{ref}$ by $\omega_{ref}$, $\delta$ becomes a molecular property which is independent of the magnetic field used to measure it. Chemical shifts are reported in parts per million (ppm), so the fraction is multiplied by $10^6$ to give an appropriate scaling. Figure 2.3 shows what effect the chemical shift can have on a peak in an NMR spectra.

![Figure 2.3 Chemical shift effect on NMR spectra peak positions.](image)

2.4 Ensemble Properties

In typical NMR experiments we are not observing a single nuclear spin, but are instead looking at a large number of spins together as an ensemble. If there are $i$ nuclei in the ensemble, each with a nuclear moment $\vec{\mu}_i$, the moments will add up to a magnetization
vector $\vec{M}$ for the ensemble given by

$$\vec{M} = \sum_i \vec{\mu}_i \quad \text{(2.17a)}$$

$$= \gamma \hbar \sum_i m_i \quad \text{(2.17b)}$$

Due to the thermal energy of the environment the spins are in, not all of the spins align parallel to the magnetic field as one might expect. In fact, there might be many different spin states depending on the nuclei being investigated.

![Figure 2.4](image)

**Figure 2.4** The bulk magnetization vector of an ensemble of spins in a magnetic field will point in the direction of the magnetic field.

The difference in the populations of spin states can be found using the Boltzmann probability distribution\(^\text{26}\)

$$\frac{N_i}{N} = \frac{g_i e^{-E_i/k_B T}}{\sum_i g_i e^{-E_i/k_B T}} \quad \text{(2.18)}$$

where $N_i$ is the number of spins in a state $i$ of energy $E_i$ and degeneracy $g_i$, $N$ is the total number of spins in the ensemble, $k_B$ is the Boltzmann constant, and $T$ is the temperature of the system. Assuming the spins are protons, then the population ratio $(N_-/N_+)$ in thermal equilibrium between the states anti-parallel and parallel to the magnetic field is given by

$$\frac{N_-}{N_+} = e^{-\Delta E/k_B T} \quad \text{(2.19a)}$$

$$= e^{-\hbar \omega_0 / k_B T} \quad \text{(2.19b)}$$
If we assume that the magnetic field is in the \( \hat{z} \)-direction with magnitude \( B_0 \), the magnetization will be

\[
M_z = (N_+ - N_-) \mu
\]  

(2.20)

The magnetization per unit volume of \( N \) magnetic moments in thermal equilibrium can be found to be

\[
M_0 = N \mu \tanh \left( \frac{\mu B_0}{k_B T} \right) \approx N \mu^2 B_0 \frac{k_B T}{k_B T}
\]  

(2.21)

where \( N = N_+ + N_- \).

This magnetization does not appear the instant the sample is placed in the magnetic field. It takes a finite amount of time for the magnetization to build up to its equilibrium value along the direction of the magnetic field. If an unmagnetized sample is placed in a magnetic field so that at \( t = 0 \), \( M_z = 0 \), then the magnetization at a later time \( M_z(t) \) can be found using the equation

\[
M_z(t) = M_0 \left( 1 - e^{-t/T_1} \right)
\]  

(2.22)

During the magnetization process energy must flow from the nuclei to the surroundings, since the magnetic energy from the spins is reduced. The surroundings which absorb this energy is referred to as the "lattice," even in the case where the sample is a liquid or a gas. Therefore the time that this energy flow occurs \( T_1 \) is referred to as the spin-lattice relaxation time, and is a characteristic of a particular sample.
2.5 **Manipulation of the Bulk Magnetization**

In thermal equilibrium an ensemble of spins placed in a static magnetic field will have a bulk magnetization, and like the single magnetic moment mentioned in section 2.1, the bulk magnetization will experience a torque from the static magnetic field

\[
\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}
\]  (2.23)

Assuming that the magnetic field lies in the \(\hat{z}\)-direction, the bulk magnetization precess around the \(\hat{z}\)-axis as

\[
\vec{M}(t) = M_0 \begin{pmatrix} \sin \omega_0 t \\ \cos \omega_0 t \\ 1 \end{pmatrix}
\]  (2.24)

To perform an NMR measurement, the magnetization of the ensemble of spins must be perturbed the out of equilibrium by irradiating the spins with photons of the same energy.
as the energy separation between the two states. The frequency of the photons for typical NMR experiments lies in the RF spectrum from a few kHz to hundreds of MHz.

Suppose we apply not only a constant magnetic field $B_0\hat{z}$, but we also apply an RF field which will create a time varying magnetic field of frequency $\omega_{RF}$ in the $x-y$ plane so that the total magnetic field can be written as

$$\vec{B}(t) = \vec{B}_0 + \vec{B}_{RF}(t)$$

(2.25)

The time varying field $\vec{B}_{RF}(t)$ is linearly polarized in the direction transverse to the static magnetic field. This can be described by two circularly polarized magnetic fields which are rotating in opposite directions. The component which rotates in the opposite direction as the spins precess does not effect the spins’ precession as long as $B_{RF} \ll B_0$, while the component which rotates in the same direction as the spins precess does effect the precession of the spins. The time varying field $\vec{B}_{RF}(t)$ can therefore be described by

$$\vec{B}_{RF}(t) = B_{RF} \begin{pmatrix} \cos(\omega_{RF} t + \varphi) \\ -\sin(\omega_{RF} t + \varphi) \\ 0 \end{pmatrix}$$

(2.26)

where $B_{RF}$ is the strength of the RF magnetic field, $\omega_{RF}$ is the frequency, and $\varphi$ is the phase offset of the field.

The magnetization vector as a function of time can most easily be solved when considering a coordinate frame rotating with $\omega_{RF}$ about $\vec{B}_{RF}$. For resonance to occur in the rotating frame to cause the spins to be perturbed we must have $\omega = \omega_0 = \gamma B_0$. Under these conditions Bloch solved Equation 2.23 to obtain

$$\frac{d\vec{M}}{dt} = \gamma \begin{pmatrix} M_y B_0 + M_z B_1 \sin(\omega_0 t) \\ M_z B_1 \cos(\omega_0 t) - M_x B_0 \\ -M_x B_1 \sin(\omega_0 t) - M_y B_1 \cos(\omega_0 t) \end{pmatrix}$$

(2.27)
The solution to these equations, using the initial condition $\vec{M}(t = 0) = M_0 \hat{z}$ is

$$
\vec{M}(t) = M_0 \begin{pmatrix}
\sin(\omega_1 t) \sin(\omega_0 t) \\
\sin(\omega_1 t) \cos(\omega_0 t) \\
\cos(\omega_1 t)
\end{pmatrix}
$$

(2.28)

where $\omega_1 = \gamma B_1$. This result shows that while the RF field is on the magnetization will precess around the static magnetic field, and the RF field simultaneously. In the rotating reference frame it appears as if the magnetization is only precessing about the RF field direction.

If the applied RF field is pulsed, in the rotating frame the magnetization will rotate by an angle $\beta$, called the flip angle, which is given by

$$
\beta = 2\pi f_{RF} t_{RF}
$$

(2.29)

where $t_{RF}$ is the duration of the RF pulse.

2.6 Relaxation

During the application of the RF pulse energy is introduced into the spin system. Once the applied RF field is turned off, the magnetization will not stay in the perturbed state forever. Given enough time the magnetization will return to thermal equilibrium through a process called relaxation. There are two types of relaxation that bring the the system back to equilibrium after an applied RF pulse, spin-lattice relaxation and spin-spin relaxation.

2.6.1 Spin-Lattice Relaxation

Spin-lattice relaxation, also known as longitudinal or $T_1$ relaxation, is the process responsible for the recovery of the longitudinal equilibrium magnetization $M_0$. The spin-lattice relaxation process involves an exchange of energy between the spin system and the surrounding thermal reservoir, refereed to as the lattice, with which it is in thermal equilibrium. This process can be described by the equation

$$
\frac{dM_\parallel}{dt} = -\frac{(M_\parallel - M_0)}{T_1}
$$

(2.30)
which has a solution

\[ M_{\parallel}(t) = M_{\parallel}(0) e^{-t/T_1} + M_0 \left( 1 - e^{-t/T_1} \right) \]  \hspace{1cm} (2.31)

where \( M_{\parallel}(t) \) is the longitudinal component of the magnetization as a function of time, \( M_{\parallel}(0) \) is the longitudinal component of the magnetization immediately after the RF pulse is turned off, \( M_0 \) is the equilibrium longitudinal magnetization, and \( T_1 \) is the spin-lattice or longitudinal relaxation time, and gives a measure of how quickly the system returns to \( \frac{1}{e} \) of its original magnetization. A small value of \( T_1 \) indicates a strong coupling between the transfer of energy from the spins to the lattice, and short times necessary to return to equilibrium. A large value of \( T_1 \) indicates a weak coupling between the transfer of energy from the spins to the lattice, and long times necessary to return to equilibrium.

**2.6.2 Spin-Spin Relaxation**

Spin-spin relaxation, also known as transverse or \( T_2 \) relaxation, is the process responsible for the recovery of the transverse magnetization back to its equilibrium value of zero. The spin-spin relaxation process involves the loss of phase coherence between the individual spins as they precess in the transverse plane. This process can be described by the equation

\[ \frac{dM_{\perp}}{dt} = -\frac{M_{\perp}}{T_2} \]  \hspace{1cm} (2.32)

which has a solution

\[ M_{\perp}(t) = M_{\perp}(0) e^{-t/T_2} \]  \hspace{1cm} (2.33)

where \( M_{\perp}(t) \) is the transverse component of the magnetization as a function of time, \( M_{\perp}(0) \) is the transverse component of the magnetization immediately after the RF pulse is turned off, and \( T_2 \) is the spin-spin or transverse relaxation time and gives a measure of how quickly the system returns to \( \frac{1}{e} \) of \( M_{\perp}(0) \).

Instead of there being a single component responsible for \( T_2 \) relaxation, there are many components which combine to make an effective \( T_2 \) relaxation time referred to as \( T_2^* \). The components responsible for the effective \( T_2 \) relaxation time include dipolar...
interactions which cause the true $T_2$ relaxation, and various time independent magnetic field inhomogeneities. The relaxation rates from these two components add together such that the effective relaxation rate is

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{\text{inhomo}}}$$

(2.34)

Figure 2.6  Spin decoherence caused by $T_2^*$ relaxation

2.6.3  Evolution of the Magnetization with Relaxation

Knowing the effects that relaxation has on both the longitudinal and transverse magnetization after a pulse is applied, the evolution in time of the magnetization can be written as

$$\vec{M}(t) = M_0 \begin{pmatrix} \cos(\omega t) e^{-t/T_2} \\ \sin(\omega t) e^{-t/T_2} \\ 1 - e^{-t/T_1} \end{pmatrix}$$

(2.35)
2.7 NMR Pulse Sequences

NMR pulse sequences are the combination of RF pulses, delays, and magnetic field gradients that make up an NMR experiment. The simplest NMR pulse sequence consists of a single RF pulse, while more complex sequences may involve thousands of pulses. The different NMR experiments make use of the fact that the magnetization is effected by different type of physical phenomena. The pulse sequence is said to be 'encoded' for the physical effect being observed such as relaxation or diffusion.

2.7.1 Free Induction Decay

As mentioned earlier, the simplest NMR experiment involves a single RF pulse. The RF pulse rotates into the transverse plane. Typically, the length of the RF pulse is chosen so that it rotates the magnetization 90° from the longitudinal direction. This is done because it gives the largest signal intensity after the RF pulse, but other pulse lengths will still produce a signal. After the RF pulse rotates the magnetization vector into the transverse plane it

![Figure 2.7](image_url)
evolves as

$$\vec{M}(t) = M_0 e^{-t/T_2} \begin{pmatrix} \cos(\omega t) \\ \sin(\omega t) \end{pmatrix}$$ (2.36)

The magnetization vector will precess around $B_0$, and the spin coherence will dephase at a rate of $T_2$ if field inhomogeneities are not considered. The precession of the spins induces a voltage in the RF coil, with the voltage decreasing as the spins dephase. This detected signal is referred to as the free induction decay (FID). The NMR signal is usually detected in quadrature so that both the real and imaginary components of the signal are detected. Usually, a Fourier transform is taken of the FID signal, which gives the chemical shift spectrum.

The intensity of the FID as a function of pulse angle and recycle delay time is

$$M_{\perp}(\theta, RD) = M_0 \sin \theta \frac{1 - e^{-RD/T_1}}{1 - \cos \theta e^{-RD/T_1}}$$ (2.37)

where $M_{\perp}(\theta, RD)$ is the measured NMR signal and $RD$ is the recycle delay.
Figure 2.8 The FID pulse sequence: (a) After a 90° pulse the NMR signal decays as a damped oscillator. This signal is called the Free Induction Decay (FID); (b) Initially the system is in equilibrium, and the magnetization vector is pointing in the direction of the static magnetic field $\hat{z}$; (c) After a 90° pulse in the $B_1$ direction the magnetization vector will be in the $x-y$ plane aligned on the $\hat{y}$ axis; (d) Once the pulse is turned off the spins will precess around $B_1$ at different rates and directions, leading to a loss of phase coherence.

2.7.2 Spin Echo

One of the most important developments in NMR was the discovery of the spin echo, which is often called the Hahn echo. This development is so important because it allows the magnetization that has been lost through dephasing to be regained. The spin echo pulse sequence refocuses inhomogeneities of the magnetic that are time independent such as heteronuclear couplings, chemical shift, or magnetic susceptibility changes. The spin echo will not refocus the loss of spin coherence brought about from entropy.

The spin echo experiment starts with a 90° pulse which rotates the magnetization into the $x-y$ plane, and the spins will begin to dephase due to inhomogeneities in the magnetic
A $180^\circ$ pulse applied at time $\tau$ will invert the phase of each spin such that the spins will refocus and produce a signal which reaches a maximum intensity at time $2\tau$. This signal is the spin echo, and the intensity of the echo is given by

$$M(2\tau) = M_0 e^{-2\tau/T_2}$$

(2.38)

where $M_0$ is the starting intensity of the FID.

Figure 2.9  Hahn Echo pulse sequence along with the evolution of the magnetization vector. The $180^\circ$ pulse will cause a refocusing of the signal at time $t = 2\tau$. 
2.7.3 \textit{CPMG}

The Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence builds on the idea of the spin echo pulse sequence. In the spin echo pulse experiment, after the spins are refocused, they begin to dephase again. The magnetization can be refocused using another 180$^\circ$ pulse as long as the measurement time $t$ satisfies $T < T_2$. Carr and Purcell$^{29}$ showed that a chain of 180$^\circ$ pulses continue refocusing the magnetization vector. Meiboom and Gill$^{30}$ presented a modification to Carr and Purcell’s pulse sequence, which compensated for small errors in the 180$^\circ$ pulse length that caused less magnetization to be returned into the transverse plane with each pulse by choosing appropriate phasing of the RF pulses. This modified sequence is referred to as the CPMG pulse sequence.

The long series of echos is referred to as an echo train, and the intensity for the $N^{th}$ echo in the train is given by

$$M_\perp(t) = M_0 e^{-ntE/T_2} \quad (2.39)$$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cpmg_sequence.png}
\caption{The CPMG pulse sequence showing multiple spin echoes at times $t = nt_E$ modulated by a $T_2$ relaxation envelope.}
\end{figure}
2.7.4 Relaxation Time Measurements

2.7.4.1 Longitudinal Relaxation Time

The most common way to measure the longitudinal relaxation time, $T_1$, is using the inversion recovery pulse sequence. The inversion recovery pulse sequence begins with a $180^\circ$ pulse which rotates the magnetization so that it lies along the negative $\hat{z}$ direction. The magnetization is then allowed to relax for a time $\tau$ at which point a $90^\circ$ pulse rotates the magnetization into the transverse plane. The $90^\circ$ pulse has the effect of rotating the longitudinal component of the magnetization after time $\tau$ into the transverse plane where it can be detected. Due to the fact that the magnetization was initially rotated along the $-\hat{z}$ axis, there will be an inversion of the signal from negative to positive as $\tau$ is increased. The intensity of the magnetization as a function of time is given by

$$M_{\perp}(\tau) = M_0 \left(1 - 2e^{-\tau/T_1}\right)$$  \hfill (2.40)

The inversion recovery is performed using a range of $\tau$ values, and the $T_1$ relaxation curve is the intensity of the acquired signal plotted as a function of $\tau$. The time at which the magnetization crosses from negative to positive occurs at $\tau = 0.69T_1$. In many systems there are more than one value of $T_1$ for different components of the system. In these systems the distribution of $T_1$ times can be found by performing an inverse Laplace transform on the relaxation curve.
Figure 2.11  Inversion recovery pulse sequence used to measure $T_1$ relaxation times.
2.7.4.2 Transverse Relaxation

There are two ways to measure the transverse relaxation. The first method is to perform several spin echo experiments, changing the echo time $\tau$ for each experiment. The maximum amplitude of the echo is measured as a function of echo time. The second method uses the CPMG pulse sequence with a fixed echo spacing, and there are enough refocusing $180^\circ$ pulses so that the magnetization at the end of the echo train is zero.

Both of these methods of measuring the transverse relaxation have their advantages and disadvantages. Using the variable spin echo experiments to make the measurement takes longer to run the experiment, but is much easier on the electronics. Using the CPMG pulse sequence accounts for the inhomogeneities in the magnetic field, and the measurement can be done in a single experiment so it takes much less time than the variable spin echo method. However, the long train of refocusing pulses can heat the sample, and can possibly exceed the duty cycle (% of time on in a given amount of time) of the RF power amplifiers used.
Figure 2.13  Transverse relaxation measurement by changing $\tau$
Porous media are common materials that are found throughout many different aspect of our lives. Examples of porous materials we see and use everyday include textiles, wood, bricks, and concrete. Porous materials even play important roles inside the human body such as in our lungs and bones. To be considered porous, a material must either have voids in the solid material, be permeable to a variety of fluids, or have voids and be permeable. The voids in porous materials, also called pores, are usually filled with a liquid, gas, or a mixture of liquids and gases. How the liquid and gases behave inside Materials that have voids and are also permeable are referred to as permeable porous materials.

3.1 Characteristics of Porous Media

There are several measurable features which can be used to characterize a porous material such as pore size (Table 3.1), pore shape (Figure 3.1), porosity, and permeability. These features strongly impact how fluids and gases behave inside the material.

3.1.1 Pore Size and Shape

An important classification of pores is according to the ability of external liquids or gases to enter the pore. We can see the two different categories of pores in Figure 3.1. The fist category are pores which are isolated from neighboring pores, and are considered closed. The second category are pores which have a path to the outside surface of the body the pore is located in, and are considered open. There are different methods of classifying open pores. One method is whether the pore is open on only one end, which are described as blind pores. Pores can also be classified by their shape. They can be cylindrical, spherical, or slit pores.
Figure 3.1 Classification of pore types\textsuperscript{32}. a) closed pore b) ink bottle c) open cylindrical d) slit pore e) pore channel f) blind cylindrical pore g) surface irregularity

Table 3.1 Classification of pores based on length scale\textsuperscript{32}.

<table>
<thead>
<tr>
<th>Pore Classification</th>
<th>$\Theta$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>micropore</td>
<td>$\Theta &lt; 2$</td>
</tr>
<tr>
<td>mesopore</td>
<td>$2 &lt; \Theta &lt; 50$</td>
</tr>
<tr>
<td>macropore</td>
<td>$\Theta &gt; 50$</td>
</tr>
</tbody>
</table>
Figure 3.2  SEM images of gas shale sample at different length scales showing the nanoscale features.
3.1.2 Porosity

The porosity of a porous material is the fraction of the bulk volume of the material that is not occupied by the solid framework of the material. The porosity $\phi$ can be expressed as

$$\phi = \frac{V_{\text{pore}}}{V_{\text{bulk}}}$$  \hspace{1cm} (3.1)

Many natural porous materials, such as sedimentary rocks, are made up by the packing of smaller grains in some arrangement. The porosity of these types of materials is independent of the grain size, or sphere diameter. The method of packing, such as cubic or rhombohedral packing of spheres, will effect the porosity. The uniformity of grain size will also effect the porosity. If smaller particles are mixed with larger grains, the porosity will be reduced. Finally, the amount of compaction applied to the material will effect the porosity. Compaction tends to close voids, and bring the particles closer together.

![Figure 3.3](image)

(a) Cubic and (b) rhombohedral packing of spherical grains, and (c) cubic packing using different sized spherical grains

There are actually two types of porosity used to characterize a material. The first is the total porosity, described earlier from the total void space in the material. The other porosity is the effective porosity, which is the ratio of the pore volume accessible from the surface to the total pore volume. The effective porosity is always less than or equal to the total porosity, but is usually less than the total porosity.
3.2 NMR Relaxation Mechanisms in Porous Media

The relaxation process in porous media is controlled by a number of different mechanisms. The three main relaxation mechanisms are the bulk relaxation, relaxation due to interactions of spins with the pore’s surface, and spins diffusing in a magnetic field gradient. All three of these mechanisms contribute to the total relaxation rate of spins in the pore.

3.2.1 Bulk Relaxation

The mechanisms for bulk relaxation were discussed earlier in Chapter 2. In most cases, the bulk relaxation rate can be ignored due to the fact that it is much slower than the rates from the other mechanisms.

3.2.2 Surface Relaxation

NMR relaxation of fluids at the surface of a pore wall was first studied by Korringa, Seevers, and Torrey\textsuperscript{34}. The group identified two mechanisms responsible for surface relaxation on the surface of a pore. The first mechanism occurs at all sites on the surface, and the other is associated with a small amount of magnetic impurities on the pore surface.
The mechanism associated with the presence of magnetic impurities, such as iron, nickel, and chromium is much stronger than the other mechanism. This means that the relaxation time of fluids in a pore will be related to the amount of paramagnetic impurities on the pore wall.

While looking at the relaxation of water in biological cells, Brownstein and Tarr\textsuperscript{35} showed that multiexponential decay is a result of both surface relaxation and diffusion of spins. They concluded that the two properties that effect the relaxation are paramagnetic impurities at the pore wall, and diffusion of spins in the pore volume. Using these two properties they found the equation for diffusion of spins in the volume of the pore can be written as

\[ D \nabla^2 m(r,t) - \frac{m(r,t)}{T_B} = \frac{\partial m(r,t)}{\partial t} \]  

(3.2)

while at the pore surface the equation for diffusion of spins is

\[ \hat{n} \cdot D \nabla m(r,t) + \rho m(r,t)|_S = 0 \]  

(3.3)

where \( m(r,t) \) is the unrelaxed spin density, \( \frac{1}{T_B} \) is the bulk relaxation rate, \( \rho \) is the relaxation rate at the solid/fluid interface (surface relaxivity), \( D \) is the diffusion coefficient of the spins in the fluid, and \( \hat{n} \) is the unit vector that is normal to the pore surface. They also showed that the magnetization

\[ M(t) = \int m(r,t)d^3r \]  

(3.4)

is given by a sum of exponential functions of time

\[ M(t) = M(0) \sum_{n=0}^{\infty} f_n e^{-t/T_n} \]  

(3.5)

where \( f_n \) are the relative amplitudes for each exponential decay, and \( \frac{1}{T_n} \) are the relaxation rates for each exponential decay. The relaxation rates, \( \frac{1}{T_n} \), are primarily determined by the geometry of the pore space, but depend strongly on the surface relaxivity \( \rho \), and the diffusion constant of the fluid \( D \).

The pore scale is given as \( l_S \), and is a reflection of the pore size. The relaxation length is

\[ l_\rho = \frac{D}{\rho} \]  

(3.6)
where $D$ is the diffusion coefficient of the fluid, and $\rho$ is the surface relaxivity. The relaxation length gives the distance a spin will diffuse before undergoing relaxation. Brownstein and Tarr related $l_S$ and $l_\rho$ to define three different diffusion regimes as shown in Table 3.3.

**Table 3.3** Diffusion regimes for NMR relaxation in pores.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Length Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast</td>
<td>$l_S \ll l_\rho$</td>
</tr>
<tr>
<td>intermediate</td>
<td>$l_\rho \ll l_S \ll 10l_\rho$</td>
</tr>
<tr>
<td>slow</td>
<td>$10l_\rho \ll l_S$</td>
</tr>
</tbody>
</table>

In the fast diffusion regime all the spins have an opportunity to contact the surface before relaxing, which would produce a mono-exponential decay rate for the spins in the pore. In the slow diffusion regime, the diffusion of the spins to the surface is not fast enough to allow all the spins to contact the surface before relaxing. The relaxation in this case gives a multiexponential decay.

In the fast diffusion limit Brownstein and Tarr found that the relaxation rate is given by

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1B,2B}} + \rho_{1,2} \frac{S}{V}$$  \hspace{1cm} (3.7)

where $\rho_1$ and $\rho_2$ are the surface relaxivities for $T_1$ and $T_2$ respectively, $S$ is the surface area of the pore, and $V$ is the volume of the pore. Pores with smaller diameters have larger values of $\frac{S}{V}$ than pores with longer diameters, therefore smaller pores will have a shorter relaxation time than larger pores.

**Figure 3.5** Relaxation of spins in a pore. Spins on the surface will have a faster relaxation rate than spins in the middle of the pore.
3.2.3 Diffusion in a Magnetic Field Gradient

During the NMR experiment, nuclear spins in a liquid or gas can move away from their initial position by diffusive motion of the atoms. If there is a magnetic field gradient present, this diffusive motion will cause $T_2$ dephasing, and can be expressed as an additional effective relaxation rate $\frac{1}{T_{2D}}$ as

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2D}},$$

(3.8)

where

$$\frac{1}{T_{2D}} = \frac{D(\gamma G t_E)^2}{12},$$

(3.9)

and $\gamma$ is the gyromagnetic ratio, $G$ the magnetic field gradient, $t_E$ the time between echoes, $D$ the self diffusion coefficient of the fluid or gas, and $T_{2B}$ the bulk relaxation time\(^{22}\). Since diffusion causes dephasing of spins, it only has an effect on $T_2$. Diffusion of spins in a magnetic field gradient does not affect $T_1$.

3.2.3.1 Internal Magnetic Field Gradients

The internal magnetic field gradient is proportional to the applied external magnetic field $B_0$, and is given by

$$g \propto \Delta \chi B_0$$

(3.10)

where $g$ is the magnetic field gradient and $\Delta \chi$ is the magnetic susceptibility difference between the pore surface and the fluid or gas inside the pore.

To look at the effect internal field gradients have on the spins, we consider the most simple case of a spherical pore of radius $R$ filled with a medium of magnetic susceptibility $\chi$ inside a spherical grain of susceptibility $\chi_g$\(^{36}\). Inside an external uniform magnetic field $B_0$ the magnetic dipole moment $\mathbf{m}$ of the pore is

$$\mathbf{m} = \frac{\mu_g - \mu}{\mu_m + 2\mu} R^3 \mathbf{B}_0$$

(3.11)

where $\mu_g = 1 + 4\pi \chi_g$ and $\mu = 1 + 4\pi \chi$ are the magnetic permeability of the grain and the medium. Assuming that all of the susceptibilities are isotropic, where all the susceptibilities
lie along the same direction, \( \mathbf{m} \) is

\[
\mathbf{m} \approx \frac{4}{3} \pi R^3 \Delta \chi \mathbf{B}_0
\]  

where

\[
\Delta \chi \equiv \chi_g - \chi = \frac{\mu_g - \mu}{4\pi}
\]  

(3.13)

The magnetic field at a distance \( r \) from \( \mathbf{m} \) is

\[
\mathbf{B}(r) = \mathbf{B}_0 + \Delta \mathbf{B}(r)
\]  

(3.14)

where

\[
\Delta \mathbf{B}(r) = \frac{3(\mathbf{m} \cdot \mathbf{r}) \mathbf{r} - |\mathbf{r}|^2 \mathbf{m}}{|\mathbf{r}|^5}
\]  

(3.15)

The magnetic field outside the pore will be nonuniform. If the pore has a spherical or ellipsoidal shape the magnetic field is uniform inside the pore, and is given by

\[
\mathbf{B} = \mathbf{B}_0 + \frac{8\pi}{3} \mathbf{M}
\]

(3.16a)

\[
= \left(1 + \frac{8\pi}{3} \chi\right) \mathbf{B}_0
\]

(3.16b)

For a non ellipsoidal shape of the grain the field may be nonuniform. In the case where grains are packed closely together, the nearby grains will contribute to the magnetic field inside the pore making it nonuniform. Solving for the spatial dependence for even simple geometries is very difficult\textsuperscript{37}, and impossible for real porous materials which have irregular pore geometries.

### 3.2.3.2 Internal Field Gradients and the Chemical Shift

In porous media internal magnetic field gradients can have a significant effect on the chemical shift of gases and liquids inside of the pores. As previously mentioned though, if the pores are spherical or ellipsoidal, not densely packed, and located within a material of constant magnetic susceptibility there will be a constant magnetic field inside the pore space. In this case there will be an overall chemical shift for all of the gases or liquids inside the pore space, but the chemical shift will be the same for all of the pores.
CHAPTER 4
INVERSE PROBLEMS

4.1 Introduction

Integral transforms are very useful tools for solving linear dynamic systems described by first order differential equations. Integral transforms have a relation of the form

\[ F(s) = \int_{\alpha}^{\beta} K(s, t)f(t) \, dt \] (4.1)

where a given function \( f \) is transformed into another function \( F \) by means of an integral. \( F \) is referred to as the transform of \( f \), and \( K \) is the kernel of the transformation. By choosing the appropriate kernel \( K \) and integration limits \( \alpha \) and \( \beta \) it can be possible to greatly simplify a problem involving a linear differential equation. In mathematics, much of Fredholm theory concerns itself with finding solutions to integral equations of the form of Equation 4.1. In many problems in science and engineering involving Fredholm integrals, \( K \) and \( F \) are the known functions, while \( f \) is the unknown that is being solved for. These type of problems are referred to as inverse problems, as opposed to forward problems which are of the type where \( K \) and \( f \) are the known functions, while \( F \) is the unknown that is being solved for.

In this chapter inverse problems will be introduced through several examples found in science in engineering, and presenting the inverse problem found in NMR relaxation data. The ill-posed nature of inverse problems, the problems this causes to their solutions, and solutions, along with methods to deal with their problems, will be presented. Finally, a discussion on algorithms specifically written to solve the inverse problem of NMR relaxation data will be presented.
4.2 Examples of Inverse Problems

The first example is from the field of image processing where an ideal image passes through some type of non-ideal optics or medium before being captured, which can lead to blurring and other distortions in the captured image. The problem of the blurring of the captured image $i_c(x,y)$ is typically modeled as a convolution of the original image $i_o(x,y)$ with a point spread function $h(x,\alpha,\beta)$. In the presence of no additional noise we can write this as:

$$i_c(x,y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} i_o(\alpha,\beta) h(x-\alpha,y-\beta) \, d\alpha \, d\beta \quad (4.2)$$

By carefully characterizing the optical elements in the system $h(x,\alpha,\beta)$ can be determined, but even then a reconstruction of the image $i_o(x,y)$ is not straightforward through a deconvolution of Equation 4.2.

The second example can be found in many different types of medical imaging such as X-ray computed tomography (CT), single photon emission tomography (SPECT), and positron emission tomography (PET). However, for the purposes of this example we will focus on CT imaging. In CT imaging X-rays are passed through an object at various angles, and the X-ray intensity is measured at each angle, giving a sinogram. The sinogram, also known as the Radon transform of the image, is given by:

$$\mathcal{R}\{f(x,y)\} \equiv g(\theta,\rho) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) \delta(x \cos \theta + y \sin \theta - \rho) \, dx \, dy \quad (4.3)$$

where $g(\theta,\rho)$ is the projection function. The sinogram contains all of the data, along with information about the X-ray beams used to create the sinogram, necessary to form the reconstructed image $f(x,y)$.

There are many other examples that could be discussed here, such as antenna design and geoseismology, but we will move on to discuss inverse problems from NMR relaxation data.
4.3 Inverse Problems in NMR Relaxation Data

From the discussion of NMR relaxation in porous media in Chapter 3 it was shown that the magnetization as a function of time can be written as

\[ m(t) = \frac{M(t)}{M(0)} = \int_0^\infty f(\tau) e^{-\frac{t}{\tau}} \, d\tau \] (4.4)

In this inverse problem we are interested in finding the distribution of relaxation times \( f(\tau) \) by measuring the magnetization as a function of time. Equation 4.4 has the form of the Laplace transform equation.

The Laplace transform is an integral transform for a piecewise continuous \( f(t) \) that is given for \( t \geq 0 \), and uses the kernel \( K(s,t) = e^{-st} \). The Laplace transform is denoted by \( \mathcal{L}\{f(t)\} \) or \( F(s) \), and is defined by the equation

\[ \mathcal{L}\{f(t)\} = F(s) = \int_0^\infty e^{-st} f(t) \, dt \] (4.5)

The form of the inverse Laplace transform integral is very similar to that of the Fourier transform\(^{45}\) as shown below, however there are major differences between the two.

\[ \hat{f}(\omega) = \int_{-\infty}^{\infty} f(x) e^{-i\omega x} \, dx \] (4.6)

The Fourier transform can be used to find frequencies present in an oscillating signal, while the inverse Laplace transform can be used to find the characteristic times of an exponential decaying signal. The most notable difference between the two transforms is that the Fourier transform is well defined and stable, and there is only one possible inverse solution. On the other hand, the inverse Laplace transform is ill-posed, and for a given exponential decay there are many possible combinations of characteristic times which will fit the solution equally well.

4.4 Ill-posed Problems

We have said that the inverse Laplace transform is ill-posed, but what exactly do we mean by being ill-posed? Hadamard proposed three properties that a problem must possess in order to be considered well-posed\(^{46}\):

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1. For all admissible data, a solution exists.

2. For all admissible data, the solution is unique.

3. The solution depends continuously on the data

The first two properties above are fairly straightforward. The third property relates to the stability of the solution with respect to the data. In other words, it requires that small changes in the data should not produce large changes to the solution. If a problem lacks any of the properties above it is by definition considered ill-posed.

In solving ill-posed problems, it is this fact that very small changes in the data produce very large changes in the solution that makes them so hard to solve. This difficulty is connected to the compactness of the kernel operator, $K$. Using Equation 4.4 as an example, the integration of $f(\tau)$ with $K(t, \tau)$ has a dampening effect on $f(\tau)$ in the sense that high frequency components in $f(\tau)$ are dampened out by the integration. This makes $m(t)$ a ‘smoother’ function than $f(\tau)$. On the other hand, taking the inverse of Equation 4.4 to find $f(\tau)$ knowing $m(t)$ and $K(t, \tau)$ will amplify any high frequency components in $m(t)$.

This behavior of ill-posed inverse problems leads to an obvious question as to the stability of any solution reached. Several regularization methods have been developed to help deal with the issue raised above.

4.5 Regularization

Regularization is the process to stabilize the inversion so that it forces a unique solution, and makes it less sensitive to noise. The process of regularization also smooths the solution returned. One of the simplest methods of regularization is the truncated singular value decomposition (SVD) method, and one of the more popular regularization methods is Tikhonov regularization.
4.5.1 Singular Value Decomposition

The singular value decomposition is a matrix decomposition method used for factorization of a real or complex rectangular matrix. Any rectangular matrix \( A \in \mathbb{R}^{m \times n} \) with \( m \geq n \) can be factored into

\[
A = U \Sigma V^T
\]  

(4.7)

where \( U \in \mathbb{R}^{m \times m} \) and \( V \in \mathbb{R}^{n \times n} \) are unitary matrices where the columns of \( U \) are eigenvectors of \( AA^T \) while the columns of \( V \) are eigenvectors of \( A^T A \). \( \Sigma \in \mathbb{R}^{m \times m} \) is a diagonal matrix of the singular values \( \sigma \) of \( A \). Singular values are the square roots of the nonzero eigenvalues of \( A^T A \). The first \( r \) spaces on the diagonal of \( \Sigma \) are filled by the singular values of \( A \), where \( r \) is the rank of \( A \).

A rank of a matrix \( M \) is the number of linearly independent rows in the matrix. Common convention sorts the values of \( \Sigma \) in descending order. From the singular values we can calculate what is known as the condition number of matrix \( M \) by taking

\[
C = \frac{\sigma(1)}{\sigma(r)}
\]  

(4.8)

where \( C \) is the condition number, and \( \sigma(1) \) and \( \sigma(r) \) are the largest and smallest singular values of the matrix respectively. The condition number represents the degree of linear independence between the columns of the matrix \( M \). This reflects the sensitivity of solutions of the matrix to inaccuracies in the data. A matrix with a large condition number is considered to be ill-conditioned. There is not a definitive condition number that defines the boundary between what is considered well-conditioned and ill-conditioned, but a generally accepted figure for a well conditioned matrix is \( C \leq 10^3 \).

4.5.2 Regularization by Truncated SVD

The first few components of the SVD hold useful information about the solution, while some of the singular values will have too much noise to be of use. By choosing to keep some eigenvalues and setting the rest to zero, the quality of the inversion can be improved.
The truncated SVD solution is computed by

$$\Sigma_k = \sum_{i=1}^{k} U_i^T M_i V_i$$  \hspace{1cm} (4.9)

where $\Sigma_k$ is the set of truncated singular values. The parameter $k$ is the truncation parameter, and must be chosen carefully such that only the desired SVD components are kept. For singular value decompositions of Fredholm integrals of the first kind, when sorted in decreasing value, the magnitude of singular values of the matrix $M$ slowly decay until they reach a plateau. The optimised value of $k$ comes from the transition between the decaying region and the flat region of the singular value magnitudes. This value of $k$ will produce a truncated SVD large enough to retain the useful components while removing those that contribute more noise than signal. An example of this can be seen in Figure 4.1. It can clearly be seen that the singular values of $K$ quickly decay towards zero, and that only a few of the singular values are needed to be kept to represent $K$.

Figure 4.1  Spectrum of singular values for the SVD of the kernel $K = e^{-t/\tau}$ with $t = (300 \mu s) \cdot N$ where $N = 1, 2, \ldots, 2048$, and $\tau$ is a 100 element vector of logarithmically spaced numbers from $10^{-5}$ to 1. The singular values of $K$ quickly decay towards zero.

There are two main benefits in applying the SVD to data. The first benefit is that the
SVD reduces the data set containing a large number of individual entries to one containing fewer individual entries, but those entries still reflects the original data. While this compression method is useful in the one-dimensional inverse Laplace transform to speed up the computation, it is critical when performing inverse Laplace transforms in higher dimensions so that the matrix sizes do not exceed the memory capability of the computer the inversion is being run on. The second benefit is that by truncating the singular values below a certain threshold regularizes (smoothes) the solution to the inverse problem\textsuperscript{51,52}.

As an example of the regularization and data compression properties of the truncated SVD method applied to data, the truncated SVD method was applied to an image of Ramses, the mascot of the University of North Carolina at Chapel Hill. The rank to which the truncated SVD represented the image was changed, and the regularization properties of truncating the SVD can be seen in Figure 4.2. Table 4.1 shows the effect varying the rank of the truncated SVD had on the number of entries and the amount of compression of the data.
Figure 4.2  Examples of data smoothing by using the truncated SVD method. As the rank of the SVD is decreased there is an overall smoothing effect on the image, until the rank is so small that the original image is not represented by the truncated data set.

Table 4.1  Compression as a function of SVD rank. As the rank of the SVD increases the number of entries representing the data set increases, and therefore the overall level of data compression decreases.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Entries (#)</th>
<th>Compression (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>original</td>
<td>2470134</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>1099200</td>
<td>55.50</td>
</tr>
<tr>
<td>25</td>
<td>274800</td>
<td>88.88</td>
</tr>
<tr>
<td>10</td>
<td>54960</td>
<td>97.78</td>
</tr>
<tr>
<td>5</td>
<td>27480</td>
<td>98.89</td>
</tr>
</tbody>
</table>
4.5.3 Tikhonov Regularization

One other popular method is Tikhonov regularization\textsuperscript{53}, which is a damped least squares method. We start with taking our ill-posed problem and writing it in tensor notation as

\[ M = KF \] (4.10)

which we can rewrite as a least squares problem with the addition of a regularization term as

\[ \chi^2 = \| M - KF \|^2 + \alpha \| LF \|^2 \] (4.11)

where $\| \cdot \|$ is the Frobenius norm, and $L$ indicates the regularisation method. We seek to minimise $\chi^2$ for the chosen $\alpha$, the regularisation factor. The regularisation factor controls the amount of smoothing applied to the final solution of the inversion. The optimal $\alpha$ for an inversion is usually chosen by performing a chi-squared analysis of the data. When the proper value of $\alpha$ is chosen, the ill-posed nature of the inversion is lessened.

Several transforms of the data are taken over a given range of $\alpha$. The values of $\chi^2$ are plotted as a function of $\alpha$, producing an L-shaped curve\textsuperscript{54}. The value of $\alpha$ that just minimises the value of $\chi^2$ and no further is used, as this is the least sensitive to random noise. Using this convention, $\alpha$ values smaller than than the optimum one are said to be over-smoothed, while larger values are under-smoothed.
Figure 4.3  The L-curve for Tikhonov regularization in log-log scale used to determine the regularization parameter $\alpha$. The optimum $\alpha$ is shown at the corner of the L, along with the regions of under and over smoothing.

4.6  Fast Inverse Laplace Transform Algorithm

Up to this point the Fredholm integral has been discussed in one dimension, but there are also many systems that can be described by two-dimensional Fredholm integrals of the first kind. In two dimensions Fredholm integrals are of the form

$$m(\tau_1, \tau_2) = \int\int k(x, y, \tau_1, \tau_2) f(x, y) \, dx \, dy + \varepsilon(\tau_1, \tau_2)$$  \hspace{1cm} (4.12)$$

where $f(x, y)$ is the joint probability density of variables $x$ and $y$, and $\varepsilon(\tau_1, \tau_2)$ is the error in $m(\tau_1, \tau_2)$. The joint probability density is the likelihood of a particular combination of $x$
and $y$. For the case where the kernel, $k$, is separable, this becomes

$$m(\tau_1, \tau_2) = \int \int k_1(x, \tau_1)k_2(y, \tau_2)f(x,y)\,dx\,dy + \epsilon(\tau_1, \tau_2) \quad (4.13)$$

When we are dealing with inverse problems which arise from data being taken we no longer have a fully continuous space to integrate over, and the integrals above need to be turned into summation operators. This allows us to write Equation 4.13 in matrix form as

$$M = K_1FK_2^T + E \quad (4.14a)$$

$$M \in \mathbb{R}^{N_1 \times N_2} \quad (4.14b)$$

$$F \in \mathbb{R}^{N_x \times N_y} \quad (4.14c)$$

$$K_1 \in \mathbb{R}^{N_1 \times N_x} \quad (4.14d)$$

$$K_2 \in \mathbb{R}^{N_2 \times N_y} \quad (4.14e)$$

where $K_1$, $F$, $K_2$, and $E$ are the discretised versions of $k_1$, $f$, $k_2$, and $\epsilon$ respectively.

The fast inverse Laplace transform algorithm developed by Venkataramanan et al. overcame many hurdles, such as computer processing and memory limitations, to provide a solution to the inverse problem in Equation 4.14. Their algorithm is an adaptation of the Butler-Reed-Dawson algorithm also used to solve Fredholm integrals of the first kind. To decrease the memory requirements from the computer their algorithm performs data compression on each of the kernels using the SVD

$$K_1 = U_1\Sigma_1V_1^T \quad (4.15a)$$

$$K_2 = U_2\Sigma_2V_2^T \quad (4.15b)$$

$$U_1 \in \mathbb{R}^{N_1 \times s_1} \quad (4.15c)$$

$$U_2 \in \mathbb{R}^{N_2 \times s_2} \quad (4.15d)$$

$$\Sigma_1 \in \mathbb{R}^{s_1 \times s_1} \quad (4.15e)$$

$$\Sigma_2 \in \mathbb{R}^{s_2 \times s_2} \quad (4.15f)$$

$$V_1 \in \mathbb{R}^{N_x \times s_1} \quad (4.15g)$$

$$V_2 \in \mathbb{R}^{N_y \times s_2} \quad (4.15h)$$

where $s_1$ and $s_2$ indicate the number of nonzero singular values of $K_1$ and $K_2$ respectively.
The compressed matrices can then be written as

\[
\tilde{K}_1 = U_1^T K_1, \quad \tilde{K}_1 \in \mathbb{R}^{s_1 \times N_x} \tag{4.16a}
\]

\[
\tilde{K}_2 = U_2^T K_2, \quad \tilde{K}_2 \in \mathbb{R}^{s_2 \times N_y} \tag{4.16b}
\]

\[
\tilde{M} = U_1^T M U_2, \quad \tilde{M} \in \mathbb{R}^{s_1 \times s_2} \tag{4.16c}
\]

where the \( \tilde{\cdot} \) indicates the compressed form of the matrix. Using these compressed forms of the matrices, the basic structure of the problem is not changed, but it can reduce the size of the kernels by up to a thousand fold for smooth kernels.

In one dimension the problem can be formulated as

\[
f = \arg\min_{f \geq 0} Q = \| \tilde{m} - \tilde{K}_0 f \|^2 + \alpha \| f \|^2 \tag{4.17}
\]

where the vectors \( \tilde{m} \) and \( f \) are obtained by lexicographically ordering matrices \( \tilde{M} \) and \( F \) respectively, and

\[
\tilde{K}_0 = \tilde{K}_1 \otimes \tilde{K}_2, \quad \tilde{K}_0 \in \mathbb{R}^{(s_1 s_2) \times (N_x N_y)} \tag{4.18a}
\]

\[
\tilde{m} = \tilde{M}, \quad \tilde{m} \in \mathbb{R}^{(s_1 s_2) \times 1} \tag{4.18b}
\]

\[
f = F, \quad f \in \mathbb{R}^{(N_x N_y) \times 1} \tag{4.18c}
\]

where \( \tilde{m} \) the compressed data, \( \tilde{K}_0 \) the compressed kernels, and \( f \) the joint density function in one dimension. Equation 4.18 can be solved by the procedure laid out by Butler, Reeds, and Dawson\(^\text{56}\), and given in terms of the one dimensional SVD compressed components in Venkataramanan\(^\text{55}\). To solve Equation 4.18 for \( f \), \( \alpha \) fixed, where

\[
f = \tilde{K}_0 \cdot c \tag{4.19a}
\]

\[
c \in \mathbb{R}^{(s_1 s_2) \times 1} \tag{4.19b}
\]

and \( c \) satisfies

\[
\tilde{m} = [G(c) + \alpha I] c \tag{4.20a}
\]

\[
I \in \mathbb{R}^{(s_1 s_2) \times (s_1 s_2)} \tag{4.20b}
\]
The vector $c$ can now be found by minimizing the convex function $\chi$ using the inverse Newton method with the first and second derivatives given by

$$\chi(c) = \frac{1}{2} [G(c) + \alpha I] c - c \cdot \tilde{m} \quad (4.21a)$$

$$\nabla \chi(c) = [G(c) + \alpha I] c - \tilde{m} \quad (4.21b)$$

$$\nabla \nabla \chi(c) = G(c) + \alpha I \quad (4.21c)$$

To choose the regularization parameter there are a number of methods available. The first is to calculate an optimum value under the assumption that the error in the data has zero mean and isn’t correlated, with the optimum value of $\alpha$ being

$$\alpha_{opt} = \frac{\sqrt{s_1 s_2}}{\|c\|} \quad (4.22)$$

Another method to calculate the smoothing parameter would be through L-curve analysis. The fit error in the compressed data domain $\chi$ would be plotted as a function of the regularization parameter $\alpha$.

4.7 Model Based Inverse Laplace Transform Algorithm

The discussion in the previous sections discussing solving the ill-posed inverse problem, and the algorithm from section 4.6 assumed that nothing is known about $f$. If information about $f$ is known and can be interjected into the solution, the ill-posed nature of the problem can be relieved and stable solutions can be found without the need for regularization.

For the case of spins inside of pores we actually have information about the system that we can use to model the functional form of $f$. From Chapter 3 we know that for spins in porous media the NMR relaxation times are inversely proportional to the surface to volume ratio of the pores the spins are in, so that the distribution of relaxation times reflects the pore size distribution. We also know from Chapter 3 that pore size distributions follow log-normal distributions. Therefore, we can model the functional form of $f$ as a log-normal distribution which has the form

$$\ln \mathcal{N} \propto e^{-\frac{(\log(T) - \mu)^2}{\sigma^2}} \quad (4.23)$$
If we have the functional form of $f$, we can set up directly the equation to minimize as a least squares minimization problem as

$$\chi^2 = |M - K_1 F K_2^T|^2$$

(4.24)

The function $\chi^2$ can be viewed as an $m$-dimensional surface with multiple minima. These minima may be due to the surface itself, or due to noise from $M$. The solution of $F$ that we wish to find is the global minimum for $\chi^2$. To find the global minimum of $\chi^2$ global optimization methods such as simulated annealing need to be used, since gradient based optimization routines generally produce local minima which aren’t necessarily the global minimum.

Simulated annealing is an optimization method introduced by Kirkpatrick\textsuperscript{57} analogous to the physical process of annealing for metals. When metals are heated to a high enough temperature there is enough energy in the system for the dislocations and internal stresses present in the system to be removed. As the system is cooled down recrystallization occurs, and if the cooling rate is low enough the system will be in the lowest possible energy state possible for the system.

**Table 4.2** Comparison between thermodynamic properties and their counterpart in the simulated annealing optimization problem.

<table>
<thead>
<tr>
<th>Thermodynamics</th>
<th>SA Optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>system states</td>
<td>feasible solutions</td>
</tr>
<tr>
<td>energy</td>
<td>cost (objective)</td>
</tr>
<tr>
<td>change of state</td>
<td>neighboring solution (move)</td>
</tr>
<tr>
<td>temperature</td>
<td>control parameter</td>
</tr>
<tr>
<td>frozen state</td>
<td>optimized solution</td>
</tr>
</tbody>
</table>

The simulated annealing algorithm, similar in nature to the Metropolis algorithm\textsuperscript{58}, in its use of statistical mechanics to establish a thermal equilibrium at a certain temperature. The simulated annealing algorithm works by defining an energy function, and in our case the energy function is $E(x) = \chi^2(x)$ where $x$ is a set of parameters that define the system.
At temperature $T$, the probability $P$ of being in the energy state $E(x)$ is

$$P \propto e^{-\frac{E(x)}{T}} \quad (4.25)$$

From Equation 4.25 we see that there is a finite probability at high temperatures that high energy states can appear. As the temperature gets lower, the probability that these higher energy states can appear becomes smaller.

The simulated annealing algorithm works by allowing the system to start at a high enough temperature so that all energy states are accessible according to Equation 4.25. Random changes are made to $x$, which changes the energy of the system. The system is allowed to stay at this temperature for enough moves for the system reach thermal equilibrium. Once thermal equilibrium is reached $T$ is lowered according to the annealing schedule, and the process is started again at this new temperature. This procedure is continued until some minimum temperature is reached. A common annealing schedule is

$$T(k) = T_0 e^{-\alpha k} \quad (4.26)$$

where $T_0$ is the initial temperature, $alpha$ is the constant which determines the cooling rate, and $k$ is the cooling step. A good rule of thumb is to set $T_0 = 2E_0$ when defining the initial parameters.

Using Equation 4.23 and Equation 4.24 we can write an equation for the energy of the system if there are $N$ different component distributions as

$$E(x) = \chi^2(x) = \sum_{i=1}^{n} \left[ m_i - \sum_{j=1}^{m} K_{ij} \sum_{k=1}^{N_i} e^{-\left( \frac{\log(T_k) - \mu_k}{\sigma_k} \right)^2} \right] \quad (4.27)$$

where $w$ controls the amplitude of the distribution, $\mu$ the center, and $\sigma$ the width. The vector $x$ is given by

$$x = (w_1, \mu_1, \sigma_1, \ldots, w_N, \mu_N, \sigma_N) \quad (4.28)$$
\[ X_0, T_0, \text{ and } E_0 \]

\[ S_{n+1} = N(S_n) \]

\[ f(S_{n+1}) \leq f(S_n) \]

Accept \( S_{n+1} \)

\[ T_{n+1} = K(T_n) \]

\[ n = n + 1 \]

Stop?

Accept with

\[ P = e^{-\frac{\Delta f}{m}} \]

Stop?

Figure 4.4  Flowchart of the simulated annealing algorithm.
4.8 Simulated Annealing Algorithm Testing

To ensure that the simulated annealing algorithm that was written performed as expected, it was tested against a set of two test functions. The first test function is given by Equation 4.29, and is a multidimensional paraboloid. This function was chosen since it simulates the algorithms behavior as it approaches a local or global minimum. For a simple test case $N = 2$ was chosen, and the resulting paraboloid is shown in Figure 4.5.

$$f(x) = \sum_{i=1}^{N} x_i^2$$  \hspace{1cm} (4.29)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure45.png}
\caption{Simple paraboloid for testing the behavior of the simulated annealing algorithm’s behavior near local and global minimums.}
\end{figure}
To test the algorithm using this function a random point was chosen on the paraboloid, and the algorithm was allowed to proceed to attempt to find the minimum of the surface \( f(0,0) = 0 \). Figure 4.6 shows the results of the testing using the first function. The random starting point is shown by the red triangle outlined in blue located near coordinates \((-30, -40)\). The pink dots represent every accepted move the algorithm made. It is interesting to note that there are a few points accepted that have a higher energy than the starting point, which shows how the simulated annealing algorithm is able to not get caught in local minimums by accepting higher energy moves at higher temperature. The final point is given by a black square, and it is located at the minimum of the paraboloid shown by the blue x at \((0,0)\).
Figure 4.6  Results of running the simulated annealing algorithm from a random starting point, indicated by a red triangle outlined in blue. The pink points indicate every accepted move of the algorithm. The final point is shown by the black square, and coincides to the surface minimum indicated by the blue x located at the point (0, 0).

The second function used to test the working behavior of our simulated annealing algorithm was De Jong’s 5th function. De Jong’s 5th function is given by Equation 4.30

\[ f(x) = 0.002 + \sum_{i=1}^{25} \left[ i + (x_1 - a_i)^6 + (x_2 - b_i)^6 \right]^{-1} \]  \hspace{1cm} (4.30)

where the vectors \( a_i \) and \( b_i \) are given by

\[ a_i = (-32, -16, 0, 16, 32, -32, -16, \ldots, 16, 32) \]  \hspace{1cm} (4.31a)

\[ b_i = (-32, -32, -32, -32, -32, -16, -16, \ldots, 32, 32) \]  \hspace{1cm} (4.31b)
This function has 25 local minima, with a global minima located at the point \((-32, -32)\). Figure 4.7 shows the surface of the function described by Equation 4.30.

![Figure 4.7 De Jong’s 5th test function has 25 local minima with a global minima value and location given by \(f(-32, -32) = 0.998004\).](image)

The first test with this function run with the simulated annealing algorithm started with a random point located on the surface shown by a red triangle outlined in blue shown in Figure 4.8. The algorithm was allowed to run, and the pink points indicate all the accepted moves made by the algorithm. It is interesting to note that many of the accepted moves were located inside of local minima, but the algorithm did not get stuck in a local minima. The stopping point is shown by a black square at the global minimum indicated by a blue x at the point \((-32, -32)\).
Figure 4.8  Simulated annealing algorithm test on De Jong’s 5th function using random starting point indicated by a red triangle outlined in blue near the point (31, 29). The pink points indicate all moves accepted by the algorithm. The algorithm eventually reached a stopping point shown by the black square at the global minimum indicated by the blue triangle.

As a final test for the simulated annealing algorithm, the starting point was chosen to be in a local minima. This is shown in Figure 4.9 where the starting point is shown as a red triangle outlined in blue. The pink points are all of the moves accepted by the algorithm. In this case all of the accepted moves are to other local minima since the probability of making the jump to the surface is very low. The stopping point is shown by a black square at the global minimum indicated by a blue x at the point (−32, −32).
**Figure 4.9** Simulated annealing algorithm test on De Jong’s 5th function using local minima starting point indicated by a red triangle outlined in blue at the point $(0, 0)$. The pink points indicate all moves accepted by the algorithm. The algorithm eventually reached a stopping point shown by the black square at the global minimum indicated by the blue triangle.
Figure 4.10  SA algorithm test on simulated CPMG data with two relaxation components and noise added. (a) Simulated data with no noise. (b) $T_2$ distribution of simulated data. (c) Simulated data with and without noise. (d) Energy of all accepted steps. (e) Simulated CPMG curve with and without noise, and the fit from the SA algorithm. (f) Ideal and SA algorithm fit $T_2$ distributions.
Figure 4.11  Statistical analysis of the error in parameter fitting using the SA algorithm for the ideal CPMG data with no noise in Figure 4.10.
4.9 Conclusions
CHAPTER 5
EXPERIMENTAL DETAILS

5.1 Introduction

NMR of materials at non-standard pressures has been found to provide a significant amount of information which cannot be obtained by any other means. One of the most widely measured class of materials using these specialized NMR techniques are proteins. NMR at low pressures has been used to observe the mutual influence of protein flexibility and hydration\(^{60}\). High pressure NMR can give information about mechanical and dynamical properties, and when pressures of up to 200 MPa are applied it allows the observation of protein denaturation at temperatures down to 255 K\(^{61}\).

Another class of materials that has been widely studied using high-pressure NMR are porous materials. Porous materials for hydrogen storage have been an important focus of research as part of an effort to develop safe fuel cells for cars that run on hydrogen fuel. Various porous materials have been measured using high-pressure NMR for this purpose such as metal hydrides\(^{62}\) and microporous carbons\(^{63}\).

Regardless of the material being studied, NMR at high pressure presents many difficulties experimentally. This chapter will describe the experimental setup and procedures used for collecting the high pressure NMR data to presented later on in this dissertation.

5.2 Experimental Setup

There are several NMR systems available in our laboratory for *in situ* adsorption isotherm measurements. Spectrometers at \(^{1}H\) frequencies of 34 MHz, 200 MHz, and 400 MHz are available, with a system at 8 MHz currently under development. The data taken in this dissertation was taken on the 200 MHz system, and the schematic of the experimental
apparatus required to measure adsorption isotherms is shown in Figure 5.1.

![Diagram of NMR system capable of high-pressure gas isotherm measurements in situ](image)

**Figure 5.1** NMR system capable of high-pressure gas isotherm measurements *in situ*.

### 5.3 High Pressure NMR Cells

There are many materials that have been used to make high pressure NMR cells in the past. Materials which are candidates must be transparent to RF radiation, and have high tensile strengths to be able to operate at the desired pressure. Examples of these materials include thermoplastics such as PEEK\(^64\) (PolyEtherEther Ketone), Vespel\(^\circledR\) SP-1 polyimide resin\(^65\), quartz\(^62\), sapphire\(^66\), and ceramics such as Alumina-toughened Zirconia Oxide (ZTA)\(^67\). The maximum pressure that a cylindrical NMR probe head can reach is a function of the tensile strength, \(\tau\), of the material and the outer and inner diameters \(d_o^2\) and \(d_i^2\), and can be approximated by\(^68\)

\[
p_{\text{max}} = \tau \ln \left( \frac{d_o^2}{d_i^2} \right)
\]  

(5.1)

Typically the high pressure NMR probe heads are designed as inserts for liquid NMR probes, so outer diameters of 5 mm and 10 mm are most often seen for the high pressure cells, which are the two standard dimensions of liquid NMR probes. Inner diameters vary
based on the design and material used, but are typically greater than 3.5 mm so that the active volume is large enough to get good signal to noise ratios.

**Table 5.1** \( p_{\text{max}} \) for different materials assuming \( d_o = 5\text{mm} \) and \( d_i = 3.5\text{mm} \). All of the tensile strength data was taken from manufacturer’s websites\(^{69-73} \).

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>( \tau ) (MPa)</th>
<th>( p_{\text{max}} ) (MPa)</th>
<th>( p_{\text{max}} ) (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vespel(^{\circledR})</td>
<td>Dupont(^{\text{TM}})</td>
<td>62.0</td>
<td>44.2</td>
<td>6,415</td>
</tr>
<tr>
<td>PEEK</td>
<td>Victrex(^{\circledR})</td>
<td>95.0</td>
<td>67.8</td>
<td>9,829</td>
</tr>
<tr>
<td>Quartz glass</td>
<td>QSil</td>
<td>50.0</td>
<td>78.0</td>
<td>11,313</td>
</tr>
<tr>
<td>Sapphire</td>
<td>Saint-Gobain Crystals</td>
<td>140</td>
<td>140</td>
<td>20,305</td>
</tr>
<tr>
<td>ZTA</td>
<td>Morgan Advanced Materials</td>
<td>350</td>
<td>250</td>
<td>36,212</td>
</tr>
</tbody>
</table>

Table 5.1 shows the calculated \( p_{\text{max}} \) for a few of the most common materials that high pressure NMR cells are made out of. Presence of defects in the quartz, sapphire, and ZTA pressure cell’s structure may drastically reduce \( p_{\text{max}} \). With the exception of the presence of defects in the body of the pressure cell itself, the limiting factor in \( p_{\text{max}} \) is most often due to how the high pressure NMR cell is sealed. High stiffness o-rings and epoxy are typically used to seal the high pressure NMR cells, and these sealing methods are prone to failure at high pressures below the \( p_{\text{max}} \) determined by the tensile strength of the material the pressure cell is made out of.

### 5.3.1 Safety Considerations

Performing NMR experiments at high pressures, especially with pressurized gases, can cause serious injury if the pressure cell fails. For this reason it is necessary to perform safety checks on any new high pressure NMR cell design to determine a safe operating range before putting it into use in the lab. The safety checks should include leak checks with the high pressure cell pressurized and immersed in water for a minimum of 12 hours to ensure that the cell will hold pressure and that there isn’t a leak in the sealing mechanisms, and tests to determine the actual burst pressure of the cell’s design.
5.4 NMR Signal Intensity to Methane Density Calibration

To measure methane adsorption isotherms on porous samples quantitatively using NMR, there needs to be a way of converting between the measured NMR intensity and the amount of methane. In Chapter 2 the NMR signal intensity was said to be proportional to the number of spins in the RF coil. In other words

\[ I_{\text{NMR}} \propto N_{\text{spins}} \]  

(5.2)

Therefore, by measuring a known number of spins in the RF coil we can find the proportionality constant between the number of spins and the NMR intensity. Because the adsorption isotherms being measured will be of methane, using methane as an NMR spin calibration for the measured NMR intensity is an obvious choice.

5.4.1 Ideal Gas

At the conditions that the isotherm measurements will be taking place in this dissertation methane is in its gas phase. Using the ideal gas law

\[ PV = N k_B T \]  

(5.3)

the number of methane molecules \( N \) in a given volume \( V \), given the pressure \( P \) and temperature \( T \) can be calculated to be

\[ N = \frac{PV}{k_B T} \]  

(5.4)

where \( k_B \) is Boltzmann’s constant. Since the number of spins in the RF coil is proportional to the number of methane molecules in the RF coil, the number of methane molecules in the RF coil is also going to be proportional to the NMR intensity. Therefore,

\[ I_{\text{NMR}} \propto N_{\text{CH}_4} \]  

(5.5)

and substituting the value for \( N_{\text{CH}_4} \) from Equation 5.4 the NMR intensity is found to be

\[ I_{\text{NMR}} \propto \frac{PV}{k_B T} \]  

(5.6)
Caution needs to be used when running the NMR adsorption isotherm measurements since modifications to the detection circuit, NMR probe or spectrometer settings will affect the intensity calibration. If any modification of these parameters is made the calibration will need to be redone. Also, due to potential errors in measuring the methane pressure and NMR intensity for a single point it is suggested that intensity calibration data be collected at multiple pressures (Figure 5.2), and the data be fitted to find the desired intensity calibration proportionality constant.

**Figure 5.2** NMR Intensity at various pressures of methane for determining the NMR intensity to number of methane molecules calibration.

Unlike liquids, whose spins relax by dipole-dipole interactions, methane’s spins relax by spin-rotation interaction. This interaction is due to the coupling between the magnetic moments of the protons and the magnetic field produced at their positions by the rotation of the molecule. This relaxation mechanism becomes more effective as the density of spins increases, and less effective as the temperature increases. For methane a simple power law
has been found to fit $T_1$ relaxation data as a function of temperature and pressure to give

$$T_{1,\text{gas}} = 2.5 \times 10^4 \frac{\rho}{T_K^{1.17}},$$

where $T_K$ is the temperature in Kelvin, and $\rho$ is the density in g/cm$^3$.

### 5.4.2 Real Gas Behavior

Figure 5.2 shows the NMR intensity at various pressures of methane taken at 285 K. According to Equation 5.6 one would expect the data to be linear, but it is clearly not linear. The ideal gas law assumes that there is no interaction between the gas molecules, but in real gases there are interactions between the gas molecules. One popular method of dealing with real gases is to include a term to the real gas equation which is related to the gas interaction. This term is called the compressibility factor $Z$.

The real gas equation of state is best represented at all but the highest pressures by

$$PV = Nk_B T Z,$$

where $Z$ is given by the series

$$Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots,$$

and $B(T)$, $C(T)$, and $D(T)$ are called the second, third, and fourth Virial coefficients. $B(T)$ is given by

$$B(T) = \lim_{V \to 0} \left( \frac{PV}{Nk_B T} - 1 \right) V \equiv \lim_{V \to 0} \mathcal{A},$$

where

$$\mathcal{A} = \frac{PV}{Nk_B T} - 1.$$  (5.11)

The third Virial coefficient is equal to the slope of $\mathcal{A}$ at zero pressure.

$$C(T) = \lim_{V \to 0} (\mathcal{A} - B) V.$$  (5.12)

Figure 5.3 shows the variation of $B(T)$ with temperature for methane, while Figure 5.4 shows the variation of $C(T)$ with temperature for methane.
Figure 5.3  Second Virial coefficients of methane\textsuperscript{76–79} as a function of temperature.

Figure 5.4  Third Virial coefficients of methane\textsuperscript{77,80,81} as a function of temperature.

Beginning with the real gas equation the number of methane molecules as a function of
the NMR intensity can be calculated to be

\[ PV = N k_B T Z \]  
(5.13a)

\[ N = \frac{PV}{k_B T Z} \]  
(5.13b)

\[ I_{NMR} = \frac{\alpha \cdot PV}{k_B T Z} \]  
(5.13c)

\[ I_{NMR} = \frac{\alpha \cdot PV}{k_B T \left[ 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} \right]} \]  
(5.13d)

where \( \alpha \) is the NMR intensity calibration proportionality constant, \( B(T) \) is the second Virial coefficient at temperature \( T \), and \( C(T) \) is the third Virial coefficient at temperature \( T \), \( P \) is the pressure, and \( V \) is the gas volume. Using appropriate values for \( B(T) \) and \( C(T) \), \( \alpha \) can be found by fitting the NMR intensity data from Figure 5.2 as a function of pressure, and the NMR intensity can be transformed into methane density. The density of a material is given by

\[ \rho = \frac{m}{V}, \]  
(5.14)

where \( \rho \) is the density, \( m \) is the mass, and \( V \) is the volume. Therefore, the density of an ideal and real gas can be expressed as

\[ \rho_{\text{ideal}} = \frac{N_{\text{ideal}}}{V} \cdot \frac{M}{N_A} \]  
(5.15a)

\[ = \frac{V \cdot I_{NMR}}{V \cdot \alpha \cdot k_B T} \cdot \frac{M}{N_A} \]  
(5.15b)

\[ = \frac{I_{NMR}}{\alpha \cdot k_B T} \cdot \frac{M}{N_A} \]  
(5.15c)

and

\[ \rho_{\text{real}} = \frac{N_{\text{real}}}{V} \cdot \frac{M}{N_A} \]  
(5.16a)

\[ = \frac{I_{NMR}}{V \cdot \alpha \cdot k_B T Z} \cdot \frac{M}{N_A} \]  
(5.16b)

\[ = \frac{I_{NMR}}{\alpha \cdot k_B T Z} \cdot \frac{M}{N_A}, \]  
(5.16c)

where \( \rho \) is the density, \( M \) is the molar mass, and \( N_A \) is Avagadro’s constant. The molar mass of methane\(^{82} \) is 16.04 g · mol\(^{-1} \). Figure 5.5 shows the methane density measured by NMR, along with the expected density from an ideal and real gas.
Figure 5.5  Density of methane at various pressures measured at 285 K using NMR, along with the expected densities assuming ideal gas behavior and real gas behavior.

Figure 5.6 shows the methane density isotherm measured by NMR at 285 K, along with methane density isotherms at various temperatures. At very low densities methane shows nearly ideal gas behavior for all of the density isotherms, while the high temperature density isotherms show ideal gas behavior unlike the low temperature isotherms.
Figure 5.6  Comparison of measured methane density using NMR at 285K and values found in literature\textsuperscript{83}.

5.5 Sample Preparation

Samples were crushed and sieved through a stack of meshes of different sizes, with the last mesh being #70 sized (250µm). Crushed samples were collected from the top of the #70 sized mesh. Samples were then placed into the NMR pressure cell, and heated to a temperature of 100°C and pumped with vacuum pump overnight. This step removes any oxygen, which is paramagnetic, from the sample and would shorten the measured NMR relaxation times. It also removes any water that is loosely bound to the surface of the grains and pores, but not the water that is bound in the clay content of the shale. Heating to 100°C also does not alter the chemical composition of the organic content of the sample.
CHAPTER 6
IDENTIFICATION OF METHANE IN PORES

6.1 Introduction

Gas shales are porous sedimentary rocks composed primarily of compacted fine-grained clay particles, which typically have porosities of $\phi \leq 0.10$, pore diameters of a few nanometers, and the majority of the porosity is found in the organic matter within the gas shale$^{33,84,85}$. As mentioned in Chapter 1, NMR is a non-destructive measurement technique that has a long history of use in the oil industry to characterize porous media, both in well-logging and in rock core analysis in the laboratory$^{11,86}$. Characterization of materials has also been performed by quantitative calibration of the measured $^1$H NMR signal intensity allowing for adsorption isotherm measurements of gases in porous samples$^{63,87}$. NMR provides unique capabilities for measuring adsorption isotherms compared to conventional techniques, such as gravimetric and volumetric$^{88}$, in that NMR is often capable of distinguishing between the local environment of molecules adsorbed on the surface of the pore and confined in the pore volume through spectroscopic or relaxation measurement techniques.

NMR adsorption isotherm measurements of gas shale core samples are impractical due to the total time required to load the gas at each pressure step in the isotherm due to the extremely low permeability of gas shales. Because of this, and due to the fact that the majority of the porosity is found in the organic matter within the gas shale, it is therefore reasonable to try measuring adsorption isotherms on crushed shale samples (Figure 6.1). To measure adsorption isotherms on gas shale samples, it makes sense to use methane as the gas the samples are exposed to because the main chemical component in natural gas is methane (Appendix C).
Figure 6.1 Crushed shale sample inside of NMR coil exposed to methane gas, with shale particle pore space (inset). Interparticle methane molecules are shown in red while methane molecules in the pore space of the crushed sample are shown in green.

From Figure 6.1 it can be seen that when making NMR measurements on a crushed porous sample exposed to high pressure methane there are four local environments that the methane molecules could be in: the volume in between the larger crushed particles (interparticle volume), adsorbed on the outside surface of the crushed particles that define the interparticle volume, the volume inside the nanopores within the organic content (nanopore volume), or adsorbed on the surface of a nanopore within the organic content. Before characterizing a porous sample can be done, it needs to be determined if NMR signals from methane residing in these four different local environments can be distinguished from spectroscopic or relaxometry measurements, such as measuring $T_2$, of crushed gas shale samples exposed to methane gas.

6.2 Results

A shale sample with high organic content which was known to have methane trapped in some of the nanopores within the organic content, along with one other shale sample which showed more typical properties, such as lower organic content and no trapped methane in the nanopores, were used in the experiments in this section. The shale sample with the trapped
methane was received already crushed, while the other sample was crushed according to the procedures outlined in Chapter 5. After loading the sample into the high pressure NMR cell, the experimental procedures outlined in Chapter 5 were followed for both samples.

### 6.2.1 Shale Sample With Trapped Methane

For the shale sample with methane trapped in some of the nanopores (RDS1), the Hahn Echo pulse sequence was used to measure the $T_2$ decay curves at various methane pressures using different $2\tau$ delay values. The CPMG pulse sequence could not be used for this sample because of the very long $T_2$ value associated with the trapped methane inside of the nanopores. Figure 6.2 shows the background spectra of the sample for a few longer values of $2\tau$. The narrow peak in the spectra with a $^1$H shift of approximately 5 ppm indicates the presence of trapped methane gas in the nanopores which was not able to be removed by pumping the sample overnight. The fact that the peak is so narrow indicates that the signal was produced by a gas, and the probability that it is a gas other than methane is very low considering the chemical composition of natural gas (Appendix C). The broader NMR signal in the spectra from a $^1$H shift of 10 to -10 ppm is most likely due to aromatic compounds from the organic content in the sample.\(^\text{89}\).
Figure 6.2 $^1$H NMR background of sample RDS1 taken using the Hahn Echo pulse sequence for long $2\tau$ values showing trapped methane, and likely aromatics from the organic content present in the sample.

Figure 6.3 $^1$H NMR spectra taken using the Hahn Echo pulse sequence for various $2\tau$ values taken at 5,000 psi for sample RDS1. The feature due to the methane in the interparticle volume (300 to -300 ppm) has a very short $T_2$ value.
Figure 6.3 shows the spectra of various values of $2\tau$ taken at 5,000 psi of methane, and the narrow peak at 5 ppm is still present indicating that the trapped methane in the nanopores can still be seen even when the crushed sample is exposed to methane gas at high pressure. As the $2\tau$ value increases the spectra changes from being very smooth and almost featureless, to being less smooth and showing many features. At long $2\tau$ values (see Figure 6.4), the features in the spectra appear as multiple peaks at different $^1H$ shift values. The multiple peaks in the range of 100 to 0 ppm indicate that there is a distribution in the nanopore sizes inside the organic content of the sample, which is not surprising considering that the nanopores were created by natural processes.

In Chapter 7 the number of methane molecules expected in the interparticle and nanopore volumes will be calculated. The calculations show that considerably more methane molecules are expected to be in the interparticle volume than in the nanopore volume, which should help in identifying the two NMR signals. Based on the strength of the $^1H$ NMR signal, along with the series of spectra at different values of $2\tau$ from Figure 6.3, it can be determined that the NMR signal from the methane in the interparticle volume has the shortest $T_2$ value, followed by the methane in the nanopores, and the trapped methane has the longest $T_2$ value.

The physical explanation for the different $T_2$ values is that the methane particles in the interparticle volume have the longest diffusion length, and are able to diffuse through much larger field gradients than the methane molecules that are in a restricted diffusion condition within the nanopores. Also, the outer surface of the shale particles is made up of clay, which has many paramagnetic ions and magnetic impurities in it, while the organic content inside of the shale particles typically has much fewer paramagnetic or magnetic impurities in it. Therefore the methane molecules in the interparticle volume will relax at a faster rate due to surface collisions than the methane molecules in the nanopores.
Figure 6.4 $^1$H NMR spectra taken using the Hahn Echo pulse sequence for various long $2\tau$ values taken at 5,000 psi for sample RDS1. The peaks associated with the methane in the nanopores which isn’t trapped (100 to -75 ppm) has a shorter $T_2$ than the methane that is trapped in the nanopores (5 ppm).

Figure 6.5 $T_2$ decay curve found using the Hahn Echo pulse sequence taken at 5,000 psi for sample RDS1. There are three main $T_2$ components present: 1) short component due to the methane in the interparticle volume, 2) middle component due to the methane in the accessible nanopores, and 3) long component due to the trapped methane inside of inaccessible nanopores.
Figure 6.5 shows the $T_2$ decay curve measurement made using the Hahn Echo pulse sequence at 5,000 psi of methane. The decay curve indicates that there is a very large short $T_2$ component, which is due to the methane in the interparticle volume. There is a very long $T_2$ component, which is due to the trapped methane inside of inaccessible nanopores. The middle $T_2$ components are due to the methane inside the nanopores which are accessible.

The methane isotherms for the three $T_2$ components, along with the sum of the component isotherms are shown in Figure 6.6. The contribution of each component to the isotherm was found by fitting a line to the long contribution, subtracting the long component contribution from each of the points in the decay curve, and fitting the remaining decay curve with two exponential functions. To determine whether the isotherm for the methane in the interparticle space was reasonable, the isotherm was fit using the Virial equation for a real gas. The isotherm for an empty NMR tube, the interparticle methane, and the Virial fits for both isotherms is shown in Figure 6.7. The empty tube corresponds to a porosity of $\phi = 1$, and for the interparticle methane the Virial fit gives a porosity of $\phi = 0.30$ which is reasonable for a random packing of spheroid shale particles (see Chapter 3).
Figure 6.6  Interparticle porosity calculation from fit of isotherm data for sample RDS1.

Figure 6.7  Interparticle porosity calculation from fit of isotherm data for sample RDS1.
6.2.2 *Shale Sample Without Trapped Methane*

For the shale sample without methane trapped in the nanopores (CVXA1), the CPMG pulse sequence was used to measure the $T_2$ decay curves at various methane pressures using an echo spacing of $300\mu$s. Figure 6.8 shows the CPMG $T_2$ decay curves for this sample. As the methane pressure increases the $T_2$ decay curve changes shape, with both a short and long relaxation component getting larger as the pressure increases. The NMR signal with the short $T_2$ component is from the methane in the interparticle volume, with the same reasoning as the shale sample with the trapped methane in some of the nanopores. The NMR signal with the long $T_2$ component is therefore from the methane in the nanopores. The change in shape of the $T_2$ decay curves as the pressure increases indicates that there is methane moving into the nanopores at higher pressures.

![Figure 6.8](image)

**Figure 6.8** CPMG $T_2$ decay curves for sample CVXA1 at various pressures using an echo spacing of $300\mu$s in the CPMG pulse sequence. The change in the shape of the decay curve as the pressure increases indicates that methane is in the pores.
Figure 6.9  $T_2$ distributions found from the CPMG $T_2$ decay curves using an echo spacing of 300µs for sample CVXAI at multiple pressures.

Figure 6.9 shows the $T_2$ distributions at various pressure obtained from performing a two component log-normal model based inverse Laplace transform (Chapter 4) on the $T_2$ decay curves shown in Figure 6.8. The peak with a mode centered at $10^{-3}$ seconds is associated with the methane in the interparticle volume. As the methane pressure increases the relaxation time does not increase as expected (Equation 3.8) because the relaxation rate in the interparticle volume is dominated by the diffusion of the methane molecules within the magnetic field inhomogeneities between the different shale particles.

The peak with a mode centered at $2 \times 10^{-3}$ seconds is associated with the methane inside the nanopores. As the methane pressure increases the relaxation time does noticeably increase as expected. This is because inside the nanopores the diffusion of the methane molecules is restricted, so the methane molecules are not able to diffuse through a large magnetic field gradient like the methane in the intergranular pores. This allows the bulk relaxation rate to have a noticeable effect as the methane pressure is increased.
Figure 6.10  Methane isotherms found from $T_2$ distributions at multiple pressures for sample CVXA1.

Figure 6.11  Interparticle porosity calculation from fit of isotherm data for sample CVXA1.
From the two component log-normal model based inverse Laplace transform (Figure 6.9) the isotherms for the methane in the interparticle volume and nanopores was determined. Figure 6.10 shows the isotherms for the methane in the interparticle volume and nanopores, along with sum total of the two components. To determine whether the isotherm for the methane in the interparticle space was reasonable, the isotherm was fit using the Virial equation for a real gas. The isotherm for an empty NMR tube, the interparticle methane, and the Virial fits for both isotherms is shown in Figure 6.11. The empty tube corresponds to a porosity of $\phi = 1$, and for the interparticle methane the Virial fit gives a porosity of $\phi = 0.41$ which is reasonable for a random packing of spheroid shale particles (see Chapter 3).

6.3 Conclusions

In conclusion it has been shown that using various NMR techniques the signal from the methane gas in the interparticle region and the methane in the nanopores can be separated. The two signals are able to be separated because of the presence of paramagnetic ions in the clay on the outside of the crushed shale particles which is not present in the organic matter which the nanopores are formed within. It is beyond the scope of work in this dissertation, but previous research has shown that different clay types have different surface relaxivities (Table 6.1). This might be used in conjunction with the NMR isotherm measurements to help identify the clay content of the sample being examined.
Table 6.1  $T_2$ measurements of clay bound water at 1 MHz and at 25°C of various types of clay, along with the calculated transverse surface relaxivities $\rho_2$.

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Amount of H$_2$O (wt %)</th>
<th>$T_2$ (ms)</th>
<th>$\rho_2$ (µm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>18.9</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>31.1</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>54.4</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>Illite</td>
<td>8.8</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>15.8</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>11.7</td>
<td>8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>17.4</td>
<td>12</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>16</td>
<td>0.7</td>
</tr>
<tr>
<td>Chlorite</td>
<td>7.5</td>
<td>5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

In the samples where there is trapped methane inside of the nanopores it is necessary to use the Hahn Echo pulse sequence to measure the $T_2$ relaxation curve due to the long $T_2$ value of the trapped methane, while in typical shale samples the $T_2$ relaxation curve can be measured using the CPMG pulse sequence. For typical shale samples Figure 6.12 shows the $T_2$ distribution of the two components. The interparticle methane has a shorter relaxation time than the methane in the nanopores, and the amount is significantly larger as well.
Figure 6.12  Identification of NMR $T_2$ signal from methane in nanopore.
7.1 Storage Mechanisms

For estimating the amount of natural gas inside of a gas shale reservoir the most important physical parameter to know is their gas storage capacity. In estimating the gas storage capacity of gas shales there are three different proposed ways that the gas can be stored within gas shales:

1. compression of gas inside pore spaces
2. adsorption of gas on pore surface
3. absorption of gas in organic content such as bitumen or kerogen

In Chapter 6 it was shown that the NMR signals from methane molecules in different environments could be separated by their $T_2$ relaxation times. By measuring the methane isotherms of the methane molecules in the different environments it is possible to identify the storage mechanisms responsible for defining the gas shale sample’s storage capacity.

7.2 Adsorption Isotherms

Adsorption is the accumulation of molecules on the surface of a material, the adsorbent. The adsorption process creates a film of the adsorbate on the adsorbent’s surface, and is brought about due to surface energy minimization. Adsorption is usually described through isotherms, which relate the amount of adsorbed gas on the adsorbent as a function of its pressure at constant temperature. An analytical model which is commonly used to describe an adsorption isotherm is Langmuir adsorption described by

$$n_{\text{ads}}(P, T) = n_\infty \frac{bP}{1 + bP},$$  \hspace{1cm} (7.1)
where $n_{\text{ads}}(P, T)$ is the number of adsorbed molecules as a function of pressure $P$ and temperature $T$, $n_\infty$ is the number of adsorption sites, and $b$ is given by

$$b = \left( \frac{\sigma}{\nu_0 \sqrt{2\pi mk_B T}} \right) e^{-E_d / k_B T}, \quad (7.2)$$

where $\sigma$ is the effective area covered by an adsorbed molecule with mass $m$, and $k_B$ is the Boltzmann constant. $\nu_0$ is the prefactor of the desorption rate constant $k = \nu_0 \times e^{E_d / k_B T}$ with a typical value of $\nu_0 = 1 \times 10^{13} \text{s}^{-1}$, and $E_d$ is the activation energy of desorption. The cross sectional area for a methane molecule is $\sigma = 1.6 \times 10^{-19} \text{m}^2$.

As mentioned earlier, the Langmuir isotherm is a commonly used model to describe the adsorption process. However, there are several different shapes of isotherms possible which have been classified by the International Union of Pure and Applied Chemistry (IUPAC), and they are shown in Figure 7.1. Type I is the Langmuir isotherm, and the physical adsorption of gases by microporous solids show this type of adsorption behavior. Type II corresponds to the physical adsorption of gases by nonporous solids, while Type IV represents the behavior of gas adsorption by mesoporous solids. Type III and IV are special cases for the adsorption behavior of water.
3.3 Adsorption Isotherm Simulations

Assuming that adsorption is taking place on the surface of a nanopore it can be seen from Equation 7.1 and Equation 7.2 that the adsorption isotherm is strongly dependent on the properties of the surface through the activation energy of desorption, and the number of adsorption sites. The number of adsorption sites is related to the surface area of the nanopore, and therefore the pore’s radius. The activation energy of desorption is going to be determined by the adsorbent, which in the case of a gas shale nanopore would be the type of organic matter that the nanopore is within. Table 7.1 lists several adsorbents that would be expected to be in gas shales, along with their energy of adsorptions for methane.

To gain a better understanding of the role the physical properties of the crushed gas shale samples has on the measured isotherms, numerical simulations were performed simulating the expected isotherm assuming a Langmuir type adsorption process. For a crushed porous sample there are two components that need to be considered in calculating the isotherm:
gas in the interparticle volume, and gas in the pore space. The following sections show the calculations of these two isotherms.

### Table 7.1  Energy of adsorption of CH$_4$ on different materials$^{94}$.  

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q$ (kJ/mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green River kerogen (type I)</td>
<td>10.3</td>
</tr>
<tr>
<td>Woodford kerogen (type II)</td>
<td>21.9</td>
</tr>
<tr>
<td>Cameo coal (type III kerogen)</td>
<td>28.0</td>
</tr>
<tr>
<td>Green River rock</td>
<td>15.1</td>
</tr>
<tr>
<td>Wood River rock</td>
<td>15.3</td>
</tr>
<tr>
<td>Coal</td>
<td>10-22</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>16-20</td>
</tr>
<tr>
<td>Zeolite</td>
<td>15.7</td>
</tr>
</tbody>
</table>

#### 7.3.1 Calculation of Interparticle Gas Adsorption Isotherm

The total number of methane molecules in the interparticle volume is given by

$$N_{\text{total}} = N_{\text{gas}} + N_{\text{surface}}$$  \hspace{1cm} (7.3)

where $N_{\text{total}}$ is the total number of methane molecules in the interparticle volume, $N_{\text{gas}}$ is the number of methane molecules in the gas phase in the interparticle volume, and $N_{\text{surface}}$ is the number of methane molecules adsorbed on the surface of the shale particles. Assuming a porosity of particle packing and knowing the volume of the sample tube, the volume of the interparticle methane gas can be calculated

$$V_{\text{gas}} = \phi_{\text{packing}} \cdot V_{\text{sample tube}}$$  \hspace{1cm} (7.4)

where $V_{\text{gas}}$ is the gas volume, $\phi_{\text{packing}}$ is the porosity of the particle packing, and $V_{\text{sample tube}}$ is the volume of the sample tube. Plugging this gas volume into the real gas equation (Equation 5.4) the number of interparticle gas molecules is given by

$$N_{\text{gas}} = \frac{P \cdot \phi_{\text{packing}} \cdot V_{\text{sample tube}}}{k_B T Z}$$  \hspace{1cm} (7.5)

The total surface area of the particles in the interparticle volume is given by

$$SA_{\text{total}} = N_{\text{particles}} \cdot SA_{\text{particle}}$$  \hspace{1cm} (7.6)
where \( SA_{\text{total}} \) is the total surface area, \( N_{\text{particles}} \) is the number of shale particles in the sample volume \( V_{\text{sample}} \), and \( SA_{\text{particle}} \) is the surface area of a single particle. The number of particles inside the sample tube is given by the ratio of the sample volume to the volume of a single particle, so the total surface area can be written as

\[
SA_{\text{total}} = \left( \frac{V_{\text{sample}}}{V_{\text{particle}}} \right) \cdot SA_{\text{particle}}.
\] (7.7)

The sample volume is calculated from the porosity of the particle packing and the volume of the sample tube, and is given by

\[
V_{\text{sample}} = (1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}}
\] (7.8)

Using this and assuming the particles have a radius \( r \), the total surface area can be calculated

\[
SA_{\text{total}} = \left[ \frac{(1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}}}{\frac{4}{3} \pi r_{\text{particle}}^3} \right] \cdot 4\pi r_{\text{particle}}^2
\] (7.9a)

\[
= \frac{3 \cdot (1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}}}{r_{\text{particle}}}
\] (7.9b)

The number of methane molecules on the particle’s surface is therefore given by

\[
N_{\text{surface}} = \frac{SA_{\text{total}}}{\sigma},
\] (7.10)

where \( \sigma \) is the cross-sectional area of the absorbate.

The total number of methane molecules in the interparticle region can now be written as

\[
N_{\text{total}} = \frac{P \cdot \phi_{\text{packing}} \cdot V_{\text{sample tube}}}{k_B T Z} + \frac{3 \cdot (1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}}}{\sigma \cdot r_{\text{particle}}}
\] (7.11)

### 7.3.2 Calculation of Pore Space Gas Adsorption Isotherm

The total number of methane molecules in the nanopores is given by

\[
N_{\text{total}} = N_{\text{gas}} + N_{\text{surface}}
\] (7.12)
where \( N_{\text{total}} \) is the total number of methane molecules in the nanopores, \( N_{\text{gas}} \) is the number of methane molecules in the gas phase in the nanopores, and \( N_{\text{surface}} \) is the number of methane molecules adsorbed on the surface of the nanopores. Assuming a sample nanopore porosity, porosity of particle packing, and knowing the volume of the cylinder the sample is in, the volume of the methane gas in the nanopores can be calculated

\[
V_{\text{confined gas}} = \phi_{\text{sample}} \cdot (1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}} \tag{7.13}
\]

where \( V_{\text{confined gas}} \) is the confined gas volume, \( \phi_{\text{sample}} \) is the sample porosity, \( \phi_{\text{packing}} \) is the porosity of the particle packing, and \( V_{\text{sample tube}} \) is the volume of the sample tube. Plugging this confined gas volume into the real gas equation (Equation 5.4) the number of confined gas molecules is given by

\[
N_{\text{confined gas}} = \frac{P \cdot \phi_{\text{sample}} \cdot (1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}}}{k_B T Z} \tag{7.14}
\]

The total surface area of the nanopores is given by

\[
SA_{\text{total}} = N_{\text{pores}} \cdot SA_{\text{pore}} \tag{7.15}
\]

where \( SA_{\text{total}} \) is the total surface area, \( N_{\text{pores}} \) is the number of nanopores in the sample tube, and \( SA_{\text{pore}} \) is the surface area of a single nanopore. The number of nanopores inside the sample tube is given by the ratio of the volume of nanopores in the sample tube to the volume of a single nanopore, so the total surface area of the nanopores can be written as

\[
SA_{\text{total}} = \left( \frac{V_{\text{pores in tube}}}{V_{\text{pore}}} \right) \cdot SA_{\text{pore}} \tag{7.16}
\]

The volume of nanopores in the sample tube is calculated from the porosity of sample, the porosity of the particle packing, and the volume of the sample tube and is given by

\[
V_{\text{sample in tube}} = \phi_{\text{sample}} \cdot (1 - \phi_{\text{packing}}) \cdot V_{\text{sample tube}} \tag{7.17}
\]
Using this, along with assumption that the particles have a radius $r$, the total surface area can be calculated

$$SA_{\text{total}} = \left[ \phi_{\text{sample}} \cdot \left(1 - \phi_{\text{packing}}\right) \cdot \frac{V_{\text{sample}}}{V_{\text{tube}}} \right] \cdot \frac{4\pi r^3}{3r_{\text{pore}}} \cdot 4\pi r^2_{\text{pore}} \quad (7.18a)$$

$$= \frac{3 \cdot \phi_{\text{sample}} \cdot \left(1 - \phi_{\text{packing}}\right) \cdot V_{\text{sample}}}{r_{\text{pore}}} \quad (7.18b)$$

With the result from the previous section the total number of methane molecules in the nanopores can be written as

$$N_{\text{total}} = \frac{P \cdot \phi_{\text{sample}} \cdot \left(1 - \phi_{\text{packing}}\right) \cdot V_{\text{sample}}}{k_B T Z} + \frac{3 \cdot \phi_{\text{sample}} \cdot \left(1 - \phi_{\text{packing}}\right) \cdot V_{\text{sample}}}{\sigma r_{\text{pore}}} \quad (7.19)$$

### 7.3.3 Gas Behavior

To simulate the isotherm for a gas given the pressure $P$, temperature $T$, and volume $V$ Equation 5.8 is used to solve for the number of molecules $N$ to get

$$N = \frac{PV}{Nk_B T Z}, \quad (7.20)$$

where $k_B$ is Boltzmann’s constant, and $Z$ is the compressibility of the gas given by the series

$$Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots \quad (7.21)$$

$Z$ can be calculated by keeping the first three terms in the series, and approximate values of $B$ and $C$ in the temperature range the experiments are conducted in for this dissertation are shown in Table 7.2. Values of $B$ and $C$ covering the temperature range 100 K to 600 K can be found in Figures 5.3 and 5.4.
Table 7.2  Second and third Virial coefficients for methane over the temperature range 273.15 to 323.15 K.

<table>
<thead>
<tr>
<th>$T$  (K)</th>
<th>$B$  ($\text{cm}^3/\text{mol}^{-1}$)</th>
<th>$C$  ($\text{cm}^3/\text{mol}^{-1}$)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>-53.37</td>
<td>2,659</td>
</tr>
<tr>
<td>283.15</td>
<td>-48.91</td>
<td>2,565</td>
</tr>
<tr>
<td>293.15</td>
<td>-44.82</td>
<td>2,477</td>
</tr>
<tr>
<td>303.15</td>
<td>-41.04</td>
<td>2,396</td>
</tr>
<tr>
<td>313.15</td>
<td>-37.51</td>
<td>2,319</td>
</tr>
<tr>
<td>323.15</td>
<td>-34.31</td>
<td>2,247</td>
</tr>
</tbody>
</table>

7.3.4 Simulation Results

Simulations of the confined and Langmuir adsorption isotherms for a single spherical pore were run, and the results are shown in Figure 7.2–Figure 7.4. Figure 7.2 and Figure 7.3 show the simulation results for isotherms of a pore with a diameter of 10 nm, with Figure 7.2 having $E_d = 10 \text{ kJ/mol}$ and Figure 7.3 having $E_d = 20 \text{ kJ/mol}$. 10 nm was chosen as the pore diameter for these two simulations because it is a very typical pore diameter found in gas shales, while the $E_d$ values were chosen as reasonable low and high values based off of the values listed in Table 7.1. Figure 7.4 shows the results of an isotherm simulation of a pore with a diameter of 1 nm, and $E_d = 15 \text{ kJ/mol}$. 1 nm was chosen as the pore diameter because it is at the low range of pore diameters found in gas shales, and the $E_d$ was chosen because it is an intermediate value according to Table 7.1.

Comparing Figure 7.2 and Figure 7.3 it can be seen that by changing the activation energy of adsorption the general shape of the isotherm is maintained, but there is an offset in the isotherm with a larger activation energy of adsorption due to the larger initial adsorption component. As can be seen from Figure 7.4, changing the pore’s diameter changes the shape of the isotherm drastically. When the pore size is large the shape of the isotherm is that of a confined gas in the pore volume with an offset due to surface adsorption. When the pore size is small the isotherm is dominated by that adsorption term, and the shape appears as that of the Langmuir isotherm.
Figure 7.2 Confined and adsorbed methane isotherm simulations for a single spherical pore with a 10 nm diameter, and $E_d = 10 \text{ kJ/mol}$.

Figure 7.3 Confined and adsorbed methane isotherm simulations for a single spherical pore with a 10 nm diameter, and $E_d = 20 \text{ kJ/mol}$.
Confined and adsorbed methane isotherm simulations for a single spherical pore with a 1 nm diameter, and $E_d = 15$ kJ/mol.

7.4 Experimental Results

Figure 7.5–Figure 7.10 show the experimental results for methane isotherm measurements for samples RDS1 and RDS2. Figure 7.5 and Figure 7.8 show the total methane isotherm along with the interparticle, nanopore, and trapped methane isotherms. The isotherm for an empty NMR tube, the interparticle methane, and the Virial fits for both isotherms for samples RDS1 and RDS2 are shown in Figure 7.6 and Figure 7.9. The isotherms for the methane in the nanopores along with the trapped methane in the sample are shown in Figure 7.7 and Figure 7.10 as a function of methane uptake (mmol of CH$_4$ per g of shale).
Figure 7.5  High pressure methane isotherm for sample RDS1 showing the total, interparticle, nanopore, and trapped components.

Figure 7.6  High pressure methane isotherm of the NMR calibration, interparticle, and Virial fits for these isotherms for sample RDS1.
Figure 7.7  High pressure methane isotherm for sample RDS1 showing the nanopore and trapped components.

Figure 7.8  High pressure methane isotherm for sample RDS2 showing the total, interparticle, nanopore, and trapped components.
Figure 7.9  High pressure methane isotherm of the NMR calibration, interparticle, and Virial fits for these isotherms for sample RDS2.

Figure 7.10  High pressure methane isotherm for sample RDS2 showing the nanopore and trapped components.
Gas shale samples with very high TOC contents are referred to as thermally immature because the shale has not reached a depth in the ground to be exposed to the pressures and temperatures necessary to convert the organic matter into methane. During thermal maturation is when the nanopores are created from the equilibrium condition from the outward pressure of the methane generated within the organic matter, and the inwards pressure from the rock above.

Both of the isotherms shown in Figure 7.11 have a Langmuir type shape, and have the characteristics of adsorption isotherms of methane gas in pores on the order of 1 nm or smaller. These two samples also are known to have very high TOC contents. This leads to the conclusion that the methane is being absorbed into the organic content instead of being adsorbed. The difference in the two storage capacities between the samples is most likely due to a difference in TOC values.

Figure 7.12–Figure 7.15 shows the experimental results for samples CVXA1–4. The $T_2$ decay curves (Figure 7.12–Figure 7.15 (a)) were all measured using the CPMG pulse sequence using a 300µs echo spacing. As the methane pressure increases the $T_2$ decay
curves for all of the samples changes shape, with both a short and long relaxation component getting longer as the pressure increases. Figure 7.12–Figure 7.15 (b) shows the $T_2$ distributions at various pressures obtained from performing a two component log-normal model based inverse Laplace transform (Chapter 4) on the $T_2$ decay curves shown in Figure 7.12–Figure 7.15 (a). In Chapter 6 the peak with the mode centered at the shorter $T_2$ value is associated with the methane in the interparticle volume, and the peak with the mode centered at the longer $T_2$ value is associated with the methane in the nanopores.

The methane isotherms for the two components, along with the sum of the component isotherms are shown in Figure 7.12–Figure 7.15 (c). The isotherms for the methane in the nanopores are shown in Figure 7.12–Figure 7.15 (d) as a function of methane uptake (mmol of CH$_4$ per g of shale). Previous studies of methane adsorption in gas shale samples have observed Langmuir type adsorption$^{94,95}$. It has been shown that phases confined in nanopores often exhibit behavior that is significantly different than that of the bulk phase$^{87,96–100}$. These effects arise from confinement inside the nanopore, and from the strong interaction of the adsorbate molecules with the walls of the pore$^{101,102}$. This interaction between the pore wall and the adsorbate molecule creates an effective pressure inside the pore that is greater than the bulk pressure outside the nanopore.

All of the nanopore isotherms for the low TOC samples (CVXA1–4) show a type V isotherm$^{32,91,103}$. These types of adsorption processes are known to be dominated by the pore size and the density of primary adsorption sites (PAS) on the pore walls$^{103–106}$. At low pressures the methane is primarily adsorbed on PAS and forms small clusters of methane. As the methane pressure increases, cooperative adsorption of these small methane clusters takes place, linking the existing smaller clusters at PAS across the pore wall. This leads to a rapid increase of adsorption.

The isotherms for CVXA1–4 exhibit low levels of adsorption at the lower methane pressure range. This suggests that the density of PAS on the nanopore walls for all of these
samples is low. If the pore surfaces had contained a high density of PAS the methane would have continually covered the pore surfaces, eventually filling the pore volume as the pressure is increased. Continuous adsorption at PAS will obscure the steep increase in the methane uptake observed in the isotherms, and the effect of pore size$^{103}$. 
Figure 7.12  Experimental results for sample CVXA1: (a) shows the $T_2$ decay curves measured using the CPMG pulse sequence with a $300 \mu$s echo spacing. (b) shows the $T_2$ distributions found from the inverse Laplace transform of the $T_2$ decay curves. (c) shows the total, interparticle, and nanopore methane isotherms found from the $T_2$ distributions. (d) shows the nanopore isotherm.
Figure 7.13  Experimental results for sample CVXA2: (a) shows the $T_2$ decay curves measured using the CPMG pulse sequence with a 300µs echo spacing. (b) shows the $T_2$ distributions found from the inverse Laplace transform of the $T_2$ decay curves. (c) shows the total, interparticle, and nanopore methane isotherms found from the $T_2$ distributions. (d) shows the nanopore isotherm.
Figure 7.14  Experimental results for sample CVXA3: (a) shows the $T_2$ decay curves measured using the CPMG pulse sequence with a 300$\mu$s echo spacing. (b) shows the $T_2$ distributions found from the inverse Laplace transform of the $T_2$ decay curves. (c) shows the total, interparticle, and nanopore methane isotherms found from the $T_2$ distributions. (d) shows the nanopore isotherm.
Figure 7.15  Experimental results for sample CVXA4: (a) shows the $T_2$ decay curves measured using the CPMG pulse sequence with a 300$\mu$s echo spacing. (b) shows the $T_2$ distributions found from the inverse Laplace transform of the $T_2$ decay curves. (c) shows the total, interparticle, and nanopore methane isotherms found from the $T_2$ distributions. (d) shows the nanopore isotherm.
Mesoporous carbons have been shown to have significant increases in their methane storage capacities in the presence of water\textsuperscript{107–110}. This has been attributed to the formation of methane hydrate inside the nanopore space, but during the measuring process methane hydrate was also formed in the interparticle space of the sorbent bed. During the measurements for this dissertation there were no unexpected increases in the methane density associated with the interparticle volume. Also, the time for the system here to reach equilibrium pressure was much less than has been previously reported as that required for the formation of methane hydrate\textsuperscript{107,111}. For these reasons methane hydrate formation inside the nanopores as the mechanism responsible for the unexpected increase in methane density in the nanopores can be ruled out.

7.5 Effect of Total Organic Carbon on Methane Storage Capacity

The organic matter present in gas shales is thought to be the primary contributor to the methane storage capacity in gas shales. This is because the porosity determines the amount of free gas stored in the gas shale, and the porosity is mostly contained within the organic content of gas shales. The microporosity (porosity due to pores with a diameter less than 2 nm) in shales has been shown to be positively correlated with TOC\textsuperscript{112–114}. Thermally mature shales have a larger microporosity, therefore thermally mature gas shales would be expected to have a higher storage capacity than immature ones.

The other two potential storage mechanisms, adsorption on pore surfaces and absorption in the organic content, should also heavily depend on the organic content present in the rock. One of the key parameters controlling the adsorption of methane on the pore surface is the energy of desorption, $E_d$. Table 7.1 shows that different types of organic matter that may be present in gas shales have different values of $E_d$, thereby controlling the adsorption behavior. The amount and type of organic content present will also effect the ability of methane to absorb into the organic content.

Previous research has shown that the methane storage capacity of gas shales is correlated
with the total organic carbon$^{94,115}$, while at the same time other studies have shown that it is not$^{95,112,116}$. With the novel measurement technique described previously in this dissertation I measured a set of gas shale samples with various TOC values measured in weight % at 5,000 psi of methane to compare the methane uptake between the samples. The results are shown in Figure 7.16.

![Figure 7.16](image)

**Figure 7.16** Methane uptake at 5,000 psi for samples CVXB1–7 as a function of total organic carbon content wt %.

Figure 7.16 indicates that there is a correlation between the methane uptake at 5,000 psi and the TOC for the gas shale samples measured. For the samples with low TOC values (less than 3 wt %) there is no evident relationship between the methane uptake and the TOC. This is the result of the uptake being dominated by the clay content of the sample at these low TOC values, and not the organic content. The measured uptakes for the low TOC samples in this dissertation is consistent with literature values for the sorption capacity of clays and other minerals which constitute the shale sample$^{115,117}$, and the presence of nanopores even at extremely low TOC levels.
7.6 Conclusions

In this chapter it’s been demonstrated that for gas shale samples with high TOC values the isotherms show that the methane is absorbing into the organic content of the gas shale, and the TOC controls the storage capacity of the gas shale. For the gas shale samples with low TOC values the isotherms shows that methane in the nanopores undergo cooperative adsorption through the non-Langmuir behavior of the isotherms. Cooperative adsorption begins in the range of 1,000–2,000 psi for the samples measured, and is indicated by the take-off of the CH$_4$ uptake in the isotherm. The presence of cooperative adsorption is significant because it provides a mechanism for the presence of a larger than expected density of methane to be present in gas shales at a given pressure. For the purpose of estimating the gas in-place this effect should be accounted for to get the total amount of methane present in a shale gas reservoir.

It has also been shown that for the shale samples measured there is a correlation between the methane uptake at 5,000 psi and TOC. At low TOC levels the uptake is controlled by the clay and mineral content, while at high TOC values the organic content controls the uptake. This conclusion is significant because it shows that it may only be necessary to measure the type of organic content and the TOC levels in the gas shale to measure the methane uptake limits, instead of having to measure an isotherm which takes significantly more time.
CHAPTER 8
CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

In this dissertation the methane storage properties of gas shales have been studied with NMR. Much of the work in this dissertation consisted of developing the laboratory equipment and software used in the analysis of the experimental data collected, along with establishing novel techniques of measuring methane storage properties of gas shales with NMR. In addition to establishing the tools and techniques necessary to make these measurements, a significant amount of time has been spent on the interpretation of the spectral and relaxation behavior of methane gas in crushed gas shale samples.

Measurements on two different types of gas shales showed two different storage properties. Gas shale samples with high TOC values showed signs of methane absorbing into the organic content, with the storage potential being controlled by the TOC value. Gas shale samples with low TOC values on the other hand demonstrated that methane in the nanopores undergo cooperative adsorption. The conclusions reached from the low TOC samples is significant because it is the first experimental evidence of a mechanism that allows for higher densities of methane to be present within gas shale nanopores than expected. This mechanism may explain why some gas shale reservoirs have significantly more natural gas than predicted. The conclusions reached on the high TOC samples are significant because it explains why reservoirs with these types of gas shales are not able to produce as much natural gas as predicted. For these gas shale formations the production is limited by the methane deabsorbing from the organic content.

Several gas shale samples with different TOC values were measured, and a correlation between the TOC and the methane uptake at 5,000 psi of methane was found. At low TOC
levels the methane uptake was determined by the clays and minerals of the sample, while at higher TOC levels the organic content was responsible for determining the methane uptake. This result shows that measuring the TOC of a gas shale sample, along with determining the type of organic carbon is present in the sample may be enough to determine the methane storage potential of the sample.

8.2 Future Work

At the time of this dissertation a variety of experiments were not possible to perform due to a lack of access to a wide variety of gas shale samples, and due to the fact that the NMR high pressure cell used utilizes an o-ring as a high pressure seal. For safety reasons, the presence of the o-ring limits the operating temperature of the NMR high pressure cell. Based on the conclusions from the work done in this dissertation, the following future work is suggested:

1. Perform high pressure isotherm measurements on a set of gas shale samples with differing types of organic carbon constituting the TOC of the sample to determine if there is a relationship between the type of organic carbon present in the sample and the storage capacity.

2. Perform high pressure isotherm measurements on a set of gas shale samples with different clay types present in the samples, but with similar TOC to determine the effect that clay type has on the storage capacity.

3. Conduct high pressure isotherm measurements on gas shale samples with different hydration levels to determine the role water plays in the storage capacity, if any.

4. Conduct high pressure isotherm measurements on gas shale samples using a different probe molecule other than methane, such as ethane or propane, to observe the effects that probe molecules with differing intermolecular forces has.

5. Conduct high pressure isotherm measurements on gas shale samples at low magnetic field to determine if the short and long relaxation components in the isotherm can still
be distinguished from each other. This will also allow the NMR data collected in the lab to be compared with NMR logging data from the field. A schematic of the system required to perform these experiments is shown in Figure 8.1.

![Figure 8.1](image_url)  

**Figure 8.1** Low field NMR system capable of low pressure isotherm measurements *in situ*.

6. Conduct high pressure gas isotherm measurements on activated carbon samples. A high pressure methane isotherm on an activated carbon sample was attempted to be taken during the course of this work. As the methane pressure was increased slightly the RF tuning of the NMR probe changed dramatically in both the tuning and matching, and as the pressure was increased again the tuning and matching continued to change. This indicates that the electronic properties of the activated carbon sample being investigated changed as a function of the methane pressure it was exposed to.
APPENDIX A

VIRIAL COEFFICIENTS OF METHANE

Table A.1  Second Virial coefficients for methane\textsuperscript{76}.

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Table A.2  Second and third Virial coefficients for methane\textsuperscript{77}.

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Table A.3  Second and third Virial coefficients for methane\textsuperscript{78}.

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Table A.4  Second Virial coefficients for methane\(^79\).

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Table A.5  Second and third Virial coefficients for methane\(^80\).

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Table A.6  Second and third Virial coefficients for methane\(^81\).

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Table B.1  Density for methane at various temperatures and pressures\textsuperscript{83}.

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APPENDIX C

NATURAL GAS CHEMICAL COMPONENTS

Table C.1  Chemical composition of natural gas\textsuperscript{118}.

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula\textsuperscript{119}</th>
<th>Typical Analysis (vol %)</th>
<th>Range (vol %)</th>
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<tr>
<td>Methane</td>
<td>CH\textsubscript{4}</td>
<td>94.9</td>
<td>87.0–96.0</td>
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<td>Ethane</td>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>2.5</td>
<td>1.8–5.1</td>
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<td>Propane</td>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>0.2</td>
<td>0.1–1.5</td>
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<td>Isobutane</td>
<td>C\textsubscript{4}H\textsubscript{10}</td>
<td>0.03</td>
<td>0.01–0.03</td>
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<tr>
<td>n-butane</td>
<td>C\textsubscript{4}H\textsubscript{10}</td>
<td>0.03</td>
<td>0.01–0.03</td>
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<tr>
<td>Isopentane</td>
<td>C\textsubscript{5}H\textsubscript{12}</td>
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<td>Trace–0.14</td>
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<td>n-pentane</td>
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<td>0.01</td>
<td>Trace–0.14</td>
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<td>Hexane</td>
<td>C\textsubscript{6}H\textsubscript{14}</td>
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<td>Nitrogen</td>
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<td>Carbon Dioxide</td>
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<td>Hydrogen</td>
<td>H\textsubscript{2}</td>
<td>Trace</td>
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REFERENCES


