NOVEL MULTIDIMENSIONAL INVERSE LAPLACE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY TECHNIQUES

By

Kathryn Elizabeth Washburn

A thesis

submitted to the Victoria University of Wellington in fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Victoria University of Wellington 2008

ii

Abstract

This thesis presents the new development and application of multidimensional inverse Laplace nuclear magnetic resonance spectroscopy techniques. We present a new NMR technique which relates the longitudinal relaxation rate of the NMR signal to the internal gradients in the sample. We perform the experiment on a large range of magnet strengths to provide experimental evidence for the theory of how internal gradient intensity scales with pore size as a function of field strength.

We make the first attempt of quantisation of two dimensional inverse Laplace experiments. We perform a transverse relaxation exchange experiment on several samples for a range of mixing times. We then integrate the peaks in the resulting spectra and plot them as a function of mixing time. By fitting the experimental results to theory, we can estimate the molecular exchange between pores of differing sizes.

We then modify the transverse relaxation experiment to include diffusion attenuation so that we can see the separate signals for oil and water. We use this to look at the effect wettability has on the movement of the different fluids between pores. We then present the first experiment to combine two inverse Laplace dimensions with a Fourier dimension. We add a propagator dimension to the transverse relaxation exchange experiment to measure how far the molecules move during the mixing time. Quantisation of the results allows us to estimate the exchange rate between pores of similar sizes in addition the exchange rate between pores of different sizes. We are also able to estimate pore radii, inter-pore spacing and tortuosity.

Lastly, we attempt a three dimensional inverse Laplace experiment by correlating transverse relaxation, diffusion, and internal gradients. While the three dimensional inversion techniques require more development, the results show resemblance to those seen from two dimensional experiments.

Acknowledgements

I'd like to start out by thanking the Harvard researcher whose functional MRI study I participated in nearly seven years ago that first started my interest in NMR. I can't remember his name and I haven't been able to figure out the study, but it sparked off an adventure that has taken me around the world. I'd also like to thank Prof. David Cory, John Georg Seland, and Uli Scheven for helping me get started with NMR. I want to take a moment to apologise for all those fuses I burnt out.

I also want to thank my PhD advisor, Prof. Paul Callaghan for all the support and guidance be has given me throughout my PhD studies. He has been an inspiration to me in his work both inside and outside the lab. My secondary supervisor, Kate McGrath, has been a great help in understanding the chemistry I encountered during my degree. Prof. Peter Northcote also provided valuable insight throughout my thesis. I acknowledge the financial support of the New Zealand Marsden fund. I also want to thank Christoph Arns at the Australian National University for the significant contribution he made to this thesis, both in his three dimensional inverse Laplace work and by providing the X-Ray CT experiments to allow external validation for my work.

I'd like to acknowledge all the people I interacted with in the lab, Mark Hunter, Antoine Lutti, Holger Egger, Brad Douglass, Allan Raudsepp, Meghan Halse, Simon Rogers, Ben Parkinson, Penny Hubbard, Kirk Feindel, Erik Tnning, and Daniel Polders. My experiences with them made my stay in New Zealand memorable.

I thank Magritek for the use of their 12 MHz system and in particular Craig Eccles for his help in coding the T1-internal gradient pulse sequence for the Kea and general data processing help. I also appreciate the access to the 900 MHz at the University of Queensland in Brisbane and Greg Pierens help there as well as Stefan Hill's assistance with the 200 MHz at Scion in Rotorua. I am very grateful to Margaret Brown for her assistance in all things administrative and Alan Rennie and Manu Pouajen-Blakiston for their services in the workshop. I acknowledge Einar Ryeng for his help with LaTeX.

I'm grateful for the aeroclub and the chemists for making sure that I wasn't all work and no play during my thesis.

I dedicate this thesis to my family, my parents George and Sharon Washburn and my older brothers George and Geoff Washburn. They've always supported my ambitions, where ever they may take me. And to my husband, Endre, whose patience and support throughout this thesis has been invaluable.

Table of Contents

	Abstract								
	Ac	knowle	dgements	v					
1	Int	roduct	ion	1					
	1.1	Thesis	Overview	2					
		1.1.1	NMR	2					
		1.1.2	Pulse Sequences	3					
		1.1.3	Porous Media	3					
		1.1.4	Inverse Laplace Transform	3					
		1.1.5	T_1 -Internal Gradients	3					
		1.1.6	Transverse Relaxation Exchange	4					
		1.1.7	Diffusion Attenuated Transverse Relaxation Exchange .	4					
		1.1.8	Propagator Resolved Transverse Relaxation Exchange .	4					
		1.1.9	Multidimensional Inverse Laplace	4					
		1.1.10	Conclusion	5					
2	Nu	clear N	Magnetic Resonance	9					
	2.1	Histor	y	9					
	2.2	Spin a	nd the magnetic moment	10					
	2.3	Quant	um mechanics	11					

	2.4	The Zeeman interaction	2
	2.5	Ensemble behaviour	4
	2.6	Boltzmann distribution	4
	2.7	Bulk magnetisation vector	5
	2.8	Semi-classical description	6
		2.8.1 Excitation	7
	2.9	Other interactions	9
		2.9.1 Dipole-dipole interaction	9
		2.9.2 Chemical shift	0
	2.10	Relaxation	0
		2.10.1 Spin-lattice relaxation	1
		2.10.2 Spin-spin relaxation	4
	2.11	Signal quality	5
		2.11.1 Scan averaging	6
		2.11.2 Temperature	6
		2.11.3 Sample size	7
	2.12	Instrumentation	7
		2.12.1 Magnet	8
		2.12.2 Transmitter	9
		2.12.3 Probe	0
		2.12.4 Field gradients	0
		2.12.5 Receiver	0
2	Dula	so Soquenços	2 2
J	2 1	Introduction 3	ე ე
	0.1 2.0	Notation 2	ე ე
	J.4	3.2.1 PF pulso 2	ט ע
		$5.2.1 101 \mathbf{pulse} \dots 5$	4

3.2.2 field gradient $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 34$

		3.2.3	signals	5
		3.2.4	delays	5
		3.2.5	Rotation	5
		3.2.6	Phase cycling 3	7
	3.3	Basic	Pulse sequences	0
		3.3.1	Free induction decay	0
		3.3.2	Spin echo	:2
		3.3.3	Carr-Purcell-Meiboom-Gill	3
		3.3.4	Stimulated echo	.5
	3.4	Relax	ometry	6
		3.4.1	Longitudinal relaxation	6
		3.4.2	Transverse relaxation	8
	3.5	Diffus	ion and flow \ldots \ldots \ldots \ldots 5	0
		3.5.1	Pulsed field gradient spin echo	0
		3.5.2	Pulsed field gradient stimulated echo 5	4
		3.5.3	Narrow pulse approximation	5
		3.5.4	Bipolar gradients	6
4	Por	ous M	edia 5	9
	4.1	Intro	duction	9
	4.2	Basic	porous media characteristics	51
		4.2.1	Pore size and shape 6	1
		4.2.2	Porosity	3
		4.2.3	Tortuosity	5
		4.2.4	Permeability	6
		4.2.5	Wettability	6
	4.3	Intern	nal gradients	7
	4.4	Trans	sport theory	9

		4.4.1 Two pore exchange theory	70
		4.4.2 Multi-pore exchange theory	73
	4.5	X-Ray Computerised Tomorgraphy	73
		4.5.1 X-Ray CT setup	74
		4.5.2 X-Ray CT imaging	74
		4.5.1 Image reconstruction	75
		4.5.2 Image analysis	76
5	Inv	erse Laplace Transform	77
	5.1	Introduction	77
	5.2	Inverse Laplace transform integral	79
	5.3	Discretisation	80
	5.4	Singular value decomposition	81
	5.5	Regularisation	83
	5.6	Inversion	85
	5.7	Two dimensional inverse Laplace transform	86
		5.7.1 Algorithm	87
	5.8	Multidimensional inverse Laplace transform	89
6	Lo	ngitudinal relaxation internal gradient correlation	95
	6.1	Introduction	95
	6.2	Theory	97
	6.3	Experimental	02
	6.4	Results and discussion	04
	6.5	Castlegate	11
	6.6	Conclusion	11
7	Tra	insverse relaxation exchange 1	13
	7.1	Introduction	13

	7.2	Transverse relaxation exchange
	7.3	Pulse Sequence
	7.4	Experimental
	7.5	Results and analysis
		7.5.1 Castlegate
		7.5.2 Fontainebleau
		7.5.3 Mt. Gambier limestone
		7.5.4 Quartz sand
	7.6	Comparision between samples
	7.7	Conclusion
8	Dif	fusion attenuated transverse relaxation exchange 131
	8.1	Introduction
	8.2	Sample Preparation
	8.3	Pulse Sequence
	8.4	Results
	8.5	Conclusions
•	Б	
9	Pro	opagator resolved transverse relaxation exchange 145
	9.1	Introduction
	9.2	Experimental
		9.2.1 Preparation
		9.2.2 Pulse Sequence
		9.2.3 Regularisation
	9.3	Analysis
	9.4	Simulations of Inter-pore diffusion
		9.4.1 Pore glass
		9.4.2 Exchange between similar size pores

	9.4.3	Exchange between different size pores
	9.4.4	Analytic simulation
	9.4.5	Probabilistic simulation
9.5	Result	s
	9.5.1	Diagram interpretation
	9.5.2	Pore Radii
	9.5.3	Inter-pore spacing
	9.5.4	Rate of exchange between pores
	9.5.5	Tortuosity
9.6	Quart	z sand two pore model $\ldots \ldots 169$
	9.6.1	Pore Radii
	9.6.2	Inter-pore spacing
	9.6.3	Rate of exchange between pores
	9.6.4	Tortuosity
9.7	Quart	z sand three pore model
	9.7.1	Pore Radii
	9.7.2	Inter-pore spacing
	9.7.3	Rate of exchange between pores
	9.7.4	Tortuosity $\ldots \ldots 175$
9.8	Fontai	inebleau
	9.8.1	Pore Radii
	9.8.2	Inter-pore spacing
	9.8.3	Rate of exchange between pores
	9.8.4	Tortuosity
9.9	Mt. G	ambier
	9.9.1	Pore Radii
	9.9.2	Inter-pore spacing

	9.9.3	Rate of exchange between pores
	9.9.4	Tortuosity
9.10	Discus	sion
9.11	Compa	arision between T_2 exchange and propagator resolved
	T_2 exch	ange experiments
9.12	Conclu	sions

1

10) Multidimensional inverse Laplace spectroscopy														189				
	10.1	Introd	uction .				•			•	•			•			•		189
	10.2	Pulse	sequence				•		•	•	•			•		•	•		191
	10.3	Regula	arisation				•		•	•	•			•		•	•		193
	10.4	Exper	imental .				•			•	•		• •	•		•	•		196
	10.5	Result	s and disc	eussion			•		•	•	•			•			•		196
	10.6	3D an	d 2D ILT	Compa	rison		•				•			•			•		202
		10.6.1	Signal to	o noise			•			•	•			•		•	•		202
		10.6.2	Transver	se Rela	xatio	n.	•			•	•			•		•	•		203
		10.6.3	Internal	gradien	ts .		•			•	•			•			•		203
	10.7	Conclu	usions				•			•	•		• •	•	•		•	•	203
11	Co	nclusio	ns																205
A	Sar	nples																	211
B	\mathbf{Pu}	blicatio	ons from	this th	nesis														225
	Bib	oliograp	ohy																227

 xiv

Chapter 1

Introduction

Porous media are a common class of materials. In particular, we are often interested in the behaviour of fluid saturated within the pores of the material. Due to difficulties with theoretical treatment of these systems, we often need to rely on experimental study of these materials. Nuclear magnetic resonance is a common technique used in the study of fluid saturated porous media as the technique is non-invasive and can be used with opaque samples. Properties of the NMR signal can give us information about the pore space and the fluids within.

Many of these NMR properties produce signals that are decaying exponentials. To extract the underlying characteristic times of these decays, we need to take an inverse Laplace transform of the signal. While one dimensional experiments can give us useful information about our system, many times we cannot reliably make identifications based on the one dimensional data. In these cases, we want to correlate two different properties or see how a particular property changes with time. In this situation, we need a way to perform a two dimensional inverse Laplace transform. For years, a two dimensional form of the inverse Laplace transform was slow, memory intensive and only possible on a supercomputer.

The relatively recent development of a fast two dimensional inverse Laplace transform has allowed for a wide range of 2D inverse Laplace experiments to be developed. The field, however, is still young and a central theme throughout this thesis is the development of new types of these pulse sequences as well as new applications for previously developed sequences and modification of them.

Firstly, we developed a new technique that correlates the longitudinal relaxation with the local magnetic field inhomogeneities produced within porous materials. We then take a previously developed technique, transverse relaxation exchange, and attempt to quantify the results. The following two chapters deal with modifications to the transverse relaxation exchange experiment. One chapter attempts a method to separate the signals of oil and water. The other chapter adds diffusion gradients to the transverse relaxation experiment to track how far fluid molecules move during the experiment. Lastly, we look to the future with an attempt at a three dimensional inverse Laplace transform correlating transverse relaxation, molecular diffusion, and internal gradients.

I Thesis Overview

1 NMR

We begin by giving an introduction to the theory behind the nuclear magnetic resonance phenomenon that is necessary to understand this thesis. We also discuss in this chapter the basics of the NMR hardware.

2 Pulse sequences

This chapter covers the basic pulse sequences that measure the various phenomena to be observed in this thesis. These fundamental sequences are the foundation for the more complicated pulse sequences developed later in this thesis. The pulse sequence notation is explained to make the pulse sequence shorthand used understandable.

3 Porous media

Chapter 4 covers the basics of porous media terminology as well as the influence the pore space has on the NMR signal. Transport equations between pores for fluid molecules are presented here. We also briefly touch on the X-Ray CT techniques used by our collaborators at the Australian National University to help validate the NMR results we obtain.

4 Inverse Laplace Transform

This chapter discusses the inverse Laplace transform, which is used to extract the characteristic times from measured decaying exponential signals. The theory behind the inversion is presented as well as the numerical techniques required to make the inversion of measured data possible.

5 T_1 -Internal Gradients

This chapter covers a novel pulse sequence we have developed to relate the longitudinal relaxation time to internal gradients present in the sample. We perform the experiment at several different magnetic field strengths to observe how the internal gradients within the sample scale as a function of applied field.

6 Transverse Relaxation Exchange

We present in this chapter the first instance of quantification of results from a two dimensional inverse Laplace transform experiment. We use the change in T_2 time of fluid molecules during a mixing period to estimate the characteristic times between pores of differing size.

7 Diffusion attenuated transverse relaxation exchange

We expand upon the basic T_2 exchange experiment. The diffusion attenuation modification uses the different diffusion coefficients between oil and water to separate their signals. This allows us to distinguish between the oil and water signals in the porous medium without the need of the spectral dimension.

8 Propagator resolved Transverse relaxation exchange

We modify the diffusion attenuation concept in this chapter. Instead of attenuating the signal from a fluid component, we use pulsed field gradients to track how far fluid molecules move during the experimental mixing time. These experiments were performed upon a single phase, water. We are then able to estimate the exchange time between similar sized pores as well as between different sized pores. The technique also allows us to estimate pore radius, inter-pore spacing, and tortuosity between pores.

9 Multidimensional Inverse Laplace

This chapter presents a three-dimensional inverse Laplace transform experiment. The inversion techniques created by our collaborator at the Australian National University need further development, but the resulting three dimensional spectra do reflect results seen in the two dimensional experiments. While this work was carried out toward the beginning of the thesis, it is placed here to better allow comparison of this emerging technique with the more established two dimensional techniques. The early nature of this work accounts for some of the less than optimal choices made for encoding parameters. The information gained from this experiment was used to fine tune values chosen for the other experiments in this thesis.

10 Conclusion

This chapter discusses the conclusions made from the experiments in the thesis, as well as presenting potential topics for future experimentation.

Part I

Theory

Chapter 2

Nuclear Magnetic Resonance

I History

The nuclear magnetic resonance (NMR) phenomenon in condensed matter was discovered independently by Felix Bloch(1) and Edward Mills Purcell(2) in 1945. They found that certain nuclei placed in a magnetic field could absorb radiation at a given frequency and then would re-emit it later at the same frequency. At first, this effect was seen as a novelty without much practical use. In 1950, two important phenomena were discovered that helped turn NMR into the extensive tool it is today. The first effect was chemical shift(3), that the precession rate of the spins is influenced by their chemical environment. This discovery is the foundation of modern NMR spectroscopy. The second phenomenon was the development of the spin echo by Erwin Hahn(4). By application of two radio frequency pulses of a particular length and strength, magnetisation can be refocused, producing an echo of the original magnetisation decay. The ability to refocus magnetisation is fundamental to nearly all NMR experiments today. Later Richard R. Ernst and Russell Varian developed Fourier transform NMR, which sped up experimentation by allowing a range of frequencies to be probed at once. In 1973, Lauterbur(5) and Mansfield(6) published the first papers on using magnetic resonance for imaging. Today, NMR is far from a static technology. With improvements in technology, computing power, and the development of new techniques, NMR is becoming more and more a vital tool in laboratory, industrial and clinical settings.

II Spin and the Magnetic Moment

The nuclear magnetic resonance phenomenon comes from the interaction of a magnetic field and the spin of a particle. Spin, \mathbf{I} , is an intrinsic angular momentum of particles, describing the symmetry of the charge distribution around the nucleus. While the description of spin as a particle rotating around its axis is sometimes used to help understand the concept of spin, one must bear in mind it is not an accurate description of reality. The angular momentum of a particle is quantified in multiples of $\hbar = \frac{h}{2\pi}$, where h is Planck's constant, in half integers for fermions and integers for bosons. Spin $\frac{1}{2}$ nuclei are generally preferred for experimental work for several reasons. First, the interaction with the electromagnetic environment is purely degenerate dipolar, so the nucleus acts similar to a bar magnet, making magnetic manipulation of the spin dynamics easier. Also, many spin $\frac{1}{2}$ nuclei, such as ${}^{1}H$, ${}^{19}F$ and ${}^{31}P$ have high sensitivity and abundance. While higher order nuclei may not have these advantages, their quadrupolar interaction enables us to study phenomena not accessible with spin $\frac{1}{2}$ nuclei. As we work exclusively with the ${}^{1}H$ nucleus in this thesis, we will not go into the details of the higher order spins.

The angular momentum of the spin creates a magnetic moment μ . The

magnetic moment is described by the equation

$$\mu = \gamma \mathbf{I} \tag{2.1}$$

where γ is the gyromagnetic ratio, which is an intrinsic constant unique to each type of nucleus. When placed in an external magnetic field \mathbf{B}_0 , the magnetic moment of the spin produces a torque that tends to align the nuclei along the direction of the field. The spins will not align directly along the applied field, however. Because of this off-axis alignment, the magnetic field exerts a torque on the spin because of its angular momentum, causing it to precess, shown in Figure 2.1. The rate at which the nuclei precess around



Figure 2.1: A spin placed in a magnetic field \mathbf{B}_0 will precess around the direction of the applied field at a rate $w_0 = -\gamma B_0$

the field is given by:

$$\omega_0 = -\gamma B_0 \tag{2.2}$$

where ω_0 is the Larmor frequency. This equation is referred to as the Larmor equation.

III Quantum Mechanics

For a spin of quantum number I, there exists in the system 2I + 1 energy levels whose angular momentum m_I values range from -I to I in integer steps. Observation of the angular momentum can be represented using an operator. For example, measurement of angular momentum along the z-axis in the basis state $|m\rangle$ would be performed as

$$I_Z|m\rangle = m|m\rangle, \qquad (2.3)$$

where I_Z is the operator and m is the eigenvalue result of the operation. An eigenvalue measurement also includes an implied value of \hbar . The quantum state of a nucleus, Ψ , is a combination of the possible $|m\rangle$ basis states given by

$$|\Psi\rangle = \sum_{m} a_{m} |m\rangle, \qquad (2.4)$$

where a_m is referred to as the complex amplitude for each state because it has both amplitude and phase. To make a measurement upon the system, we use

$$\langle \Psi | I_Z | \Psi \rangle = \sum_m |a_m|^2 m \,. \tag{2.5}$$

The quantity $\langle \Psi | I_Z | \Psi \rangle$ is referred to as the expectation value. For a single nucleus, a measurement has a probability of $|a_m|^2$ to return the value of m. To look at the dynamics of the system, we use Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle,$$
 (2.6)

where H is the Hamiltonian. For a time invariant case, this reduces to

$$|\Psi(t)\rangle = \exp\left(-\frac{iHt}{\hbar}\right)|\Psi(0)\rangle.$$
 (2.7)

IV The Zeeman Interaction

The Zeeman interaction describes the case of an isolated nucleus in a magnetic field. The Hamiltonian of this system is:

$$H = -\mu \cdot \mathbf{B_0} \,. \tag{2.8}$$

The Hamiltonian to measure an individual energy state is written as

$$H = -\hbar\gamma B_0 I_Z \,, \tag{2.9}$$

where I_Z is the angular momentum operator along the z-axis. The energies of these states are

$$E_m = -\gamma \hbar m_I B_0 \,. \tag{2.10}$$

For spin $\frac{1}{2}$ nuclei, there are two stable states, parallel and anti-parallel to the



Figure 2.2: Spins aligning parallel to the \mathbf{B}_0 are in the low energy state and are called "Spin up". Those that align anti-parallel are in the high energy state and are called "Spin Down".

applied field. The lower energy state $E_{\uparrow} = -\frac{\gamma\hbar B_0}{2}$ is referred to as spin up. Similarly, the high energy state $E_{\downarrow} = +\frac{\gamma\hbar B_0}{2}$ is called spin down. The energy difference between the levels is $\Delta E = \gamma\hbar B_0$. A spin can transition from one energy state to the other by absorption or emission of a photon of this energy. It is the emission and absorption of photons from spins transitioning between the high and low energy states that induces the voltage in the NMR coil that we detect as the NMR signal. At present day magnet strengths, the energy difference between the levels is very small, about $10^{-5} kT$, where k is the Boltzmann constant and T is the temperature. Therefore, a large collection of the spins is required to obtain a detectable signal. Because of the high number of spins required for detection, we can then use ensemble theory to describe the behaviour of the spins.

V Ensemble Behaviour

As we cannot detect single nuclear spins with present day apparatus, we consider a system composed of a large number of spins in the same state. For this case, a measurement would return the mean of eigenvalue results weighted by the probability of each state of m occurring, $|a_m|^2$. However, when we work with a real sample, all the nuclei are not all in the same state $|\Psi\rangle$, but will have many different states. We consider each state to be a sub-ensemble and within each sub-ensemble we consider all the nuclei to be identically prepared. To take this into account, we perform an average over all the possible sub-ensembles to give us:

$$\overline{\langle \Psi | I_Z | \Psi \rangle} = \sum_{\Psi} p_{\Psi} \langle \Psi | I_Z | \Psi \rangle , \qquad (2.11)$$

where p_{Ψ} is the probability of each state Ψ . This value is considered the ensemble average. For the simplest nontrivial case of spin $\frac{1}{2}$, at thermal equilibrium the spins will either be in the low energy state $m = -\frac{1}{2}$ or the high energy state $m = +\frac{1}{2}$. The expectation value for this will be:

$$\overline{\langle \Psi | I_Z | \Psi \rangle} = \frac{1}{2} \left(\overline{|a_{\frac{1}{2}}|^2} - \overline{|a_{-\frac{1}{2}}|^2} \right)$$
(2.12)

where the expectation value is determined simply by the difference between the populations of the high energy and low energy states.

VI Boltzmann Distribution

To find the difference in the populations of spin states, we apply the Boltzmann probability distribution

$$\frac{N_i}{N} = \frac{g_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_j g_j \exp\left(-\frac{E_j}{kT}\right)},$$
(2.13)

where N_i is the number of molecules in a state *i* of energy E_i and degeneracy g_i , N is the total number of molecules in the system, k is the Boltzmann constant, T is the equilibrium temperature, and *j* represents all the different energy states. For the energy difference of $\hbar \gamma B_0$ between two adjacent energy levels, this becomes

$$\overline{|a_{\pm\frac{1}{2}}|^2} = \frac{\exp\left(\frac{\pm\hbar\gamma B_0}{2k_B T}\right)}{\exp\left(-\frac{\hbar\gamma B_0}{2k_B T}\right) + \exp\left(\frac{+\hbar\gamma B_0}{2k_B T}\right)}$$
(2.14)

Thus, the ratio between the two spin populations can be given by

$$\frac{n_{\downarrow}}{n_{\uparrow}} = \exp\left(\frac{\Delta E}{k_B T}\right) \,. \tag{2.15}$$

Because the condition $\hbar \gamma B_0 \ll k_B T$ is satisfied for current day magnet strengths at room temperature, we may simplify equation 2.14 to

$$\overline{|a_{\pm\frac{1}{2}}|^2} = \frac{1}{2} \left(1 \pm \frac{\hbar\gamma B_0}{2k_B T} \right) \,. \tag{2.16}$$

VII Bulk Magnetisation Vector

For magnetic fields producible today, the difference in spin populations is about 1 in 10^5 . Because of the small difference between energy levels and the

nearly equivalent spin population at room temperature, roughly 10^{14} spins are presently required to produce a detectable signal at room temperature. This makes NMR a relatively insensitive method compared to other spectroscopic techniques. Fortunately for us, even a small amount of sample contains multitudes of atoms and the difference in spin populations leads to an excess of magnetisation in the lower spin state, resulting in a bulk magnetisation vector, shown in Figure 2.3. Common convention places the bulk magnetisation vector along the z-axis. The magnetisation vector can



Figure 2.3: The excess spins in the low energy state will produce a bulk magnetisation vector \mathbf{M} which precesses around $\mathbf{B}_{\mathbf{0}}$.

be found by taking the expectation value of the system:

$$\overline{\langle M_Z \rangle} = N_S \hbar \gamma \langle \Psi | I_Z | \Psi \rangle \tag{2.17}$$

where N_S is the number of spins in the system per unit volume. The expectation value is described by

$$\overline{\langle M_Z \rangle} = N_S \sum_{m=-1}^{I} \overline{|a_m|^2} \hbar \gamma m \qquad (2.18)$$

and we then substitute this into equation 2.16, to obtain the bulk magnetisation vector

$$\overline{\langle M_Z \rangle} = \frac{N_S \gamma^2 \hbar^2 I(I+1)}{3k_B T} B_0.$$
 (2.19)

VIII Semi-Classical Description

Using this bulk magnetisation vector, we can now stray from a purely quantum mechanical approach. While this approach holds true for all situations we will be considering in this manuscript, there are cases beyond the scope of this thesis where the semi-classical approach will break down and a return to quantum mechanics is necessary.

The excess of spins in the lower state will lead to a bulk magnetisation vector. Like the individual magnetic moments mentioned in Section 2.2, the bulk magnetisation will experience a torque in the applied magnetic field:

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \tag{2.20}$$

If we assume our applied magnetic field lies along the z-axis as $\mathbf{B} = B_0 \mathbf{k}$, the bulk magnetisation vector \mathbf{M} precesses as:

$$M_x(t) = M_0 \sin \omega_0 t ,$$

$$M_y(t) = M_0 \cos \omega_0 t ,$$

$$M_z(t) = M_0.$$
(2.21)

1 Excitation

To perform an NMR measurement, we must perturb the spins away from equilibrium. Excitation of the spins can be achieved by irradiating the sample with photons of the same energy as the energy separation between the two states. For current equipment, the frequency ω of the photons in that energy range falls into the radio frequency spectrum. Using a radio frequency (RF) pulse on the system, a magnetic field, **B**₁, is created orthogonal to that of the applied **B**₀ field. The bulk magnetisation vector then proceeds to rotate about **B**₀ and **B**₁ simultaneously. The Hamiltonian of the excitation can be described by:

$$H = -\gamma B_0 I_Z - 2\gamma B_1 \cos(\omega t) I_X \tag{2.22}$$

The RF radiation of the transverse field is linearly polarized. This is described as two counter-rotating circularly polarized magnetic fields. There is the component

$$\mathbf{B}_{1\mathbf{r}}(t) = B_1 \cos(\omega t)\mathbf{i} - B_1 \sin(\omega t)\mathbf{j}, \qquad (2.23)$$

which rotates in the same direction as the spins precess. The non-resonant component

$$\mathbf{B_{1nr}}(t) = B_1 \cos(\omega t)\mathbf{i} + B_1 \sin(\omega t)\mathbf{j}, \qquad (2.24)$$

rotates in the opposite direction of the spins. The oppositely rotating magnetic field has virtually no influence on the system, provided $B_1 \ll B_0$, as it oscillates too fast to influence the spin system and can be neglected. Therefore, the applied transverse field can be solely described by:

$$\mathbf{B}_{1}(t) = B_{1}\cos(\omega t)\mathbf{i} - B_{1}\sin(\omega t)\mathbf{j}. \qquad (2.25)$$

Equation 2.22 then simplifies to

$$H = -\gamma B_0 I_z - \gamma B_1 \cos(\omega t) I_x. \qquad (2.26)$$

Dealing with the system in the laboratory frame can quickly become cumbersome, so we perform a reference frame shift. We now consider our reference frame to be rotating at the Larmor frequency such that $\mathbf{B_1}$ appears stationary. This produces a much-simplified picture of the excitation such that the Hamiltonian in the rotating reference frame is:

$$H_{rot} = -\gamma \left(B_0 - \frac{\omega}{\gamma} \right) I_z - \gamma B_1 I_x \tag{2.27}$$

The resonance phenomenon corresponds to $\omega = \omega_0 = \gamma B_0$. Solving equation 2.20 for a **B** vector that now includes both **B**₀ and **B**₁, Bloch obtained(1):

$$\frac{dM_x}{dt} = \gamma \left(M_y B_0 + M_z B_1 \sin(\omega_0 t) \right)$$
(2.28)

$$\frac{dM_y}{dt} = \gamma \left(M_z B_1 \cos(\omega_0 t) - M_x B_0 \right) \tag{2.29}$$

$$\frac{dM_z}{dt} = \gamma \left(-M_x B_1 \sin(\omega_0 t) - M_y B_1 \cos(\omega_0 t) \right)$$
(2.30)

Using the unexcited state, $M(t) = M_0 \mathbf{k}$, for the initial condition, the solution of the equations becomes:

$$M_x = M_0 \sin(\omega_1 t) \sin(\omega_0 t)$$

$$M_y = M_0 \sin(\omega_1 t) \cos(\omega_0 t)$$

$$M_z = M_0 \cos(\omega_1 t),$$
(2.31)

where $\omega_1 = \gamma B_1$.

IX Other Interactions

So far, we have focused solely upon the Zeeman interaction, but there also exist four other types of interactions that provide terms in the spin Hamiltonian: chemical shift, J-coupling, the dipole-dipole interaction, and the quadrupolar interaction(7). The largest term by far in the Hamiltonian is the Zeeman interaction, which is on the order of megaHertz. The four other terms are significantly smaller and can be treated as first order perturbations. We will briefly cover chemical shift and the dipole-dipole interaction as the topics appear in the rest of this manuscript. The other two interactions are not relevant to this thesis and will not be discussed.

1 Dipole-Dipole interaction

Each nuclear spin has a magnetic field surrounding it. When two spins come near each other, each will be influenced by the magnetic field of the other spin. This interaction is described by:

$$H_D = \frac{\gamma^2 \hbar^2}{r^3} \left(\mathbf{I_1} \cdot \mathbf{I_2} - \frac{3(\mathbf{I_1} \cdot \mathbf{r})(\mathbf{I_2} \cdot \mathbf{r})}{r^2} \right)$$
(2.32)

The interaction is mainly intra-molecular but can be inter-molecular. For liquids, the molecules are generally moving quickly enough that this interaction averages out to zero. For solids, that is not the case and special steps are often necessary to suppress the interaction. Anisotropic liquids will often have a residual dipole-dipole moment as well.

2 Chemical Shift

Chemical shift is the workhorse of NMR spectroscopy. Electrons surrounding a nucleus shield it slightly from the applied magnetic \mathbf{B}_0 field. The external field causes a current to arise in the electrons of a molecule. In turn, a magnetic field is produced to oppose the current, which affects the total magnetic field felt by the nucleus. The slight difference in magnetic field means that the nucleus will precess at a slightly different frequency than the Larmor frequency, given by

$$\omega_0^j = -\gamma^j B_0 (1+\delta^j) \tag{2.33}$$

where ω_0^j is the chemically shifted Larmor frequency and δ^j is the chemical shift. This effect can be seen by taking a Fourier transform of a Free Induction Decay, discussed further in Section 3.3.1. The extent to which the magnetic field of a particular nucleus is affected depends on its neighbours, how they are bonded, and their proximity. This makes chemical shift an excellent method for compound and structural identification.

X Relaxation

Brief examination of the equations 2.31 shows that the description of the excited magnetisation behaviour is not yet complete. Rotation cannot be the only motion of the spins, as there is no way for the system to return to equilibrium after excitation. There exist two types of relaxation to bring the system back to equilibrium, spin-lattice relaxation and spin-spin relaxation.

1 Spin-Lattice Relaxation (T_1)

Spin-lattice relaxation, longitudinal relaxation, is the process by which the spins come to thermal equilibrium with their surrounding environment. The relaxation occurs by energy transfer from the excited spins via the dipolar interaction into the lattice, which acts as a thermal reservoir. In the semiclassical description, longitudinal relaxation is the return of the magnetisation vector to equilibrium along the z-axis. The time it takes for a system to have dropped to $\frac{1}{e}$ of its deviation from the original magnetic intensity is referred to as the T_1 time.

For spins to dissipate energy into the lattice, they must interact with fluctuations at or near the Larmor frequency. Because of this, T_1 is dependent upon the applied magnetic field. The T_1 time of a sample will be different at 2 MHz than at 600 MHz. As the spins move, they will experience fluctuating magnetic fields(8) and hence the spin Hamiltonian fluctuates. These fluctuations are described by a characteristic time of the random motion, τ_c . The local spin Hamiltonian has a time varying part, b(t), that experiences a time correlation,

$$G(\tau) = \overline{b(t)b(t+\tau_c)}, \qquad (2.34)$$

which is averaged over the ensemble of molecules. This correlation function for isotropic random motion becomes

$$G(t) = G(0) \exp\left(-\frac{t}{\tau_c}\right) \,. \tag{2.35}$$

The Fourier transform of G(t) gives the spectral density function:

$$J(\omega) = \int_{-\infty}^{\infty} G(0) \exp\left(-\frac{t}{\tau_c}\right) \exp\left(i\omega t\right) dt$$
$$= \bar{b^2} \frac{\tau_c}{1 + \omega^2 \tau_c^2}$$
(2.36)

where $J(\omega)$ represents the amplitude and range of frequencies of the fluctuating local field. We consider the behaviour of $J(\omega)$ for an isotropic rotational dipole model to obtain(9):

$$J^{(0)}(\omega) = \frac{24}{15r_{ij}^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}$$
$$J^{(1)}(\omega) = \frac{4}{15r_{ij}^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}$$
$$J^{(2)}(\omega) = \frac{16}{15r_{ij}^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}$$
(2.37)

The influence of the dipolar interaction upon longitudinal relaxation can then be given as(8):

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 \frac{3}{2} I(I+1) \left[J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)\right]$$
(2.38)

When we substitute in equation 2.37 to the above equation, we obtain

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{2\gamma^4 \hbar^2 I(I+1)}{5r^6} \left[\frac{\tau_c}{1+\omega_0^2 \tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2 \tau_c^2}\right].$$
 (2.39)


Figure 2.4: T_1 and T_2 relaxation times as a function of τ_c^{-1} .

One can see from equation 2.39, that as the Larmor frequency increases, this will lead to an increase in T_1 as well. Plotting equation as a function of τ_c^{-1} (Figure 2.4), we see that T_1 has a minimum when the Larmor frequency is on the order of the correlation time. Freely tumbling molecules have higher energy than the Larmor frequency and therefore will have a long T_1 time. Similarly, spins in large molecules or solids will be moving at a rotational rate that is much slower than the Larmor frequency, also leading to long T_1 times. Some solids such as silver can have T_1 relaxation times of days! Spins in molecules moving at a medium rate, such as soft biological tissues, have a rotational energy near that of the Larmor frequency, leading to short T_1 times. In the semi-classical description, the relaxation process is described by:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \,. \tag{2.40}$$

The solution for the individual components of equation 2.40 is

$$M_z(t) = M_z(0) \exp\left(-\frac{t}{T_1}\right) + M_0\left(1 - \exp\left(-\frac{t}{T_1}\right)\right).$$
(2.41)

When the T_1 value is observed in the rotating reference frame in the presence of the B_1 field, it is referred to as $T_{1\rho}$.

2 Spin-Spin Relaxation (T_2)

Spin-spin relaxation, transverse relaxation, occurs when the spins come to equilibrium among themselves. After excitation, the spins precess precisely in unison. As time progresses, interaction of the spins with each other causes their precession to lose synchronisation. The transverse relaxation is caused by the loss of phase coherence between the spins. The time it takes the system to drop to $\frac{1}{e}$ of the original magnitude of the transverse signal is referred to as the T_2 time. Several different components make up the effective T_2 interaction: the true T_2 relaxation caused by dipolar interactions, and various time independent inhomogeneities in the magnetic field lead to further coherence loss. Unlike the pure T_2 relaxation, transverse relaxation from inhomogeneities is reversible through a spin echo experiment (Section 3.3.2). The two transverse relaxation components give the effective relaxation:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2^{inhomo}}.$$
(2.42)

 T_2^* is generally on the order of a few milliseconds in porous materials. In the case of a fluctuating dipolar relaxation mechanism, the relation of T_2 to frequency and τ_c is described by(8)

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 \frac{3}{2} I(I+1) \left[\frac{1}{4} J^{(0)}(0) + \frac{5}{2} J^{(1)}(\omega_0) + \frac{1}{4} J^{(2)}(2\omega_0)\right] . \quad (2.43)$$



Figure 2.5: Spin decoherence of T_2^* relaxation

When we assume the isotropic rotational motion again, equation 2.43 becomes

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4 \hbar^2 I(I+1)}{r^6} \left[\frac{3}{5}\tau_c + \frac{\tau_c}{1+\omega^2 \tau_c^2} + \left(\frac{2}{5}\right) \frac{\tau_c}{1+4\omega^2 \tau_c^2}\right].$$
 (2.44)

 T_2 is not nearly as sensitive to magnetic field strength as is T_1 , but it tends to decrease slightly with increased magnetic field. The sensitivity of magnetic phase coherence to the environment makes the transverse magnetisation an excellent probe of the molecular environment. Except for a rare and unique case(10), the T_2 relaxation time must always be less than or equal to the T_1 . Unlike T_1 , there is no minimum for T_2 when the Larmor frequency is near τ_c (Figure 2.4). For liquids, the T_2 time is usually on the order of the T_1 relaxation time. For solids or viscous liquids, the T_2 time can be as short as a few microseconds. The semi-classical description of transverse relaxation is described by

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2} \tag{2.45}$$

The solution to this equation is simply

$$M_{x,y} = M_{x,y}(0) \exp\left(-\frac{t}{T_2}\right)$$
(2.46)

XI Signal Quality

As shown in equation 2.19, the NMR signal is relatively weak; it is only because we have so many spins that we are able to obtain a detectable signal. The equation governing ${}^{1}H$ NMR signal to noise is given for a water sample by(11)

$$\left(\frac{\rho_0}{\sigma_f}\right) = \left(\frac{t}{a^2}\right) \left(\frac{T_2}{T_1}\right) \left(\frac{f^{\frac{7}{2}}}{2.8 \times 10^{-15}}\right) (\Delta x)^3 \tag{2.47}$$

where $\left(\frac{\rho_0}{\sigma_f}\right)$ is the signal to noise ratio, t is experiment time, a is the RF coil radius, f is the spectrometer frequency, and $(\Delta x)^3$ the sample volume. Because of the weakness of the NMR signal, several techniques exist to improve signal quality.

1 Scan Averaging

One technique to improve the signal to noise is signal averaging. Assuming identical starting conditions, the NMR signal from a sample will be identical each time. The noise, except for external RF interference, will be random. If N successive scans are added, the NMR signal will grow at a rate of N. The noise, however, will only grow at a rate of \sqrt{N} . By having several scans, a previously weak signal can be distinguished from the noise. Unfortunately, signal averaging experiences the law of diminishing returns, such that the more scans performed, the less each additional scan improves the acquired signal. We can gain a factor of 2 signal to noise improvement by going from 2 scans to 8; gaining a factor of 2 improvement from 1024 scans would require 4096 scans.

2 Temperature

From Boltzmann's equation (2.15), we can see that the difference in energy states is temperature dependent. By lowering the temperature of the sample, the difference between the populations will increase, which in turn gives better signal to noise. While lowering sample temperature is an effective way to improve sensitivity, this is often not a practical option for many experiments. However, in the sensitivity equation 2.47, the thermal noise term is given by(12)

$$\sigma_t = (4k_B T_C \Delta f R)^{\frac{1}{2}} \tag{2.48}$$

where T_C is the coil temperature, Δf is the bandpass filter, and R is the coil resistance. By lowering the temperature of the coil, the thermal noise can be reduced and signal to noise improved. Current cryoprobes, where the coil is kept at 4 K, can give an improvement in signal to noise up to a factor of 4 over ordinary probes.

3 Sample size

Two competing size factors arise in the signal to noise equation. First is the $(\Delta x)^3$ of sample volume. The more sample used, the more spins are present, so a stronger signal is obtained. Therefore, increasing sample volume is a possible solution to improve signal quality. For situations that involve minute amounts of sample, this is not possible. In such a case, shrinking the coil is another option, as a smaller value of a in equation 2.47 will improve signal to noise as well. To take advantage of this behaviour, microcoils have been developed to measure minute amounts of sample or image at resolution not possible with normal sized coils. The diameter of coil that optimises the trade off between the large sample volume and small coil size is approximately 15



Figure 2.6: Simplified schematic diagram of an NMR system

mm.

XII Instrumentation

There are many parts to an NMR system setup; a simplified diagram is shown in Figure 2.6. We will discuss here some of the major portions of an NMR system.

1 Magnet

For high magnetic field situations, a superconducting magnet is most commonly used. Coils of niobium and tin wire are surrounded by liquid helium to keep them at 4 K; the temperature required for superconductivity is approximately 20K. An outer dewar of liquid nitrogen is used to reduce the heat leak of the helium and hence the helium boil-off rate as liquid helium is costly. Once electrically charged, the coils of superconducting metal provide a stable magnetic field that can be maintained indefinitely. NMR experiments generally require an extremely homogeneous magnetic field to improve resolution. For this, additional coils called superconducting shims surround the main coils to enable correction of field inhomogeneities.

For some situations a non-superconducting magnet may be more desirable. These include setups that need to be mobile, such as oil well logging tools, or for low magnetic field work. For these cases, rare earth magnets are typically used. In addition, experiments have been performed using the earth's magnetic field(13; 14). This field, while very weak, has homogeneity far beyond what we can obtain with other types of magnets. The extreme homogeneity of the earth's field can produce sub-hertz linewidth in the NMR spectral dimension, allowing for ultra-high resolution spectroscopy(15).

2 Transmitter

The next portion of the NMR setup is the transmitter. The pulse program software controls the functions of the transmitter, which produces the RF radiation to excite the nuclei. The transmitter has three main components: the synthesizer, the pulse gate and the amplifier. The RF synthesizer produces an oscillating electrical signal at a given frequency. The phase of this signal may be changed throughout experimentation.

The next component is the pulse gate. When we irradiate the sample, we typically wish to apply the RF pulse for only a very brief period of time. The pulse gate serves as a very fast switch that allows the RF wave to pass through when opened. The last component of the RF transmitter is the RF amplifier. The amplifier increases the strength of the RF signal produced by the synthesizer to the level necessary to irradiate the sample. From the amplifier, the signal travels to the duplexer. The duplexer has two functions. Its function here is to divert the strong RF signal to the probe instead of the receiver.

3 Probe

The probe has many functions. Physically, it places the sample in the homogeneous magnetic field within the bore of the magnet. The probe also contains the resonator coil that is used to excite the sample and, in turn, detect the NMR signal. Most NMR setups detect in quadrature, meaning that two signals are detected so that clockwise and counter-clockwise rotation can be detected. The two signals are the in-phase and quadrature signals which become the real and imaginary portions of a complex signal and thus used to find the Fourier transform of the signal.

4 Field gradients

While for many situations we want a homogeneous magnetic field, there are times we purposely make the magnetic field inhomogeneous. Magnetic field gradients are linear gradients which are applied to the sample to change the uniform \mathbf{B}_0 field to a spatially dependent one. If these gradients are applied briefly during experimentation, they are referred to as "pulsed". Physically, the magnetic field gradients are a set of additional coils around the probe designed to produce a linear magnetic gradient throughout the sample. The pulse programmer will also control the field gradients if the system is fitted with them.

5 Receiver

After signal detection, the duplexer's second function is now to take the weak received RF signal and divert it to the pre-amplifier. The pre-amplifier increases the voltage of the signal to a more convenient level with which to work. The signal then travels to the receiver. At the receiver, the signal needs to be processed so that the signal oscillates at a rate that can be handled by the analogue to digital converter (ADC). For high field magnets, the signal as measured oscillates at several hundred MHz, which is beyond the capabilities of present day analogue to digital converters. To change the signal into a form the ADC can manage, a quadrature receiver compares the measured signal to a reference signal produced by the synthesiser to give an offset frequency:

$$\Omega^0 = \omega^0 - \omega_{ref} \,, \tag{2.49}$$

where Ω^0 is the relative Larmor frequency, ω^0 is the measured signal, and ω_{ref} is the reference signal. The offset signal Ω^0 usually oscillates around 1 MHz, a rate which can be handled by the ADC. Once the data has been digitised, the results are then saved for processing and analysis.

Chapter 3

Pulse sequences

I Introduction

Pulse sequences are the series of RF pulses, delays and field gradients that make up a nuclear magnetic resonance experiment. They can range from a simple, single RF pulse to a highly complex sequence containing thousands of pulses and elaborate gradients. Pulse sequences are used to make the magnetisation sensitive to various phenomena, and therefore are commonly said to be "encoding" for certain effects, such as diffusion, imaging, or relaxation. In this chapter, we present several basic pulse sequences that are commonly used in NMR research. These often serve as the building blocks for more complicated NMR experiments, including the pulse sequences developed for this thesis.

II Notation

Throughout this thesis, we will refer to diagrams of pulse sequences, which act as a shorthand for the series of events during an experiment. The axis



Figure 3.1: An RF pulse which rotates the magnetisation vector 180° around the -x-axis

upon which the symbols appear represents time, so that we can see how different pulses and delays are applied relative to each other. While these diagrams are useful to understand how a sequence is carried out, they are not a literal depiction. Experimental delays are generally not to scale. Similarly, while the height of a particular symbol may change throughout the sequence to indicate a change of intensity relative to itself in an experiment, there is no relation between the heights of differing symbols. Symbol choice varies slightly from author to author, so we explain here the particular notation used for this thesis.

1 RF Pulse

A vertical, solid rectangle represents an RF pulse. The angle of the RF pulse is indicated above it by a number in degrees. Often, a subscript will be added to the number to indicate which axis the magnetisation is being rotated around.

2 Field gradient

Magnetic field gradients are depicted as hollow trapezoids. A field gradient pulse above the time axis indicates a positive gradient, below the axis, a negative gradient. The term δ indicates the duration of the applied pulse.



Figure 3.2: Magnetic field gradient pulse of length δ

3 Signal

NMR signal is represented either as a "sinc-like" function, in the case of echoes, or half a sinc-like function for free induction decays.



Figure 3.3: NMR signal

4 Delays

These are depicted as spaces between pulses or gradients. If the length of the delay is important for calculations, it will be given a symbol, usually τ or Δ .

5 Rotation

For NMR experimentation, the magnetisation vector needs to be rotated through different angles and directions so that the spins can undergo the



Figure 3.4: Rotation of the magnetisation vector from along the z-axis. The red arrow indicates the applied B_1 field. a) Rotation 90° about the x axis b) Rotation 90° about the -x axis c) Rotation 90° about the y axis

necessary interactions to encode for the desired effect. In the semi-classical description, the angle by which the magnetisation vector is rotated is governed by

$$\theta = \frac{180}{\pi} \tau \gamma B_1, \qquad (3.1)$$

where θ is the angle rotated in degrees, τ is the RF pulse duration, and B_1 the applied magnetic field produced by the RF pulse. Therefore, a 90° pulse is an RF signal of a duration long enough to pivot the magnetisation vector 90° around an axis. Changing either the pulse duration or the RF field strength can control the pulse angle. Thus, to produce a 180° pulse, an RF pulse of twice the length or twice the amplitude of the 90° pulse RF field is needed.

The direction of the axis around which the magnetisation vector rotates is controlled by the phase of the RF pulse that produces B_1 . The magnetisation will rotate around the perturbing magnetic field such that the vector moves in the plane perpendicular to B_1 , shown in Figure 3.4. The rotation is clockwise for +x and +y phases while counterclockwise for -x and -y phases.

6 Phase Cycling

As we can see from Figure 3.4, the phase of the NMR signal depends on the phase of the applied RF pulse. If we perform the same experiment, but with the pulses 180° out of phase to each other, adding the two scans together will result in the two signals canceling each other out. If we have the phases of only some pulses alternating 180° to each other, we can cause some signals to cancel and other signals to be added coherently. This property enables another method, called phase cycling, to improve signal quality. While phase cycling does not improve the signal to noise ratio, it does serve to better the acquired signal by selecting out the desired NMR signal and correcting for



Figure 3.5: CYCLOPS phase cycle. Changing the phase of the RF pulse and receiver by 90° and then addition of the two signals will correct for the two receivers being slightly out of phase. Continuing the cycle with the $(180^\circ, 180^\circ)$ - $(270^\circ, 270^\circ)$ will serve to cancel unwanted signal contribution from multiple pulses

imperfections in the NMR hardware.

In pulse sequences containing multiple pulses, the additional pulses may produce unwanted signal. When we run multiple scans of an experiment, we will often have a set of different phases for each of the pulses in the experiment that we cycle through. Then, when the measured signal from the different scans are added together, the unwanted signal can be made to cancel while the desired signal is added together in a coherent superposition. The sequence of different phases used in the experiment is referred to as its phase cycle.

The simplest phase cycle is a $(0^{\circ}, 0^{\circ})$ - $(180^{\circ}, 180^{\circ})$ phase cycle, where the initial RF excitation pulse and the receiver phase alternate 180° between experiments. Because the receiver is alternating with the initial RF pulse, the signal from the first 90° pulse adds coherently while the phase from the other pulses as well as any DC background from the amplifier appears to switch sign and any resulting signal from them will cancel.

Another common method of phase cycling is the CYCLOPS cycle(16), which helps corrects for errors between the real and imaginary receivers. The procession of the initial RF pulse and receiver for the CYCLOPS cycle is $(0^{\circ}, 0^{\circ})$ - $(90^{\circ}, 90^{\circ})$ - $(180^{\circ}, 180^{\circ})$ - $(270^{\circ}, 270^{\circ})$. Often the two receivers for quadrature detection are not perfectly 90° out of phase with each other, which will lead to artefacts in the Fourier transformed spectrum. By addition of two signals 90° out of phase, the slight errors are corrected for, shown in Figure 3.5. The cycle then continues to shift the phase of the initial RF pulse and receiver 180° and 270° to cancel unwanted signal from pulses other than the initial pulse in the sequence.



Figure 3.6: Free induction Decay Pulse Sequence. a) Initial state of the magnetisation vector b) excitation with a 90° pulse c) the magnetisation begins to dephase. The precession of the magnetisation vector in the transverse plane can be seen by the oscillation in the signal while the rate of the decay envelope is dependent on T_2^*

III Basic experiments

1 Free Induction Decay

The simplest nuclear magnetic resonance experiment is the single pulse experiment. A single RF pulse excites the spins so that the magnetisation vector rotates into the transverse plane, as in Figure 3.6. Most commonly, the single pulse experiment is performed with a 90° pulse, as that gives the most intensity. The single pulse takes the initial magnetisation $M_0\mathbf{k}$ and

places it in the transverse plane where it evolves as:

$$\mathbf{M}(t) = [M_0 \cos \omega_0 t \,\mathbf{i} + M_0 \sin \omega_0 t \,\mathbf{j}] \exp(-\frac{t}{T_2}) \tag{3.2}$$

The magnetisation vector subsequently rotates around B_0 , dephasing at a rate of T_2 , and slowly decays back to equilibrium as a function of T_1 . This precession induces a voltage in the RF coil, which we detect as the free induction decay (FID). The FID is usually detected in quadrature so that both imaginary and real portions of the signal are detected. A Fourier transform of these signals will give the NMR chemical shift spectrum.

If there exist inhomogeneities in the magnetic field, the decay is a function of T_2^* instead of the pure T_2 interaction. The resolution of the NMR spectrum is limited by the linewidth, which is dependent on the T_2^* value. The shorter the T_2^* , the broader the linewidths in the transformed spectrum will be, possibly obscuring the finer structures. This is shown in Figure 3.7. For high-resolution spectroscopy, this makes an extremely homogenous magnetic field paramount, whereas for other types of experiments where we are not concerned with the chemical spectrum, this is not as important. The intensity of the FID as a function of pulse angle and repetition times is

$$M_y(\theta, \tau_R) = M_0 \sin(\theta) \frac{\left(1 - \exp\left(-\frac{\tau_R}{T_1}\right)\right)}{\left(1 - \cos(\theta) \exp\left(-\frac{\tau_R}{T_1}\right)\right)}$$
(3.3)

where $M_y(\theta, \tau_R)$ is the measured signal and τ_R is the repetition time. The maximum intensity results when θ is 90°. A pulse angle of less than 90° will still produce a signal, albeit less than the maximum intensity. If experiments are too closely spaced, $\tau_R \approx T_1$, the magnetisation will not have time to fully return to equilibrium. Only the portion of the spins that have relaxed from the previous experiment will be excited by the subsequent one, leading to a loss of measured intensity.



Figure 3.7: Simulated FID and subsequent Fourier transform of the same chemical shift with a) long T_2^* b) short T_2^* . Real signal is in blue, imaginary in orange. The short T_2^* increases the linewidth such that the two peaks cannot be resolved in the Fourier transform

2 Spin Echo

The spin echo, sometimes called a Hahn echo, is one of the most important developments for modern nuclear magnetic resonance techniques because it allows the magnetisation that has been lost through dephasing to be regained. The spin echo will refocus time independent variations of the magnetic field, such as heteronuclear couplings, chemical shift, or susceptibility changes but not the loss of fundamental spin-spin coherence brought about by entropy.

A 90° pulse puts the magnetisation into the x - y plane. The transverse

magnetisation begins to dephase due to inhomogeneities in the magnetic field. Application of a 180° pulse at time τ will invert the phase of each spin such that the spins will refocus and produce a signal at time 2τ . This signal is referred to as a spin echo. The original experiment by Hahn(4) used two 90_x° pulses to produce an echo. Improved equipment later allowed the inversion of the magnetisation using a 180_x° pulse, producing a negative echo along the -y axis. The more common convention today uses a 180_y° pulse to produce an echo along the +y axis for better refocusing of the magnetisation.

The intensity of the resulting echo is given as

$$M(2\tau) = M_0 \exp\left(-\frac{2\tau}{T_2}\right) \,. \tag{3.4}$$

where M_0 is the intensity of the original free induction decay.

3 Carr-Purcell-Meiboom-Gill

In the spin echo experiment, after the magnetisation has been refocused, it begins to dephase again. However, it is possible to refocus the magnetisation using another 180° pulse so long as the measurement time $t < T_2$. Carr and Purcell(17) were the first to implement a chain of 180° pulses to continue refocusing the magnetisation vector. However, the phase choice of the pulses was such that small errors in the 180° pulse length were cumulative, so that with each echo, less and less magnetisation was returned to the transverse plane to be refocused. Meiboom and Gill (18) later adjusted the relative phases of the pulses to compensate for this, in which the small errors would self correct by having the magnetisation vector rotate around the y-axis instead of the x-axis, so that the magnetisation is refocused along the positive y-axis. The modified Carr-Purcell-Meiboom-Gill sequence is commonly called a CPMG for the sake of brevity. A long sequence of these echoes is often referred to



Figure 3.8: Spin Echo Pulse Sequence. a) Initial state of the magnetisation vector b) an applied 90° pulse along the x-axis causes the magnetsation vector to rotate around B_1 to lie along the y-axis. c) the magnetisation vector begins to dephase d) a 180° pulse causes the magnetisation to rotate around the y-axis to lie along the -y axis, where the magnetisation begins to refocus e) the magnetisation has refocused, producing a spin echo f) the magnetisation begins to dephase again



Figure 3.9: Carr-Purcell-Meiboom-Gill pulse sequence

as a CPMG train. The intensity for any given echo in the train is described by

$$M(2n\tau) = M_0 \exp\left(-\frac{2n\tau}{T_2}\right).$$
(3.5)

where n is the n^{th} echo.

4 Stimulated Echo

A variation on the spin echo experiment is the stimulated echo, shown in Figure 3.10. The stimulated echo is useful for experiments where the T_1 time is much longer than the T_2 time. The system is excited with the application of a 90° pulse. A time τ later, another 90° pulse is used to then store the dephased transverse magnetisation back along the z-axis for a time τ_1 . Only one component of the transverse magnetisation, either the x or y, can be stored by the 90° pulse along the z-axis. The magnetisation now experiences only the much slower T_1 relaxation. Finally, a third 90° pulse is used to place the magnetisation back into the transverse plane. The magnetisation refocuses and produces a signal, the stimulated echo. Unlike the spin echo, the amplitude of the stimulated echo is only one half that of the original due to the loss of one of the components of the transverse magnetisation from the second 90° pulse:

$$M(2\tau + \tau_1) = \frac{M_0}{2} \exp\left(-\frac{2\tau}{T_2}\right) \exp\left(-\frac{2\tau + \tau_1}{T_1}\right).$$
 (3.6)

IV Relaxometry

The study of the spin mechanisms which return the systems to equilibrium is referred to as NMR Relaxometry. These relaxation mechanisms can tell us a wealth of information about the system, such as fluid properties or material structure.

1 Longitudinal Relaxation

The most common way to perform a T_1 measurement is through the inversion recovery sequence. The inversion recovery sequence begins with a 180° pulse that places the magnetisation along the negative z-axis. The magnetisation is then allowed to relax for a time τ_{T_1} and then a 90° pulse excites the magnetisation into the transverse plane. This places the longitudinal magnetisation remaining after time τ_{T_1} into the transverse plane where it is detected. Because the magnetisation was initially placed along the -z-axis, we will see an inversion of the signal from negative to positive as the magnetisation relaxes. The intensity of this magnetisation is a function of time as:

$$M_y(\tau_{T_1}) = M_0\left(1 - 2\exp\left(-\frac{\tau_{T_1}}{T_1}\right)\right)$$
(3.7)

The inversion recovery experiment is performed with a range of values of τ_{T_1} and the T_1 relaxation curve is the intensity of the acquired signal plotted as a function of τ_{T_1} , shown in Figure 3.12. The time which the magnetisation crosses from the negative to the positive occurs at $\tau_{T_1} = 0.69T_1$. However, in



Figure 3.10: Stimulated Echo Pulse Sequence a) Unexcited state b) an applied 90° pulse along the x-axis causes the magnetisation vector to rotate around B_1 to lie along the y-axis. c) the magnetisation vector begins to dephase d) a 90° pulse causes the magnetisation to rotate around the x-axis to lie in the y-z plane e) magnetisation left in the transverse plane decays away f) a third 90° pulse returns the remaining magnetisation to the x-y plane g) the magnetisation refocuses h) a stimulated echo is produced, only half the amplitude of the original echo i) magnetisation begins to dephase again

many cases, there exists more than one value of T_1 in the system. For these situations, performing an inverse Laplace transform on the relaxation curve, discussed in chapter 5, will give the distribution of T_1 times in the sample.

2 Transverse Relaxation

There are two ways to perform a transverse relaxation experiment. The first is to perform several single echo spin echo experiments. The echo time, τ , for each experiment is varied and the maximum amplitude of the resulting echo is measured as a function of the echo time, shown in Figure 3.13. The second method uses a CPMG train, where the echo spacing is fixed and the number of refocusing 180° pulses varied. The maximum amplitude of each spin echo in the CPMG train is recorded.

Both methods have their advantages and disadvantages. The fixed echo time experiment can avoid bias from inhomogeneities in the magnetic field. The fixed echo time experiment can also obtain the T_2 relaxation of the sample in a single experiment, making it more time efficient. However, the long train of refocusing pulses can heat the sample and have a heavy duty cycle, possibly exceeding the capabilities of the spectrometer. The variable echo experiment takes longer, but is less demanding upon the equipment. Temperature control is also easier because less energy is transferred into the sample.



Figure 3.11: Inversion Recovery pulse sequence a) Initial magnetisation vector b) the magnetisation is inverted using a 180° pulse c) the magnetisation is allowed to relax for a time τ_{T1} d) the remaining longitudinal magnetisation is placed into the transverse place for detection e) the magnetisation dephases



Figure 3.12: Measured inversion recovery magnetisation intensity as a function of τ_{T1}

V Diffusion and Flow

1 Pulsed Field Gradient Spin Echo (PGSE)

Whereas many other methods to study fluid flow and diffusion require a transparent sample and fluids or tracer particles to observe the movement of fluids, NMR can detect fluid displacement in opaque samples and in a non-invasive manner. Two main methods are used for detection of fluid diffusion and flow, the Pulsed Field Gradient Spin Echo and the Pulsed Field Gradient Stimulated Echo. While a wide manner of variations on these sequences exist, we focus on the core elements and modifications relevant to this thesis.

The pulsed field gradient spin echo combines the spin echo experiment with magnetic field gradients to 'tag' molecules to look at their motion. Shortly after the initial 90° excitation, a linear pulsed field gradient is applied



Figure 3.13: Transverse relaxation measurement using a variable τ echo spacing

to the sample. The spins now experience a magnetic field $B_0 + \mathbf{r} \cdot \nabla B$, where B is the component of magnetisation parallel to B_0 from the much smaller applied field gradients and \mathbf{r} is the location in the sample. The magnetic field gradient can be defined by $\mathbf{g} = \nabla B$. The application of the field gradient causes a spatially dependent phase shift in the spin bearing molecules by changing their precession rate to:

$$\omega_{eff} = \omega + \gamma \mathbf{r} \cdot \mathbf{g} \tag{3.8}$$

where ω_{eff} is the effective Larmor frequency. The gradient is applied for a time δ so that the spin-bearing molecules are tagged with the spatially dependent phase shift

$$\Phi = \gamma \delta \mathbf{g} \cdot \mathbf{r} \,. \tag{3.9}$$

Note that this equation assumes that δ is sufficiently short that negligible



Figure 3.14: Pulsed field gradient spin echo pulse sequence

molecular motion has occurred over that time interval. The molecules are left to move for a given evolution time, $\frac{\Delta}{2}$. A 180° pulse is then applied to invert both the magnetisation as well as the phase shift. A time $\frac{\Delta}{2}$ after the 180° pulse, another gradient of equal intensity and duration is applied to refocus the magnetisation. This imparts a second additional phase shift, which is added to the first, inverted phase shift:

$$\Delta \Phi = (-\Phi_1) + (\Phi_2). \tag{3.10}$$

For molecules that have not moved, the two phase shifts will be equal, so the second gradient cancels the phase shift of the first gradient, giving a net phase shift of zero. For molecules that have moved during the evolution time, the second gradient will not completely cancel the initial phase shift and the molecules will have a residual phase shift. If a molecule has moved to position \mathbf{r}' after the evolution time, the phase shift is given as

$$\Delta \Phi = \gamma \delta \mathbf{g} \cdot (\mathbf{r} - \mathbf{r}') \,. \tag{3.11}$$

The movement of a single particle is reflected by the self correlation function

$$P_s\left(\mathbf{r}|\mathbf{r}',\mathbf{t}\right) \tag{3.12}$$

which describes the probability that a particle which started off at \mathbf{r} is located at \mathbf{r}' a time *t* later. However, as NMR is currently unable to measure a single spin, we work with large numbers of spins. Therefore, we tend to use the average propagator instead, given by(19)

$$\overline{P_{s}(\mathbf{R},t)} = \int P_{s}(\mathbf{r}|\mathbf{r}+\mathbf{R},t) \rho(\mathbf{r}) d\mathbf{r}$$
(3.13)

where $\rho(r)$ is the probability of finding a particle at **r**. Equation 3.13 describes the likelihood of any particle to have a displacement **R** after a time *t*. The average propagator relation does not concern us with where precisely the particles have moved, but only how far.

In the PGSE experiment, the residual phase shift of the molecules serves to attenuate the amplitude of the subsequent echo

$$M(\mathbf{g}, \delta, \Delta) = M_0 \int \rho(\mathbf{r}) \int P_S(\mathbf{r} | \mathbf{r}', \Delta) \exp\left[i\gamma \delta \mathbf{g} \cdot (\mathbf{r} - \mathbf{r}')\right] d\mathbf{r}' d\mathbf{r}.$$
 (3.14)

We see from equation 3.13 that we can then simplify this behaviour to the average propagator:

$$M(\mathbf{g}, \delta, \Delta) = M_0 \int \overline{P_s}(\mathbf{R}, \Delta) \exp\left[i\gamma\delta\mathbf{g} \cdot \mathbf{R}\right] d\mathbf{R}$$
(3.15)

To further simplify our calculations, we define a reciprocal space

$$\mathbf{q} = \frac{\gamma \delta \mathbf{g}}{2\pi} \tag{3.16}$$

so that equation 3.15 now becomes

$$M(\mathbf{q}, \Delta) = M_0 \int \overline{P_s}(\mathbf{R}, \Delta) \exp\left[i2\pi\mathbf{q} \cdot \mathbf{R}\right] d\mathbf{R}.$$
 (3.17)

Examination of equation 3.17 shows that $M(\mathbf{q}, \Delta)$ divided by M_0 and $\overline{P_s}(\mathbf{R}, \Delta)$ are Fourier conjugates of one another. Therefore, we can recover the average propagator behaviour by Fourier transformation of the signal we obtain from the PGSE experiment.

The average propagator theory can be related to diffusion via Fick's second Law

$$\frac{\partial \overline{P_s}}{\partial t} = D\nabla^2 \overline{P_s} \tag{3.18}$$

If we assume the initial condition of zero displacement for the molecules, $\overline{P_s}(\mathbf{R}, 0) = \delta(\mathbf{R})$, and the boundary condition $\overline{P_s}(\mathbf{R}, \Delta) \to 0$ when $\mathbf{R} \to \infty$, we obtain

$$\overline{P_s}(\mathbf{R}, \Delta) = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \exp\left[-\frac{\mathbf{R}^2}{4Dt}\right].$$
(3.19)

However, in an NMR experiment, we will typically only encode for diffusion along one axis. In this situation the average propagator becomes

$$\overline{P_s}(Z,\Delta) = \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{Z^2}{4Dt}\right].$$
(3.20)

Solving for the substitution of equation 3.20 into equation 3.17, we obtain the measured signal from a PGSE experiment in the short δ limit(20)

$$M(q,t) = M_0 \exp\left[-4\pi^2 q^2 D\Delta\right] . \qquad (3.21)$$

2 Pulsed Field Gradient Stimulated Echo (PFGSTE)

In many cases we want to study the diffusion or flow in a sample over a longer period of time than the transverse relaxation will permit. In this situation, we can use a pulsed field gradient stimulated echo experiment. Once we have used the gradients to apply a phase shift to the spins, instead of just refocussing the magnetisation with a 180° pulse, we use a 90° pulse to store the magnetisation in its shifted state along the z-axis. We then wait for a time Δ before using another 90° pulse to return the magnetisation to the transverse plane. As with the regular stimulated echo experiment, the time Δ is limited by T_1 . Once the magnetisation is back in the transverse plane, we apply the second set of gradients to apply a phase shift to the



Figure 3.15: Pulsed field gradient stimulated echo pulse sequence

magnetisation. The drawback with the technique is that, as with the normal stimulated echo, the signal amplitude is only half that of a spin echo. The signal attenuation from the PFGSTE is described by

$$M(q,t) = \frac{M_0}{2} \exp\left[-4\pi^2 q^2 D\Delta\right] \,. \tag{3.22}$$

Other than the loss of amplitude due to the loss of one of the transverse components during storage, the theory is the same as that of the pulsed field gradient spin echo experiment.

3 Narrow Pulse Approximation

For our calculations, the gradient pulses have been treated as delta functions. In reality, this is not the case as the gradient pulse must have a finite width to impart the phase shift upon the spins. For a situation where $\delta \ll \Delta$ and any characteristic time associated with restricted diffusion, the duration of the gradient pulse is considered sufficiently short that the pulse length can be treated as a delta function for all practical purposes. For these cases, we are said to be in the narrow pulse approximation.

If we cannot assume $\delta \ll \Delta$, we then must modify the equation to account

of the finite gradient times, which then results in the measured signal being described by (20)

$$M(q,t) = M_0 \exp\left[-4\pi^2 q^2 D(\Delta - \frac{\delta}{3})\right].$$
(3.23)

As our gradients are relatively weak and our δ finite, this is the form we will use throughout this thesis.

4 Bipolar Gradients

In many situations where we want to measure diffusion, there exist background gradients in the system. The way we avoid the unwanted influence of the added dephasing from these background gradients during diffusion measurements is through bipolar gradients, which break a long gradient pulse into two parts.



Figure 3.16: Bipolar gradients

The first field gradient pulse in the pair imparts a phase shift of:

$$\Phi_1 = \gamma \mathbf{g} \cdot \mathbf{r} \tag{3.24}$$

A 180° pulse then inverts the phase shift. The second pulse in the bipolar pair now imparts a negative phase shift

$$\Phi = (-\Phi_1) + (-\Phi_2) \tag{3.25}$$

to continue the dephasing of the spins. However, any resulting dephasing that came about from background gradients in the first gradient pulse will be inverted and cancelled during the second gradient pulse. The bipolar gradients can also be used to compensate for flow during the application of the gradient. The inversion will undo the added dephasing from the molecules flowing through the applied field gradients.

The bipolar pulsed field gradients also have the added advantage that they can be used to avoid the interaction between the applied field gradients and local inhomogeneities in the magnetic field caused by some samples. Some techniques to remove this interaction often require long phase cycles(21; 22) or spoiler gradients(23; 24). Sørland(25) showed that by using unequal bipolar gradients, the interaction can be removed with only a simple four step phase cycle, greatly decreasing the required experiment time.
Chapter 4

Porous Media

I Introduction

Porous media are a class of materials that are common in research, industry, and our everyday lives. Some are obvious, such as rocks, wood, or bone. Others are less apparent, such as meat, chemical reactors, and clay. A fundamental question in porous material research concerns the behaviour of fluid within a porous medium. This behaviour is important to a wide range of applications, from oil recovery to medicine(26) to food science. Despite its importance, the behaviour of fluid in these materials, particularly at the microscopic level, is often poorly understood, even after decades of research. The irregular shapes of pores make them difficult to model; transport equations cannot be solved at the microscopic level of porous media, as the pore geometry is too complex. In the case of multi-phase saturation, detailed knowledge of the distribution of fluid phases throughout the porous medium is also needed. In addition, surface effects between the pore surface and saturating fluid can greatly influence how fluid moves through the medium(27; 28). The difficulty in theoretical treatment of these systems makes experimental work with porous media particularly important.

Nuclear magnetic resonance has been widely used for studies in fluid saturated porous media(29; 30; 31; 32; 33; 34; 35; 36; 37; 38; 39; 40). The technique is non-invasive and can be used upon opaque samples; use of the diffusion and flow techniques mentioned in the previous chapter can be used to look at the movement of fluids without a need for sample transparency nor tracers. NMR also has the advantage of being a bulk volume spectroscopy technique; the entire sample contributes to the measured signal. Other types of spectroscopy, such as IR or UV, only characterise the surface of a large sample via reflectance.

There exist different types of NMR techniques depending on the pore scale one wishes to investigate. For the smallest pores on the order of nanometres, cryoporometry(41; 42) is the main technique, using NMR to measure the size dependent freezing point depression that occurs in nanometre scale pores. For pores on the millimetre scale, the pore space can be imaged directly. The techniques in this thesis focus on the intermediate range, where pores are on the micron scale. It is these length scales where diffusion and relaxometry techniques are most useful. For larger pores, the behaviour of fluid in the pores is indistinguishable from that of bulk fluid. Depending on the systems, sometimes micron-sized pores can be imaged directly as well, though we will not cover that in this thesis.

As the samples used for this thesis are geological in nature, we focus mostly upon the particular properties of geological porous media. The techniques developed later herein, however, have the potential for application beyond rocks and granular materials and a few examples are given. While an important branch of NMR work is being performed using hyperpolarised gases to probe the structure of porous materials(43; 44; 45; 46), we limit our study to liquids. Descriptions of the samples used and the X-ray CT analysis of the samples can be found in Appendix A of this thesis.

II Basic Porous Medium Characteristics

A porous medium is described by several basic features such as porosity, pore size, pore shape, permeability, tortuosity, and wettability. How fluids behave in a porous medium is greatly influenced by these properties. We give here an overview of the various characteristics and some of the influence they have on NMR measurements.

1 Pore size and shape

The size of the pores influences the amount of fluid the medium can contain. The shape and size of pores is important with regards to fluid transport throughout the medium. Delineating a porous medium into individual pores can be very tricky. In modeling porous materials, we will often simplify the pore geometry to a series of connected spheres, boxes, or occasionally cylinders. In real world systems, the pore geometries are usually irregular and what constitutes a pore is not as clear cut. In image analysis of the pore space, it is often difficult to say precisely where one pore ends and another begins, or whether an area of void space is a single pore or made up of several smaller pores. NMR takes another approach to estimate pore size in a system.

As pore size influences the NMR relaxation rate, it can be used to find the volumetrically weighted pore size distribution. Brownstein and Tarr discussed the influence that the pore scale and the relaxation rate had on the signal in a porous material (47). The pore scale is defined as l_s , which reflects the pore size. The relaxation length is given as

$$l_{\rho} = \frac{D_0}{\rho} \,, \tag{4.1}$$

where D_0 is the fluid diffusion coefficient and ρ is surface relaxivity. This length gives the distance a spin-bearing molecule will diffuse before the magnetisation relaxes. If $l_s \ll l_{\rho}$, then we are said to be in the fast diffusion limit. All the fluid molecules have an opportunity to probe the pore surface before relaxing, producing a mono-exponential relaxation decay rate for the pore. If $l_s \gg l_{\rho}$, the diffusion of the molecules no longer overcomes the relaxation at the pore surfaces and the relaxation in the pore is not uniform, producing a multi-exponential decay.

When we are in the fast diffusion limit, the relationship between pore size and relaxation time can be described by the equation(33):

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2}^{bulk}} + \rho_{1,2} \frac{S}{V}$$
(4.2)

where ρ_1 and ρ_2 are the surface relaxivities for T_1 and T_2 relaxation respectively. Larger pores have a smaller surface area to volume ratio, producing longer relaxation times, while smaller pores have a larger surface area to volume ratio that gives shorter relaxation times. The larger the surface to volume ratio is, the more often fluid molecules will encounter the pore surface and experience surface relaxation.

An inverse Laplace transform of the relaxation signal, discussed further in Chapter 5, gives the distribution of T_1 or T_2 relaxation times, which usually mirrors the distribution of pore sizes in a sample. This relation between pore size and relaxation will be referred to multiple times throughout this manuscript, as it is a major foundation of the experiments of this thesis.

The surface relaxivity, ρ , reflects the interaction of a fluid with the pore surface. This interaction is manifested by an increase in the rate of magnetisation relaxation. The surface relaxivity for T_1 , ρ_1 , comes from the ability of the dipole-dipole interaction to induce transitions between the spin energy states(48). In bulk fluid, the dipole-dipole interaction is averaged out by molecular tumbling. When the fluid molecules come into contact with the pore surface, this tumbling is hindered and the energy of the spins can be transferred to the environment. As mentioned in Chapter 2, energy can only be exchanged with the environment if the frequency is near the Larmor frequency. As the Larmor frequency increases with applied field, it is less likely that the Larmor frequency and the hindered molecular tumbling frequency will overlap. Consequently, ρ_1 will decrease with increased applied magnetic field.

The frequency dependence of ρ_2 is more uncertain. Again, ρ_2 comes about by the pore surface preventing the fluid molecules from tumbling freely. In the case of ρ_2 , the dipolar interaction leads to additional dephasing of the spin coherences, leading to increased T_2 relaxation. This behaviour is field independent. In addition, the proximity to paramagnetic impurities in the porous material may lead to additional dephasing of the spin coherence. This effect is field dependent. Unfortunately, internal gradients have confounded attempts to qualify a frequency dependence of ρ_2 .

When the two types of surface relaxivities are compared, the T_2 relaxation tends to be more strongly influenced by the surface relaxivity than T_1 . Therefore, T_2 relaxation is often preferred for pore size studies as it gives a more detailed reflection of the pore space.

2 Porosity

Porosity is the measure of the void space in a sample. The complete measure of porosity of a sample is referred to as the total porosity, which can be found



Figure 4.1: Different classification of pores(49)

using the NMR signal intensity. The fluid signal intensity in the sample is measured and compared to the signal intensity of a known volume of the saturating fluid to determine the volume of fluid present in the sample. Division of the fluid volume by the total sample volume yields the total porosity of the sample.

Of particular importance is the open or effective porosity. Effective porosity is the ratio of the pore volume accessible from the surface of the sample to the total pore volume. Fluid contained in the open pores is considered reducible and can be recovered while fluid in closed pores is considered irreducible and cannot be recovered. In geological samples, this closed porosity usually comes about through metamorphosis of the pore space due to geological pressures. For other materials, the closed porosity usually comes about during manufacture. In addition, fluid bound in capillaries or clay is also considered closed, as the fluid in them also cannot be obtained even though they may be connected to the sample surface. The effective porosity of a sample is generally less than its total porosity, as most systems have at least some porosity cutoff from the rest of the system. Current techniques to determine the effective porosity using NMR are imprecise. The most commonly used method is to declare a cutoff time in the T_2 spectrum, and any signal that occurs below the cutoff time is considered closed. The cutoff times are empirical values given to various classes of geological materials.

3 Tortuosity

The tortuosity of a sample is defined as the complexity of the flow path. The greater the path length a fluid molecule must take to travel a given distance, the greater the tortuosity of the sample. There are a variety of different ways to attempt to quantify tortuosity. The simplest and most practical of these is to define tortuosity as the ratio between the length of a curve and the distance between its end points. The tortuosity of a sample can vary with the length scale under observation; the tortuosity may be low for a short length scale but become higher at larger observation scales. In NMR, the tortuosity of a sample can sometimes be deduced by comparing how far the molecules actually traveled to how far unrestricted molecules would have traveled in the same period of time. We define tortuosity here as

$$t = \frac{D_0}{D_{eff}},\tag{4.3}$$

though some sources will use the inverse of this relation. The tortuosity of a medium will impact the movement of fluid throughout it, so it is an important factor with regards to fluid behaviour in a porous material. Measurement of tortuosity in tumors, for example, is an important tool in selecting a cancer treatment option(50).

4 Permeability

Permeability is a measure of the amount of interconnected porosity and the ease of which fluid can travel through the sample. This is commonly described in terms of Darcy's law:

$$Q = \frac{\kappa A}{\mu} \frac{P_a - P_b}{L} \tag{4.4}$$

where Q is the volumetric flow rate, κ is the permeability, A the cross sectional area, μ is the dynamic viscosity, L is the distance between the two points a and b, and $P_a - P_b$ is the pressure drop between the two points. The more pressure required to reach a given flow rate, the less permeable the porous system is. Darcy's law only holds true for laminar flow.

The permeability of a system is described in two ways, absolute permeability and effective permeability. The absolute permeability of a sample is the ability of a single fluid to flow throughout it. The effective permeability of sample is its ability to transport a particular fluid in the presence of other, immiscible fluids. The absolute permeability of a system is roughly related to porosity. In general, the greater the porosity of the system, the higher its permeability. This is because the greater amount of void space in a sample usually makes it easier for fluid to flow through the pores. However, situations do arise where this does not hold true, for example if the pore throats connecting the pores are narrow.

5 Wettability

Many materials exhibit a property called wettability. The wettability of a substance is its "preference" to be in contact with one fluid phase over another. A water-wet material prefers to be in contact with water over oil and the reverse is true for an oil-wet material. This preference is caused by the surface chemistry of the material. The simplest way to measure wettability is to place a drop of fluid on a surface and to measure the contact angle the drop makes with the surface. Low contact angles mean the surface is wetting, high contact angles mean the surface is non-wetting, and a contact angle of about 90° means the surface is non-preferential.

Unfortunately, the contact angle method to determine wettability is applicable to only certain geometries. Contact angle measurements are not practical in porous materials and so other methods to try to determine wettability have been developed. Several experimental NMR techniques(51; 52; 53; 54) have been performed to estimate wettability. These experiments tend to focus on determining which phase is predominantly in contact with the pore surfaces. Wettability is considered to be an important factor in the effective permeability of a porous system.

III Internal Gradients

Internal gradients have been briefly mentioned previously in this manuscript. Here, we give a more thorough treatment of the topic. The magnetic susceptibility of a material χ is the extent to which it will magnetise when placed in a magnetic field. When there exists a magnetic susceptibility difference between materials in a sample, for example between a porous matrix and a saturating fluid, local magnetic fields with associated local magnetic field gradients develop at the interfaces. These local fields superpose with the applied magnetic field \mathbf{B}_0 , such that the effective magnetic field is no longer homogeneous throughout the sample. The spatial variations of inhomogeneities in the local magnetic field are referred to as "internal gradients".

The main factors governing the strength of these gradients depend on the susceptibility difference between the materials, the applied magnetic field, and the pore size, though grain size, pore shape, and the geometry of the pore network also have an influence. The internal gradient intensities are roughly inversely proportional with pore size and scale linearly with applied field strength as

$$g \sim \Delta \chi B_0 \tag{4.5}$$

where g is the local magnetic field gradient experienced by the spins and $\Delta \chi$ is the magnetic susceptibility difference between the fluid and pore surface.

We consider the simplest case of an isolated spherical pore of radius R, filled with a fluid of magnetic susceptibility χ_p embedded in a material of susceptibility $\chi_m(55)$. When the system is subjected to the applied magnetic field **B**₀, the magnetic moment produced by the pore is given as

$$\mathbf{m} = \frac{\mu_p - \mu_m}{\mu_p + 2\mu_m} R^3 \mathbf{B_0} \tag{4.6}$$

where **m** is the magnetic moment, $\mu_p = 1 + 4\pi\chi_p$ and $\mu_m = 1 + 4\pi\chi_m$ are the magnetic permeability for the pore and medium respectively. For the case of isotropic susceptibilities, where the magnetic susceptibilities are the same in all directions, **m** becomes

$$\mathbf{m} \approx \frac{4}{3} \pi R^3 \Delta \chi \mathbf{B_0} \tag{4.7}$$

The magnetic field a distance \mathbf{r} from \mathbf{m} is given as

$$\mathbf{B}(\mathbf{r}) = \mathbf{B}_0 + \Delta \mathbf{B}(\mathbf{r}), \qquad (4.8)$$

where

$$\Delta \mathbf{B}(\mathbf{r}) = \frac{3(\mathbf{m} \cdot \mathbf{r})\mathbf{r} - |\mathbf{r}^2|\mathbf{m}}{|\mathbf{r}|^5}.$$
(4.9)

The magnetic field outside the sphere will be non-uniform. An ellipsoidal pore will produce a uniform magnetic field within the pore space, but most other pore geometries will produce non-uniform magnetic fields within the pore. Solving the spatial dependence for even simple geometries such as cylinders is non-trivial(56), and impossible in most real world porous systems as they are irregular. Again, this underscores the importance of experimental porous material research.

Most systems consist of more than one pore. When multiple pores exist in close proximity to one another, the magnetic field is a superposition of the dipoles:

$$\Delta \mathbf{B}(\mathbf{r}) = \sum_{k} \Delta B_d(\mathbf{r} - \mathbf{r}_k)$$
(4.10)

where $\mathbf{r}_{\mathbf{k}}$ is the center of the dipole k and ΔB_d is the local dipolar field centered at $\mathbf{r}_{\mathbf{k}}$. However, due to the \mathbf{r}^{-3} dependence, variations in the applied magnetic field occur mostly within the pore as opposed to between different pores. Due to the difficulty in calculation of ΔB , we often attempt to characterise it in our systems experimentally.

IV Transport theory

The majority of this thesis is concerned with tracking the movement of fluid between pores as a function of time. We present in this section some of the basic theory behind fluid movement using a two pore exchange theory and then touch upon a three pore exchange situation.

1 Two Pore Exchange Theory

We begin with the simple case of two connected pores, A and B. Fluid molecules are able to move between the two pores

$$A \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} B \tag{4.11}$$

with the steady state constraint

$$k_{AB}N_A = k_{BA}N_B. aga{4.12}$$

The number of molecules in the pores are N_A and N_B respectively. We are considering the steady state condition, so the value of N_A and N_B must remain constant. Over an interval of time t, the spin populations of the pores at any point in time are described by: N_{AA} , which began in A and currently reside in A, N_{AB} , which began in A but have migrated to B, N_{BB} , which began in B and currently reside in B, and N_{AB} , which began in B but migrated to A. The initial conditions for this system are:

$$N_{AB} = N_{BA} = 0$$

$$N_{AA}(0) = N_A$$

$$N_{BB}(0) = N_B$$
(4.13)

No molecules have exchanged yet, so all molecules reside in their starting pores. Because of the steady state condition, at any point in time

$$N_{AA}(t) + N_{BA}(t) = N_A$$
$$N_{BB}(t) + N_{AB}(t) = N_B$$
(4.14)

To find the rate at which molecules move from pore A to pore B and vice versa, we use the Bloch-McConnell equations(57):

$$\frac{dN_{AA}}{dt} = -k_{AB}N_{AA} + k_{BA}N_{AB}$$

$$\frac{dN_{BB}}{dt} = -k_{BA}N_{BB} + k_{AB}N_{BA}$$

$$\frac{dN_{AB}}{dt} = k_{AB}N_{AA} - k_{BA}N_{AB}$$

$$\frac{dN_{BA}}{dt} = k_{BA}N_{BB} - k_{AB}N_{BA}$$
(4.15)

We can then use the relations

$$N_{AA} = N_A - N_{AB}$$
$$N_{BB} = N_B - N_{BA} \tag{4.16}$$

to reduce from four equations to two:

$$\frac{dN_{AB}}{dt} = k_{AB}(N_A - N_{AB}) - k_{BA}N_{AB}$$
$$\frac{dN_{BA}}{dt} = k_{BA}(N_B - N_{BA}) - k_{AB}N_{BA}$$
(4.17)

This then simplifies to

$$\frac{dN_{AB}}{dt} = k_{AB}N_A + (-k_{AB} - k_{BA})N_{AB}$$
$$\frac{dN_{BA}}{dt} = k_{BA}N_B + (-k_{AB} - k_{BA})N_{BA}$$
(4.18)

To aid in solving the equations, we change into matrix notation. Our equations can now be written in the form

$$\frac{d\mathbf{N}}{dt} = \mathbf{AN} + \mathbf{C} \tag{4.19}$$

where

$$\mathbf{A} = \begin{pmatrix} -k_{AB} - k_{BA} & 0\\ 0 & -k_{AB} - k_{BA} \end{pmatrix}, \qquad (4.20)$$

$$\mathbf{N}(\mathbf{t}) = (N_{AB}, N_{BA}), \qquad (4.21)$$

and

$$\mathbf{C} = (k_{AB}N_A, k_{BA}N_B). \tag{4.22}$$

The solution to these linear differential equations is

$$\mathbf{N}(t) = \exp(\mathbf{A}t)(\mathbf{N}(t=0) + \mathbf{A}^{-1}\mathbf{C}) - \mathbf{A}^{-1}\mathbf{C}$$
(4.23)

For our initial condition N(t = 0), we simply have

$$\mathbf{N} = (0,0) \tag{4.24}$$

In addition, to solve equation 4.23, we then need to take the inverse of matrix **A**, which is:

$$\mathbf{A}^{-1} = \frac{1}{(-k_{AB} - k_{BA})(-k_{AB} - k_{BA})} \begin{pmatrix} (-k_{AB} - k_{BA}) & 0\\ 0 & (-k_{AB} - k_{BA}) \end{pmatrix}$$
(4.25)

To simplify our equations, we set a dummy variable

$$\mathfrak{x} = (-k_{AB} - k_{BA})(-k_{AB} - k_{BA}). \tag{4.26}$$

We can now enter our matrices \mathbf{A} , \mathbf{A}^{-1} , \mathbf{C} into equation 4.23. As the initial matrix $\mathbf{N}(\mathbf{0})$ was simply zero, that term goes away so when we substitute our values into 4.23, we obtain

$$N(t) = \exp\left(\frac{(-k_{AB} - k_{BA} & 0)}{0 & (-k_{AB} - k_{BA})}\right) \times \frac{1}{2} \left(\frac{(-k_{AB} - k_{BA} & 0)}{0 & -k_{AB} - k_{BA}}\right) \times \left(\frac{k_{AB}N_A}{k_{BA}N_B}\right) - \frac{1}{2} \left(\frac{(-k_{AB} - k_{BA} & 0)}{0 & -k_{AB} - k_{BA}}\right) \times \left(\frac{k_{AB}N_A}{k_{BA}N_B}\right)$$
(4.27)

Because \mathbf{A} is a diagonal matrix, the exponential of the matrix is simply the exponential of each matrix element. This then reduces to

$$N(t) = \frac{1}{\varpi} \left(\begin{array}{c} (-k_{AB} - k_{BA})N_{AB} \exp((-k_{AB} - k_{BA})t) \\ (-k_{AB} - k_{BA})N_{BA} \exp((-k_{AB} - k_{BA})t) \end{array} \right) - \frac{1}{\varpi} \left(\begin{array}{c} (-k_{AB} - k_{BA})N_{AB} \\ (-k_{AB} - k_{BA})N_{BA} \end{array} \right)$$
(4.28)

and then further simplifies to

$$\begin{pmatrix} N_{AB}(t) \\ N_{BA}(t) \end{pmatrix} = \frac{1}{k_{AB} + k_{BA}} \begin{pmatrix} N_{AB}(1 - \exp(-(k_{AB} + k_{BA})t)) \\ N_{BA}(1 - \exp(-(k_{AB} + k_{BA})t)) \end{pmatrix}$$
(4.29)

With the above equations, it is now a simple matter to solve for $N_{AA}(t)$ and $N_{BB}(t)$

$$\begin{pmatrix} N_{AA}(t) \\ N_{BB}(t) \end{pmatrix} = \frac{1}{k_{AB} + k_{BA}} \begin{pmatrix} N_A - N_{AB}(1 - \exp(-(k_{AB} + k_{BA})t)) \\ N_B - N_{BA}(1 - \exp(-(k_{AB} + k_{BA})t)) \end{pmatrix}$$
(4.30)

The characteristic time of exchange between the pores A and B can then be described as:

$$\lambda = \frac{1}{k_{AB} + k_{BA}}.\tag{4.31}$$

2 Multi-pore Exchange Theory

The Bloch-McConnell equations can be expanded from two site exchange up to theoretically any number of sites in the form:

$$\frac{dN}{dt} = -\sum_{j\neq i} k_{ij} N_{ii} + \sum_{j\neq i} k_{ij} N_{ij}$$
(4.32)

However, the analytical solution of more than two sites quickly becomes intractable and provides little useful information on the dynamics of the system(58). Fitting simulations of molecular movements based on the three pore equations could be used to find more precise exchange times from measured data, but is beyond the scope of this PhD.

V X-Ray CT

To provide additional validation of our experimental NMR results, we worked with collaborators at the Australian National University, who performed X- Ray CT experiments upon the samples. We provide here a brief overview of the X-Ray CT process and the subsequent analysis.

1 X-Ray CT Setup

The X-Ray CT machine used for characterisation is a home built setup. The X-ray source (X-Tek RTR-UF225), sample platform (Newport RV120PP), and CCD camera (Roper PI-SCX100:2048) plus scintillator are all on a sliding rail. This allows the distances between the components to be varied such that the magnification factor can range from near unity to over a 100. The X-ray source produces X-rays in the energy range of 30-225 $\frac{kV}{mA}$ with a 2-5 μm spot size. The rotation stage has accuracy up to 1 millidegree. The CCD camera has a $70 \times 70 \, mm^2$ active area with 2048 × 2048 16-bit pixels.



Figure 4.2: X-Ray CT setup

2 X-Ray CT Imaging

The source produces X-rays by focusing a high energy electron beam onto a metal target. The interaction between the energetic electrons and the metal produces polychromatic X-rays via bremsstrahlung, X-rays with a wide range of energies. The sample is then bombarded with the resultant Xrays. Photons will be attenuated as the X-rays pass through the sample. The extent of absorption depends on the structure and composition of the material. In addition, when polychromatic X-rays travel through a sample, the lower energy x-rays, called soft x-rays, are more easily attenuated than the hard x-rays of higher energy. As the beam passes through the sample, the loss of the soft x-rays will leave only the hard x-rays, causing the beam to be more penetrating, referred to as beam hardening. The X-rays are pre-filtered, usually with a piece of aluminium, to avoid this phenomenon.

Opposite the X-Ray source is an array of detectors, which measure the number of photons that have managed to penetrate through the sample. These days, a CCD camera is usually used for photon detection. The measured array of photon intensities is referred to as a slice. The sample is then rotated slightly and the sample is irradiated with X-rays again. This procedure is repeated until the sample has been rotated through 360°. The number of rotations necessary for proper imaging is governed by:

$$N_{\theta} = \left(\frac{\pi}{2}\right) N_w \tag{4.33}$$

where N_w is the pixel width of the detector.

3 Image Reconstruction

To produce an image, the projections must be a linear interaction between the probe and sample. This unfortunately is not the case for X-ray tomography, which is dominated by the X-ray attenuation. To over come this, Beer's law of attenuation(59) is used to manipulate the data into a linear form. Once the data has been linearised, the data is pre-processed and then reconstructed using the Feldkamp algorithm. This processing is performed at the Australian Partnership for Advanced Computing (APAC) national facility on a Compaq AlphaServer super-computer.

4 Image Analysis

Once the image has been reconstructed, several pore properties were calculated. Two methods were used to estimate pore size. The simplest method is that of inscribed spheres, where we determine the largest radii of spheres that could fit into the pores of the sample. While this method is useful for spherical pores, it can be inaccurate for more irregular pores. The second method is that of pore partitioning. This technique calculates the volume of a pore and then finds the radius of a sphere of equivalent volume. The inter-pore spacing was also calculated in two methods. The first is the centre of mass calculation, which gives the centre of the sphere to be its centre of gravity. The second, the Euclidean distance transformation, considers the centre of the pore as the centre of the largest sphere that can fit into the pore. The distance between the pore centres and their nearest neighbours was then calculated. The distances between the pore centres were calculated as both volume-weighted and pore-weighted. In the volume weighted calculation, the inter-pore spacings are weighted by the average of the pore volumes of the associated pores. For the pore weight calculation, each pore had the same weight. Tortuosity was estimated by solving the Laplace equation for diffusivity in the image.

Chapter 5

Inverse Laplace Transform

I Introduction

The inverse Laplace transform is a method to extract characteristic times from exponential decays. For a given mono-exponential decay

$$M(t) = \exp\left(\frac{-t}{\tau}\right) \tag{5.1}$$

M is the measured signal, t is time and τ is the characteristic time. From Figure 5.1, we can see that short characteristic times produce fast exponential decays while long characteristic times produce slow exponential decays. Even if the exponential decay has multiple components, the inverse Laplace transform can return the characteristic times for the different components.

Many of the measured NMR properties produce signals that are decaying exponentials. The ability to take the decaying exponential signals and transform them into distributions of these properties has the potential to give us a wealth of information about our systems. This makes the inverse Laplace transform an invaluable tool in materials characterisation. The ability to perform two dimensional Laplace inversions is relatively recent(60; 61) and this



Figure 5.1: Simulated exponential decays transformed by a 1D Inverse Laplace Algorithm

thesis focuses on the development of several new 2D inverse Laplace spectroscopy techniques. Therefore, the inverse Laplace transform is an integral part of this work, so in this chapter we seek to provide a basic introduction to the theory behind it.

II Inverse Laplace Transform Integral

The inverse Laplace transform is used to analyse linear dynamic systems, which are described by first order differential equations. The Laplace integral is(62):

$$F(s) = \int_0^\infty f(\tau) \exp(-s\tau) d\tau, \qquad (5.2)$$

where F(s) is the signal and $f(\tau)$ is the transform. The equation is a linear operator.

The measured data in an inverse Laplace experiment is similar in form to equation 5.2, where a set of characteristic times gives a signal in the time domain. The data has the structure of a Fredholm integral of the first kind(63)

$$m(t) = \int f(\tau)k_1(t,\tau)d\tau + \epsilon, \qquad (5.3)$$

where m(t) is the system's measured response as a function of t, $k_1(t,\tau)$ is a known function of variables t and τ reflecting the physics of the problem, $f(\tau)$ is the probability density to be estimated and ϵ is the known error characteristic of the measurement. The measure of the variability of a function's derivatives is described as smoothness. The smaller the variability, the smoother the function is considered to be. The integration of $f(\tau)$ with $k_1(t,\tau)$ serves to dampen the high frequency components, making m(t) a smoother function than $f(\tau)$; the low variability of $k_1(t,\tau)$ averages out the variations in $f(\tau)$. Therefore, taking the inverse of the data to find $f(\tau)$ from m(t) tends to intensify the high frequency components of $f(\tau)$. For an ideal system, this would not be a problem. Unfortunately, real measurements contain noise, and these small perturbations in the measured data can lead to large perturbations in the resulting $f(\tau)$. Because of this, the inversion of Fredholm integrals with smooth kernels is considered an ill-conditioned problem; small changes in the data can lead to large changes in the resulting distribution. Obviously, this behaviour leads us to question the stability of the inverse Laplace transform, and several regularisation methods (section 5.5) have been applied to improve the stability of the transform.

The form of the inverse Laplace integral is very similar to that of the Fourier transform. Whereas the Fourier transform is used to find frequencies present in an oscillating signal, the inverse Laplace transform is used to the find the characteristic times of a decaying exponential. However, there exists a critical difference between the two transforms. The Fourier transform is well defined and stable; there is only one possible inverse solution. The inverse Laplace transform, on the other hand, is ill-posed. For a given exponential decay, there are a multitude of possible combinations of characteristic times which will fit the solution equally well. By applying regularisation, we average out the small variations in the solution to add stability to the inversion so that a unique solution can be found. There is no general analytic method that will take measured data and produce a stable, unique solution. Therefore, when it comes to inverting measured data, we must move away from the integral form of the inverse Laplace transform and resort to a numerical solution instead.

III Discretisation

As mentioned, we cannot solve the inverse Laplace equation analytically for measured data so we need to use numerical methods to perform the inversion. We change the continuous integrals into discrete matrices of the form

$$M = KF + E \tag{5.4}$$

where M is the measured data, K is the kernel, F is the probability density and E is noise. These variables are in the real domain such that

$$M \in \Re^{m},$$

$$K \in \Re^{m \times n},$$

$$F \in \Re^{n},$$

$$E \in \Re^{m}.$$
(5.5)

The inverse Laplace transform attempts to determine F given the measured data and the kernel. The size of F and its range are supplied by the user. While F does not necessarily need to be the same size or smaller than M, it is considered good practice as the additional points would be redundant; no additional information is gained through the extra points as we are limited in the extent of our information from the number of our experimentally acquired points. While the acquisition axis is given by the measurement, affecting Mand K, F and K share the inversion axis, which is user supplied during a separate post-processing step and controls the space in which the solution is searched for. K contains the set of possible solutions. For example, for a transverse relaxation experiment, a single element of K could be

$$K_{ij} = \exp\left(-\frac{t_i}{T_{2j}}\right) \,. \tag{5.6}$$

Solving for F involves finding the contribution of each K_j , a column of K representing a discretised exponential decay, to the solution.

IV Singular Value Decomposition

The singular value decomposition (SVD) is a matrix decomposition method (64; 65)used for factorisation of a real or complex rectangular matrix and is

performed to reduce a dataset containing a large number of values to one that contains fewer values but yet still reflects the variability of the original data. While this compression method can be useful in the one dimensional inverse Laplace transform to speed up the computation, it is critical for higher dimensions of the inverse Laplace transform so that the matrix sizes do not exceed the computer system's capabilities.

Any $m \times n$ rectangular matrix M can be factored into

$$M = U\Sigma V^{T} = (orthogonal)(diagonal)(orthogonal)$$
(5.7)

U and V are unitary matrices where the columns of U $(m \times m)$ are eigenvectors of MM^T while the columns of V $(n \times n)$ are eigenvectors of M^TM . Σ is a diagonal matrix of the singular values (σ) of M. Singular values are the square roots of the nonzero eigenvalues of M^TM . The first r spaces on the diagonal of Σ are filled by singular values, where r is the rank of M. A rank of a matrix is the number of linearly independent rows in the matrix. Common convention sorts the values of Σ in descending order. From the singular values we can immediately calculate the condition number of the matrix M by taking

$$C = \frac{\sigma(1)}{\sigma(r)} \tag{5.8}$$

where C is the condition number, and $\sigma(1)$ and $\sigma(r)$ are respectively the largest and smallest singular values of the matrix. The condition number represents the degree of linear independence between the columns of the matrix M, which means whether any of the columns in the matrix can be written as linear combinations of other columns in the matrix. 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.

V Regularisation

Regularisation is the process to stabilise the inversion algorithms so that they force a unique solution and are less sensitive to noise. Regularisation also helps return smooth solutions. The Non-Negative Least Squares (NNLS) algorithm (66) often used in the inverse Laplace transform tends to produce solutions consisting of numerous sharp peaks. While these solutions do fit the exponential decay, they are non-physical, as most of the physical phenomena we investigate involve smooth distributions of values instead of sharp, discrete values.

The simplest regularisation method is truncation of the singular value decomposition (67). While some of the singular values will have too much noise to be of use, the first components of the SVD hold useful information about the solution. Therefore, 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

$$\Sigma_k = \sum_{i=1}^k U_i^T M_i V_i \,, \tag{5.9}$$

where Σ_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. Two main issues arise with truncated singular value decompositions: the regularisation

has no positivity constraint, and knowledge of the unknown solution F is needed to determine the optimal cutoff value.

Another method is Tikhonov regularisation(68), which is a damped least squares method. We start with an ill-posed system M = KF, where F is a column vector of size n, M is a column vector of size m, and K is an $m \times n$ matrix. We then rewrite the problem as:

$$\chi^2 = \| KF - M \|^2 + \alpha \| LF \|^2 .$$
 (5.10)

where $\|\cdot\|$ indicates the sum of the matrix elements squared, sometimes referred to as the Frobenius Norm(69; 65), and *L* indicates the regularisation method, in this case Tikhonov regularisation. We seek to minimise χ^2 for the chosen α , the regularisation factor, which regulates the amount of smoothing applied to the inversion. The optimal α for an inversion is usually chosen by performing a chi-squared analysis of the data. When the proper value of α is chosen, the ill-posed nature of the inversion is lessened. The inversion tries to minimise the difference between the measured and calculated signal. Because of the noise in the acquired signal, there will be numerous possible minima, hence the ill-posed nature of the inversion. With regularisation, the influence of noise is reduced so that the multitude of minima will be smoothed into a single minimum.

Several transforms of the data are taken over a given range of α . The values of χ^2 are plotted as a function of α , producing an L-shaped curve(70), shown in Figure 5.2. The value of α that just minimises the value of χ^2 and no further is used, as this value is the least sensitive to random noise. By our convention, α values smaller than this value are over-smoothed, while larger values are under-smoothed. The quadratic nature of the Tikhonov regularisation forces a unique solution.

Tikhonov regularisation combined with truncated SVD using a large trun-



Figure 5.2: The L-shaped curve used for α value optimisation. The correct alpha value is at the start of the χ^2 plateau.

cation parameter k for compression has been used for regularisation for the majority of the inverse Laplace transforms performed in this thesis. A third method of regularisation is mentioned briefly in the chapter on multidimensional inverse Laplace techniques.

VI Inversion

Regardless of the regularisation method used, the actual inversion for the differing methods is performed by minimising the sum of squared differences between the measured and calculated data

$$\min \sum \| M - KF \|^2 + \alpha \| LF \|^2 .$$
 (5.11)

The non-negative least squares method is often employed, which minimises for F but contains the constraint that the solution elements of F must be positive. The NNLS algorithm simply limits the possible test solutions to positive values:

$$\hat{F} = \underset{F \ge 0}{\operatorname{argmin}}(\chi^2). \tag{5.12}$$

VII Two Dimensional Inverse Laplace Transform

While a one dimensional inverse Laplace transform gives useful information about a system, in many cases the results are ambiguous. In multi-phase systems, we are often unable to reliably identify the different fluid components in the inverted one dimensional spectrum. The inverse Laplace transform is unable to resolve features less than a factor of three apart(71), which can lead to features of the true probability distribution being blurred together in the inverse Laplace spectrum. In addition, we may want to see how differing parameters such as T_1 , T_2 or diffusion coefficients are correlated with one another. Therefore, to gain better understanding about our systems we move to two dimensions. The Fredholm integral in two dimensions is of the form

$$M(\tau_1, \tau_2) = \iint k(x, y, \tau_1, \tau_2) f(x, y) dx dy + \epsilon(\tau_1, \tau_2), \qquad (5.13)$$

Where f in the two dimensional situation is the joint probability density of the two variables x and y. The joint probability density is the likelihood of a particular combination of x and y. For the case of separable kernels, where the two kernels contain no dependence upon each other, this becomes

$$M(\tau_1, \tau_2) = \iint k_1(x, \tau_1) k_2(y, \tau_2) f(x, y) dx dy + \epsilon(\tau_1, \tau_2).$$
 (5.14)

Once again, solving the equation exactly is not possible so we return to numerical methods. The equation can be converted to a matrix of the form

$$M = K_1 F K_2^T + E (5.15)$$

where K_1 , F, and K_2 are the discretised k_1 , f, and k_2 respectively.

VIII Algorithm

The equation for optimisation of the joint probability density function is given as:

$$\min \sum_{r=1}^{R} \| M - K_1 F K_2^T \|^2 + \alpha \| LF \|^2 .$$
 (5.16)

Again, the algorithm tries to estimate F by testing a range of potential values to find the solution that minimises the difference between the measured data and the calculated data. Until recently, the 2D inverse Laplace transform was too computationally intensive to be performed on anything but a supercomputer. Pseudo-2D inversions have been attempted(72), using multiple 1D inverse Laplace transforms. While these often produce passable results, they can be unreliable as they do not take in to consideration the full 2D landscape. The pseudo-2D inversion breaks the data up into 1D slices and inversion of these slices is not influenced by the other slices. As the data in the other slices may, in reality, have an influence upon a particular slice, the pseudo-2D inversion is a poor solution.

A more elegant solution is to use a minimiser to search through the possible solution space for the optimal fit between measured and calculated data. While this is a much more reliable method compared to the pseudo-2D inversion, the size of the kernels often exceeds available computer memory. However, with the increases in computing power, this possibly may no longer be a limitation in the near future.

The Fast 2D inverse Laplace transform developed by Elden et al.(64) and Venkataramanan et al. (60) overcame the limitations of speed and memory requirements. They decreased the memory requirements by performing data compression using a singular value decomposition upon each of the kernels K_1 and K_2 :

$$K_1 = U_1 \Sigma_1 V_1^T$$
$$K_2 = U_2 \Sigma_2 V_2^T.$$

The smooth nature of the kernels means that much of the data in the matrix is redundant and therefore performing a SVD upon the kernels typically allows the data to be compressed by three orders of magnitude. The compressed matrices are then written as

$$\begin{split} \tilde{K}_1 &= U_1^T K_1 \\ \tilde{K}_2 &= U_2^T K_2 \\ \tilde{M} &= U_1^T M U_2 \,, \end{split}$$

where $\tilde{\cdot}$ indicates the matrix has been compressed via SVD. The data is then transformed into a 1D matrix

$$\tilde{K} = \tilde{K}_1 \otimes \tilde{K}_2$$

$$\tilde{m} = \begin{bmatrix} \tilde{M} \end{bmatrix}_{1d}$$

$$f = \begin{bmatrix} F \end{bmatrix}_{1d},$$
(5.17)

where \tilde{m} , \tilde{K} and f are the measured data, the kernels and the density function respectively in 1D, $[]_{1D}$ represents the conversion to one dimension and \otimes indicates the tensor product. The reason for this conversion is that the number of singular values needed to describe the matrix converted into a vector is smaller than the number needed to describe it as a matrix. This gives us

$$\tilde{m} = \tilde{K}f + \tilde{e} \tag{5.18}$$

The resulting form for inversion is now similar in form to the equation for 1D inversion. This equation is then substituted into a minimiser algorithm for optimisation

$$\min \sum \| \tilde{m} - \tilde{K}f \|^2 + \alpha \| Lf \|^2 .$$
(5.19)

With the compressed data and the reduced dimensionality, the computation is much less memory intensive than with the original matrices and can be performed on a personal computer in a few minutes. The development of fast inverse Laplace transforms has allowed for a wide range of 2D inverse Laplace spectroscopy experiments to be produced(60; 61; 54; 73; 74; 75).

IX Multidimensional Inverse Laplace Transform

Expansion of the Fredholm integral to a third dimension for a 3D inverse Laplace experiment gives us the equation

$$M(\tau_1, \tau_2, \tau_3) = \iiint k_1(x, \tau_1) k_2(y, \tau_2) k_3(y, \tau_3) \Im(x, y, z) dx dy dz + \epsilon(\tau_1, \tau_2, \tau_3)$$
(5.20)

The integral can, in principle, be expanded indefinitely to n dimensions. Discretization is more problematic. The 1D and 2D framework using matrix products is not sufficient for higher dimensional inversions. Instead, tensor products must be used. For the 2D case, a contracted product of two tensors is given by

$$\sum_{k,l} k_{ijkl} f_{kl} = m_{ij} \tag{5.21}$$

or

$$\langle K, F \rangle_{3,4} = M \tag{5.22}$$

where

$$K \in \Re^{(N_1 \times N_2) \times (N_x \times N_y)} \tag{5.23}$$

$$M \in \Re^{(N_1 \times N_2)} \tag{5.24}$$

$$F \in \mathfrak{R}^{(N_x \times N_y)} \tag{5.25}$$

M exists in modes 1 and 2 of the tensor while F exists in modes 3 and 4 of the tensor. A mode of a tensor refers to a data acquisition or inversion axis. The contraction gives the inverse Laplace transform of the respective dimensions. We can expand this form for higher dimensions

$$\sum_{k,l} k_{ijklmn} f_{lmn} = m_{ijk} \tag{5.26}$$

or

$$\langle K, F \rangle_{4,5,6} = M \,, \tag{5.27}$$

where

$$K \in \mathfrak{R}^{(N_1 \times N_2 \times N_3) \times (N_x \times N_y \times N_z)}, \tag{5.28}$$

$$M \in \mathfrak{R}^{(N_1 \times N_2 \times N_3)}, \tag{5.29}$$

$$F \in \Re^{(N_x \times N_y \times N_z)} . \tag{5.30}$$

Now M exists in modes 1,2, and 3 of the tensor while F exists in 4,5, and 6. The inversion of the multidimensional transform is then similar to the two dimensional transform, where we seek to optimise the difference between the measured and calculated results

$$\min \sum \| M - \langle K, F \rangle_{4,5,6} \|^2 + \alpha \| LF \|^2 .$$
 (5.31)

In theory, these tensor modes can be expanded to any number of higher dimensions, though the computational power for such inversions limits the practicality of such high dimensional experiments.

Part II

Experimental
Chapter 6

T1- Internal Gradients

I Introduction

Now that we have covered the basic theory, we move to the experimental work performed in this thesis. We begin by discussing a novel two dimensional inverse Laplace technique that we have developed for characterising internal gradients within the pore space.

Nuclear magnetic resonance (NMR) experiments on heterogeneous porous media are often performed at low magnetic fields(29; 30; 31; 32; 33; 34; 35; 36), with proton Larmor frequencies on the order of a few megahertz. Even at these low fields, the heterogeneous nature of the samples will still produce internal gradients as discussed in Chapter 4, interfering with NMR measurements in a variety of ways. The inhomogeneities in the magnetic field will shorten T_2^* , causing a broadening of the linewidths in chemical spectra. The interaction between the internal gradients and applied field gradients can produce distorted images and inaccurate diffusion measurements. The internal gradients can introduce a bias in transverse relaxation and diffusion measurements due to extra dephasing of the signal.

However, NMR research in heterogeneous materials has not been limited to low field (37; 38; 39; 40), as increased field strength confers advantages, such as higher signal to noise, small sample requirements, and long relaxation times. As the majority of this thesis concerns itself with experiments performed on heterogeneous porous media at 400 MHz, we are particularly interested in the influence of internal gradients upon measurements. With their dependence on field strength, as shown in equation 4.5, these internal gradients become more prominent at higher magnetic fields. What may have been a negligible effect at low field often becomes a serious concern at high field. This makes the internal gradients present in a sample for a given field strength an important factor to consider when designing experiments, particularly at high field. In some situations, the side effects of internal gradients are small enough to safely be ignored. In other cases, special steps must be taken to avoid confounding the experiment and many techniques have been developed to deal with the unwanted side effects of internal gradients. The line broadening caused by the internal gradients can make identification of chemically shifted components in the spectral dimension impossible. Pines et al.(76) have tried to overcome this using magic angle spinning. This technique spins the sample at a particular angle such that the rotation will cause the interaction between the applied field and internal gradients to go to zero. Seland et al. (54) used diffusion attenuation to distinguish between oil and water in porous systems. Diffusion attenuation is discussed further in Chapter 8. Cotts(77) and Sørland (78; 79) have developed bipolar gradient sequences to compensate for interactions between the applied and internal gradients in diffusion experiments. Many of these methods are incorporated into the new techniques developed in this thesis.

Despite their potential to distort experiments, the internal gradients within

a sample are not always a nuisance. Because of their dependence on characteristics of the pore space, several techniques have been developed to take advantage of internal gradients to find pore shape, pore connectivity or wettability. (55; 54) We present in this chapter a novel 2D inverse Laplace NMR technique which correlates internal gradients with T_1 relaxation. There exist multiple motivations for these experiments. First, the technique is a new method to assist better understanding of the distribution of internal gradients as a function of pore size, particularly at high field. By contrast with the measurement of T_2 or the restricted diffusion coefficient, measurement of T_1 relaxation is not susceptible to the presence of internal gradients. This makes it ideal for use at high and ultra-high fields where internal gradients could potentially be significant. We also want to know the range of intensities of internal gradients that will be produced by our samples so we can determine the effect they may have on other experiments in this thesis. Lastly, by performing the experiments at multiple field strengths, we also undertake the first experimental study of how internal gradients in differing pores sizes scale as a function of applied field to test the theoretical predictions.

II Theory

Internal magnetic field gradients affect transverse magnetisation by enhancing the loss of spin coherence as spin-bearing molecules diffuse through the inhomogeneities. The additional decoherence produces attenuation in the measured signal, leading to a potential bias in the T_2 measurement. Were the spin-bearing molecules to remain stationary, the local magnetic fields would be time-invariant and the decoherence which arises from the distribution of local fields could be reversed by the spin-echo process. However, these molecules diffuse in the case of liquids imbibed in porous media. This has the effect that the magnetic fields experienced by the spins are time varying, leading to a subtle motional averaging process in the evolving phases of the ensemble of spins. To understand this process it is helpful to define a length scale l_g over which a molecule must diffuse for significant irreversible dephasing to occur. This length is defined by (80)

$$l_g = \left(\frac{D_0}{\gamma g}\right)^{\frac{1}{3}},\tag{6.1}$$

where D_0 is the diffusion coefficient of the fluid and γ is the gyromagnetic ratio. Of course, in a porous medium, that gradient will change, typically over distances on the length scale of structural features.

For a CPMG pulse sequence with echo spacing t_E , the distance traveled between echoes is on the order of $l_E = (D_0 t_E)^{\frac{1}{2}}$. Provided $l_E \ll l_g$, the echo attenuation between successive pairs of echoes is small and the cumulative attenuation over many echoes is the result of the successively small dephasing. The size of the local gradient can readily be seen by changing the echo spacing of a Carr-Purcell-Meiboom-Gill (CPMG) (17; 18) train. As the echo spacing is increased, the apparent dephasing rate of the spins increases. This increased relaxation rate arises from diffusion through the internal gradients while the relaxation due to T_2 remains constant(33).

While absolute gradients scale linearly with the applied field strength as $\Delta \chi B_0$, it may be shown that there is an upper limit to the effective gradient which can be measured, namely when the structural features have length scales on the order of l_g . These maximum possible measured gradients within a sample are given by the relation(80):

$$g_{max} \approx \left(\frac{\gamma}{D_0}\right)^{\frac{1}{2}} (\Delta \chi B_0)^{\frac{3}{2}}$$
 (6.2)

while the associated structural length scale is given by l_s . There is a critical length of l_s , defined as

$$l^* = \left(\frac{D_0}{\gamma \Delta \chi B_0}\right)^{\frac{1}{2}}.$$
(6.3)

For pores larger than l^* , the fluctuations in gradient as molecules diffuse mean that the local gradients are averaged over the dephasing length. As l_s begins to approach l^* , the measured effective gradient begins to approach g_{max} . For pores smaller than l^* , the dephasing of the CPMG echo signal which occurs over the echo time t_E , such that $l_E \ll l_s$, arises from a local gradient which is effectively constant. Hence, the overall echo train attenuation may be calculated by averaging over the distribution of gradients in the ensemble of spins.

The technique for measurement of internal gradients is a modified CPMG sequence that capitalises upon the changing echo amplitude as a function of echo spacing. We take a constant interval of time t_0 and vary the number of 180° pulses, which refocus the magnetisation. Thus, the echo spacing t_E for an individual experiment is

$$t_E = 2\tau_n = \frac{t_0}{n}, \qquad (6.4)$$

where n is the number of 180° pulses in the time period. As we increase the number of pulses in this time period, the spin-bearing molecules have less time to diffuse through the internal gradients, lessening the dephasing effect. In some situations, below a certain τ_n , the intensity of the measured echoes will plateau. For these cases, the echo spacing is sufficiently short that the influence of internal gradients upon the signal has become negligible. For the experiments performed here, in which variable echo spacings are used, the observation of a signal after several echoes requires that the condition $l_E \ll l_g$ is satisfied for all measurements.

In the "local gradient" regime, the echo amplitude of a CPMG echo train in the presence of internal gradients is described by:

$$M(t_i) = \sum_j f_j \exp\left[-\frac{t_i}{T_{2j}}\right] \int_j P_j(g) \exp\left[-\frac{\gamma^2 g^2 \tau_n^2 D t_i}{3}\right] dg^2 \tag{6.5}$$

where f_j is the volume fraction of pore sizes that produce a transverse relaxation time T_{2j} , $P_j(g)$ is the volume fraction of pore sizes that produce an internal gradient of strength g, τ_n is the echo spacing and t_i the echo train time.

Only in the rare situation of a mono-disperse pore space can the magnitude of internal gradients be found uniquely. For poly-disperse porous materials, the internal gradients are coupled to pore size, and the internal gradient values will be widely dispersed. To separate different gradient components, the multiexponential decay can be analysed using 1D inverse Laplace methods. However, due to the resolution limits of the inverse Laplace transform, in some situations individual components may not be able to be resolved using a 1D inversion, leading to large, broad peaks. A more effective separation results if the gradients can be correlated with other parameters also dependent on pore size and a 2D inversion performed. One approach followed by Sun and Dunn is to use T_2 relaxation to decouple the internal gradients from pore size. However, a T_2 measurement can be susceptible to the influence of internal gradients. At very high applied fields, there is concern that the echo spacing of a CPMG cannot be made short enough to overcome the influence of very strong internal gradients. To avoid this possible situation, we instead choose to use the T_1 times of a system, which are related to pore size as:

$$\frac{1}{T_1} = \frac{1}{T_1^{bulk}} + \rho_1 \frac{S}{V}, \qquad (6.6)$$

where T_1^{bulk} is the T_1 relaxation time of the bulk fluid, ρ_1 is the surface relaxivity of the system, S is the pore surface area and V is the pore volume.

Both the values of T_{1bulk} and ρ_1 are frequency dependent, as mentioned in Chapters 2 and 4 respectively. T_{1bulk} increases as a function of field strength while ρ_1 decreases.

Figure 6.1 shows a pulse sequence in which both T_1 relaxation and the internal gradient dephasing effects are correlated. The signal attenuation for this pulse sequence is given by:

$$M(\tau_{T1}, \tau_n) = \Sigma_j f_j^0 \exp(\frac{-t_0}{T_{2j}}) \iint F_j(T_1, g^2) (1 - 2 \exp\left[-\frac{\tau_{T1j}}{T_1}\right]) \\ \times \exp\left[-\frac{\gamma^2 g^2 \tau_n^2 D t_0}{3}\right] dT_1 dg^2 + \epsilon(\tau_{T1}, \tau_n)$$
(6.7)

where $F_j(T_1, g^2)$ is the joint probability density and ϵ is the experimental noise. We can treat the T_2 relaxation during the internal gradient interval, t_0 , as a constant and ignore it in the inversion calculations as it will be the same for all experiments at different τ_n and constant t_0 . It will therefore result in a fixed intensity weighting for each T_{2j} . Similarly, the amount of T_1 relaxation that occurs during the internal gradient encoding interval can be considered a constant and ignored as well. However, the effect of T_2 cannot be ignored as a whole in the experiment. The 180° pulses serve to correct for the reversible spin decoherence caused by the local inhomogeneities, but the underlying irreversible spin-spin relaxation is unaffected. Therefore, any signal which has a T_2 time shorter than the internal gradient interval will decay away and not appear in the T_1 -g plot. In addition, while the T_2 relaxation will not affect the peak locations in our experiment, it will influence the intensity of the peaks. If quantification of the spectra is to be performed, the intensity should be corrected using values of T_1 and T_2 obtained from T_1-T_2 and T_2-g correlation experiments.

III Experimental

The experiments were performed on a Magritek 12 MHz Kea and Bruker 200 MHz Avance, 400 MHz Avance II and 900 MHz Avance II+ spectrometers. Two samples were used: Mt. Gambier limestone and tight packed quartz sand. X-ray CT images of the samples are shown in Appendix A. The samples were saturated with distilled water before experimentation and held at a constant temperature of 25°C for the duration of the experiments. Using the inhomogeneous linewidth, we calculated the magnetic susceptibility differences for the quartz sand and Mt. Gambier limestone to be $\Delta \chi = 30 \times 10^{-6}$ and $\Delta \chi = 9 \times 10^{-6}$ respectively. This technique compares the linewidth of the Fourier transformed spectra of a bulk fluid and the fluid imbibed in a material. The broadening in the linewidth can be related to the magnetic susceptibility difference as(81)

$$\Delta v \approx \frac{\gamma \Delta \chi B_0}{2\pi} \,. \tag{6.8}$$

We used these values to determine the critical length l^* , shown in Table 6.1. As the majority of the pores in both the sand and Mt. Gambier samples are

Sample	Mt. Gambier	Quartz Sand
12 MHz	$0.4\mu{ m m}$	$0.3\mu{ m m}$
200 MHz	$0.1\mu{ m m}$	$0.06\mu{ m m}$
400 MHz	$0.08\mu{ m m}$	$0.04\mu{ m m}$
900 MHz	$0.05\mu{ m m}$	$0.03\mu{ m m}$

Table 6.1: Calculated critical lengths

larger than our calculated critical lengths, we believe we can reliably apply the local field gradient assumption and assume free diffusion through the



Figure 6.1: Pulse sequence for the T_1 -g experiment.

internal gradients for all field strengths. The T_1 encoding was performed in 30 steps, ranging from a τ_{T1} of 1 ms to 1500 ms. For the internal gradient encoding, the length of the t_0 intervals were 60 ms, 40 ms, 32 ms and 19.2 ms at 12 MHz, 200 MHz, 400 MHz and 900 MHz respectively. The length of this interval is the time necessary for the measured echo of the longest echo spacing to be completely attenuated. There were 40 steps for internal gradient encoding, with the number of refocusing 180° pulses ranging from 1 to 400. The number of refocusing pulses was selected so that the echo intensities reached a plateau for the shortest values of τ_n . The data were Fourier transformed along the acquisition dimension and the resulting peak was integrated, producing a 2D plot of τ_{T1} versus τ_n . A 2D inverse Laplace transform was applied to the time domain data to give a 40×30 matrix. The α value chosen for regularisation of the inverse Laplace transform minimized the value of χ^2 and no further. Because the experiments measure the internal gradients as a function of diffusion, we then use the diffusion coefficient of $2.3 \times 10^{-5} cm \, s^{-1}$ for water at room temperature. We assume we are in the free diffusion limit for the internal gradient interval, as the molecules will only diffuse 5-10 μ m during that time, which is less than the pore size for most pores in the samples.



Figure 6.2: T₁-g plots for the tight packed quartz sand at a) 12 MHz b) 200 MHz
c) 400 MHz d) 900 MHz. A, B, and C arrows indicate the tracked intensity

IV Results and Discussion

Figure 6.2 and 6.3 show the measured internal gradients for the quartz sand and Mt. Gambier samples as a function of the different field strengths. Surprisingly, even at the ultra-high field of 900 MHz there exists signal at relatively low internal gradients. The maximum measured gradients are on the order of ~ 10^5 G cm⁻¹. This value seems high, though is reasonable when compared to measurements made by other researchers(80; 73; 54). We note that the relation $l_E \ll l_g$ holds true even for these high internal gradient strengths. The largest measured internal gradients are calculated using only



Figure 6.3: T₁-g plots for the Mt. Gambier limestone at a) 12 MHz b) 200 MHz
c) 400 MHz d) 900 MHz. A, B, and C arrows indicate the tracked intensity

the very early decay of the CPMG, for which τ_n is short and hence the condition $l_E \ll l_g$ is still satisfied.

For the most part, the distribution of internal gradients stays the same for the different magnetic field strengths. This indicates that the signal measured at the higher applied fields is still representative of the pore space. The results of Winkler et al.(82) raised a concern that at high magnetic fields, strong internal gradients might crush most of the signal through rapid dephasing of the spins so that the measured signal might come from only a small fraction of the fluid present. However, in the Mt. Gambier sample, the peak of highest intensity at low field strength disappears at the higher fields. We believe the peak has moved to internal gradient strengths higher than we can currently measure due to machine limitations, so it appears some loss of signal does occur at higher applied fields. If τ_n and the number of 180° pulses exceeds the duty cycle capabilities of the spectrometer, the transmitter will often shut down. This became an issue with attempting shorter τ_n at 200 and 400 MHz. At 900 MHz, moving to shorter τ_n was possible due to the newer spectrometer technology, but was hampered by the fact a cryoprobe was used for experimentation. The cyroprobe's limits with regards to pulse duration, power and frequency are not as robust as a regular probe, so attempting shorter τ_n was considered unwise. Alternatively, the peak may reside at internal gradients beyond g_{max} . For this situation, the $l_E \ll l_g$ relation is no longer satisfied, and the strong internal gradients will not affect the CPMG train such that we can measure them.

For internal gradient measurements, working at high field may actually enable us to probe a greater proportion of the pore space as the value of l^* becomes smaller with increased field. While incomplete sampling of the pore space is not a concern for the samples used here, this could potentially be an issue for samples with lower magnetic susceptibility differences. For example, mudstones often have low magnetic susceptibility differences between water. As the pore sizes can be extremely small in mudstones, the internal gradients for a significant portion of the pore space would be unable to be probed at low field. However, for the CPMG decay to be affected by internal gradients, l_E must be less than l^* to encode for these pores. This is usually not a concern with modern equipment, but as mentioned can become a problem with the duty cycle for older spectrometers.

Using our estimated susceptibility differences and equation 6.2, we calculate the expected maximum gradients present in the samples and compare

Sample	Mt. Gambier	Quartz Sand
12 MHz	$10^{1.8}$	$10^{2.5}$
200 MHz	$10^{3.6}$	$10^{4.3}$
400 MHz	$10^{4.1}$	$10^{4.8}$
900 MHz	$10^{4.5}$	$10^{5.3}$

Table 6.2: Maximum Calculated gradients

Table 6.3: Maximum Measured gradients

Sample	Mt. Gambier	Quartz Sand
12 MHz	$10^{3.0}$	$10^{2.3}$
200 MHz	$10^{4.1}$	$10^{3.9}$
400 MHz	$10^{4.1}$	$10^{4.3}$
900 MHz	$10^{4.5}$	$10^{4.8}$

them to our measured values, shown in Tables 6.2 and 6.3. For the Mt. Gambier sample, the maximum measured gradients for 400 MHz and 900 MHz agree well with calculations. At the lower field strengths, there is a measured peak found at gradients higher than the calculated values. This may arise from an area of paramagnetic impurity in the sample which has a higher than average $\Delta \chi$. If we ignore this anomalously high gradient peak, our measured values at these field strengths agree better with theory. The sand sample follows the general trend, but consistently has slightly lower measured values than the calculated maximum gradients. It is possible that a higher gradient signal component exists at these internal gradient strengths, but at such a low intensity compared to the other signal present that they are below the resolution threshold on the inverse Laplace transform. For the low field, the T_1 times for the different internal gradient strengths are nearly the same. As we increase field strength, we begin to see better distinction of the peaks in the T_1 dimension, highlighting better resolution in the T_1 domain as an advantage of working at higher magnetic fields in these samples. However, as we increase field strength, we seem to lose some resolution in the internal gradient dimension, particularly in the sand sample.

We now consider how the internal gradients and T_1 relaxation times scale as a function of B_0 for both the sand and Mt. Gambier samples. In our spectra, we see several distinct regions of intensities which reflect different sizes in the pore space within the sample. To aid in tracking the signal between field strengths, we assign letters to different regions of the signal. The signal components arising from larger pores in the samples, labeled as A and B, are easy to track because of distinctive peaks. Unfortunately, with the smaller pores at higher applied fields, we lose distinguishing peaks, so we simply choose to follow the maximum measured intensity for each spectrum, which we label C. For consistency with the Mt. Gambier sample, we track the maximum intensity for the second highest peak at 12 MHz and 200 MHz due to the loss of the highest gradient peak at higher field strengths. Error bars were calculated using the peak locations from repeated measurements.

Internal gradients strengths as a function of field strength are shown in Figure 6.4 with the best fit lines shown in Table 6.4. For both A and Bpeaks the magnetic field scaling is approximately unity. For the C peak the internal gradients scale as a function of $B_0^{1.3}$. These results agree well with the theory put forth by Hürlimann(80); the larger pores scale as approximately B_0 whereas the maximum observable gradients, corresponding to small pores approaching l^* , scale at up to $B_0^{1.5}$. For the smaller pores where $l_s < l^*$, the local gradients will be averaged out by diffusion. If $l_s = l^*$, the strength of the gradient is such that diffusion can no longer average the local gradient of the pore and the effective gradients can approach the limit of $B_0^{\frac{3}{2}}$.

Figure 6.5 shows T_1 as a function of field strength with the best fit lines shown in Table 6.5. The T_1 values of the A and B peaks scale as a function of $B_0^{0.5}$, which agrees with the T_1 frequency dependence of $T_1 \propto \omega^{0.5}$ in water saturated porous media seen by Korb et al. (83). For the C limit, T_1 scales only as $B_0^{0.4}$. While surface relaxation is known to decrease with increased field strength, cursory examination of equation 6.7 shows that as the T_1 of the saturating fluid increases with field strength, a broader distribution of T_1 values will be produced from the surface relaxivity for a given pore size distribution. This explains the increase in resolution we see in the T_1 domain. Because of this scaling, nearly an order of magnitude in T_1 relaxation time is gained between the low field and the high field experiments. The increased T_1 relaxation time is a particular advantage for exchange experiments (75; 84; 85). With proper bipolar gradients and sufficiently short echo times(77), diffusion exchange and transverse relaxation exchange experiments can take advantage of the long T_1 times to increase the mixing times, which allows longer length scales within the material to be probed without sacrificing the reliability of the measurements.

Mt. Gambier	g^2	T_1	Quartz Sand	g^2	T_1
А	$B^{1.1}$	$B^{0.49}$	А	$B^{1.1}$	$B^{0.48}$
В	$B^{1.1}$	$B^{0.47}$	В	$B^{1.0}$	$B^{0.48}$
С	$B^{1.3}$	$B^{0.42}$	С	$B^{1.3}$	$B^{0.42}$

Table 6.4: Scaling Factors



Figure 6.4: Internal Gradient intensity as a function of field strength for a) Mt. Gambier and b) Quartz Sand as a function of magnetic field strength with best fit lines



Figure 6.5: T_1 relaxation time as a function of field strength for a) Mt. Gambier and b) Quartz Sand as a function of magnetic field strength with best fit lines

V Castlegate

The experiments were also attempted for a third sample, Castlegate sandstone. Experiments were performed twice at the 900 MHz. During the second set of experiments at 900 MHz, we noted that the Castlegate sandstone signal looked remarkably different than compared to the initial experiments. The previously short FID signal with strong internal gradients had lengthened and resembled more the sand sample than the previous experiments. Upon removing the sample from the magnet, we noticed that the sandstone had disintegrated from solid stone into sand at the bottom of the tube. While we were unable to complete experimentation with this sample, this shows the significant influence that the structure of the material has upon the internal gradients present.

VI Conclusion

We provide experimental evidence that the effective internal gradients present in a sample can scale as B_0 while maximum observable gradients can scale at up to $B_0^{\frac{3}{2}}$. Our results show that it is possible to reliably perform experiments on even highly heterogeneous samples at high fields and that advantages come at these high fields. For these samples, the T_1-g correlation is a useful initial experiment to estimate the expected internal gradients. The large internal gradients that arise at high field can be accessed through short echo spacing and those that are too high given the shortest experimentally available t_E will not contribute to the measured signal. We find evidence that there is some signal loss at high applied fields. Here, one must bear in mind that the 900 MHz data may possibly not represent a complete picture of the system. We anticipate as spectrometer technology improves, we will be able to measure the higher gradients in the sample even at the highest fields, helping to rectify this loss of signal. Interesting future work could combine our technique with the MAS techniques developed for internal gradient suppression. Our findings certainly encourage the use of these high and ultra-high field strengths for a broader range of samples.

Using this technique upon our samples helped confirm that the experiments in the rest of the thesis can be performed reliably at 400 MHz without the unwanted influence of internal gradients. The portion of the signal we work with in the rest of the thesis exists at relatively low internal gradients, up to strengths of 10^2 G cm⁻¹. While this is not negligible, it is comparable to the internal gradients seen in some samples at low applied B_0 , so work with these samples is possible at 400 MHz. However, special steps must be taken to avoid bias in our measurements. As our applied field gradients are on the order of internal gradients in our samples at 400 MHz, we must utilise bipolar gradients for the diffusion measurements to avoid unwanted interaction between the two magnetic fields. In addition, we need to keep our echo spacings for CPMG measurements sufficiently short. A pared down version of the T_1 -g experiment was used to decide the t_E times. As mentioned, in some samples the echo intensity will plateau if the echo spacing is made sufficiently short that the internal gradient influence is negligible. We ran the experiments without the T_1 encoding. By looking at the value of τ_n where the signal plateaus, we can determine the echo spacing that is short enough to avoid the influence of internal gradients upon T_2 measurements.

Chapter 7

Transverse Relaxation Exchange

I Introduction

Now that we have satisfied ourselves that the presence of internal gradients in our samples will not distort our results at 400 MHz, we turn to a different sort of two dimensional inverse Laplace NMR experiment. The T_1 -g experiment was a correlation experiment, which relates two different properties of a sample together. In this chapter we describe a 2D exchange experiment, where one property is measured on the same nuclear magnetisation, but at two successive times, the two measurements then being plotted against each other. Diagonal peaks represent signal from molecules where the property has remained unchanged, while exchange is indicated by the presence of off-diagonal intensity. Until recently these methods were restricted to the frequency domain(86), yet many NMR properties, such as relaxation or diffusion, are associated with exponential decays. We present here for the first time how 2D inverse Laplace experiments may be used to quantitatively monitor molecular exchange processes, choosing as a simple example the relaxation-relaxation exchange for liquid molecules imbibed in a porous medium.

II Transverse relaxation exchange

As mentioned in Chapter 4, the distribution of transverse relaxation times reflects the distribution of pore sizes within a sample; in general, larger pores have longer T_2 relaxation times and smaller pores have shorter T_2 times. Assuming we are in the fast diffusion limit, this relation is governed by(33):

$$\frac{1}{T_2} = \frac{1}{T_2^{bulk}} + \rho_2 \frac{S}{V}$$
(7.1)

where T_2^{bulk} is the T_2 relaxation time of the bulk fluid, ρ_2 is the surface relaxivity, S is the pore surface area and V the pore volume. In transverse relaxation exchange, we begin the experiment with a T_2 measurement to take a "snapshot" of where the fluid molecules are located within the porous medium. We can then turn off the influence of T_2 by storing the magnetisation along the z-axis. While the magnetisation is stored along the z-axis, it does not experience T_2 relaxation, only the longer T_1 relaxation. The magnetisation is stored for a mixing time τ_m , during which the spin-bearing molecules are allowed to diffuse freely. Depending on the pore structure, length of τ_m and the diffusion coefficient of the fluid, some fluid molecules may move to new environments. At the end of this mixing time, a second T_2 measurement is performed. By observing how the T_2 values change between the two points in time, we can then compare where molecules were located at the start of the experiment and where they were located a time τ_m later.

The resulting form of the inverted spectra, shown in Figure 7.1, is similar in form to that of the VEXSY Fourier experiment(87) or the DEXSY inverse



Figure 7.1: Transverse relaxation exchange spectrum for a simulated fluid filled two-pore system. Molecules that started in the small pore and remained in the small pore (AA) appear along the diagonal at a short T_2 time. Similarly, molecules that began in the large pore and remained there (BB) appear along the diagonal at a long T_2 time. Molecules that have exchanged pores during the mixing time (AB, BA) appear on the off diagonal

Laplace transform experiment (75). Signal that appears along the diagonal comes from spin-bearing molecules in their original environment, while signal on the off-diagonal comes from the molecules which have shifted environments during the mixing time. For a porous medium, if the T_2 value of a molecule changes during the mixing time, this is indicative, but not conclusive, that the fluid molecule has moved to a pore of another size.

The first T_2 exchange experiment was performed by Lee et al.(72) in 1993. This, however, was not a true 2D inverse Laplace experiment. Whereas true



Figure 7.2: Transverse relaxation exchange pulse sequence

two dimensional ILT experiments are performed by taking the inversion over a two dimensional set of data, Lee and co-workers produced a brute force pseudo-2D solution from multiple 1D inversions. While they managed to obtain relatively good results, this technique is unreliable because it does not take into account the complete 2D solution space as discussed in section 5.8. The first true 2D T_2 - T_2 exchange experiment was performed by McDonald and Korb(35) to demonstrate the movement of water between differing environments in concrete, but they did not undertake quantification, nor follow the dependence of intensities over a range of mixing times.

III Pulse Sequence

The pulse sequence begins with a 90° excitation pulse to place the magnetisation in the transverse plane. We then perform a T_2 encode using the fixed echo spacing method to avoid the influence of internal gradients in our samples; we have a loop consisting of n 180° pulses. After the first T_2 encode interval, a second 90° pulse stores the magnetisation along the z-axis for the mixing time τ_m . A third 90° pulse returns the magnetisation to the transverse plane. The fixed echo spacing CPMG allows us to make efficient use of time, encoding the second T_2 measurement simultaneously as acquisition by recording the amplitude of each of the *m* echoes. The experiment is then repeated with an increased value of *n*. The value of *n* starts small at the beginning of the experiment and is increased logarithmically until *n* is equal to *m*. We use a simple four-step phase cycle to ensure that all of our signal derives solely from the initial 90° pulse.

The way data is acquired for our transverse relaxation exchange experiment produces very asymmetric data sets. Generally the number of different values of n are on the order of tens whereas the number of m is often several thousand. A transform of such a highly asymmetric data set can lead to the blurring or loss of features in the resulting inverse Laplace spectrum. Therefore, we pick out from the second CPMG train the echoes corresponding to the first encode times. This gives us a square matrix upon which to perform our inversion. The equation for the inverse Laplace transform of the transverse relaxation exchange experiment can be described by:

$$M(t_1, t_2) = \iint \exp(-\frac{t_1}{T_2^1}) \exp(-\frac{t_2}{T_2^2}) F(T_2^1, T_2^2) dT_2^1 dT_2^2 + \epsilon(t_1, t_2)$$
(7.2)

where T_2^1 and T_2^2 are the T_2 values of the molecules for the first and second encodes respectively and $F(T_2^1, T_2^2)$ is the joint probability density.

IV Experimental

The number of points acquired, echo spacings, and mixing times used depended on the sample. For the Castlegate sandstone, the transverse magnetisation relaxed quite quickly. In addition, the T_1 time was relatively short and the exchange between differing T_2 environments fast. Thus, for the mixing times we chose values of 1 ms, 10 ms, 20 ms, 30 ms, 40 ms, 60 ms, 80 ms, 120 ms, and 160 ms. Because of the concern of high internal gradients in this sample, we had a very short echo spacing of $50 \,\mu s$. We used 42 points in the first T_2 encode interval and 1024 points in the second T_2 encode. After symmetrisation, we had a 42×42 matrix which we transformed into a 32×32 inverse Laplace spectrum.

For the other three samples, the magnetisation relaxed more slowly, so we needed more points to fully acquire the signal decay. These samples acquired 66 points in the first T_2 encode interval and 4096 points in the second T_2 encode. Internal gradients were less in the other three samples than in the Castlegatesample, so we had a longer echo spacing of $150 \,\mu$ s to help minimise the issues of sample heating. The T_1 relaxation times for these samples were much longer, so longer exchange times could be probed. For the mixing times, we chose $50 \,m$ s, $100 \,m$ s, $150 \,m$ s, $200 \,m$ s, $250 \,m$ s, $300 \,m$ s, $350 \,m$ s, $400 \,m$ s, $450 \,m$ s, $500 \,m$ s and $550 \,m$ s. These times were also chosen to aide comparison with later experiments in this thesis. We transformed the symmetrised 66×66 matrix into 40×40 inverse Laplace spectra.

V Results and analysis

Due to oscillatory transients in the CPMG echo train(88), the first few points of the signal decay could not reliably be used towards inversion. This resulted in the loss of a weak peak at short T_2 times in the inverse spectra for the Fontainebleau, Mt. Gambier and quartz sand samples.

Most of the plots have three to four diagonal peaks, except the Fontainebleau with only two. This seems contradictory with respect to the X-Ray pore size distribution results in Appendix A, as those present a smooth distribution of pore sizes. The distinct peaks in the T_2 exchange spectra are an artefact of the inverse Laplace transform. The inverse Laplace transform has a tendency to "pearl" data(74), taking a continuous distribution and breaking it up into distinct peaks. While this behaviour could be problematic for some experiments, it is beneficial for us because it serves to bin the data, making integration of the peaks easier. The total measured signal intensity is conserved despite pearling behaviour in the inverted signal distribution.

Looking at the intensity of the peaks in the spectra as a function of mixing time, we see that the off-diagonal peaks appear to grow in their intensity, while the on-diagonal peaks tend to decrease. To quantify this effect, we integrated the intensity of the peaks, combining the intensity of the complimentary cross peaks. Some problems arise in assigning peak intensity due the resolution issues of the inverse Laplace transform. The cross peaks have a tendency to bud off from the diagonal peaks. The diagonal peak will begin to spread outward from the diagonal, before the cross peak finally appears as a distinct peak at a later mixing time. This sometimes can make proper assignment of intensity difficult.

The absolute intensity of the peaks was normalised by the total integrated intensity for the given mixing time to correct for T_1 relaxation. We then plotted the intensity of the diagonal and off-diagonal peaks as a function of mixing time. Using the two pore exchange theory from Section 4.4.1, we fitted the off-diagonal data using a least squares calculation to obtain the characteristic times. We then used the characteristic times from the cross peaks to calculate and plot the rate of decay of the diagonal peaks. These, in general, showed good agreement with the measured data. We discuss now the behaviour for the different samples individually.



Figure 7.3: Castlegate T_2 exchange spectra for a) 1 ms b) 30 ms c)80 ms and d) 160 ms

1 Castlegate

The Castlegate sample produces four diagonal peaks at 0.2 ms, 1.6 ms, 8 msand 32 ms labeled A, B, C and D respectively. The spectra show quick



Figure 7.4: Castlegate peak intensities as a function of mixing time a) Off-diagonal intensity and b) Diagonal Intensity

exchange between the A, B, and C peaks while peak D does not appear to exchange at all with the other peaks. While it is possible this signal comes from isolated vuggy pores, analysis of the X-ray CT data suggests that this is not probable. Instead, it is more likely that there has not been sufficient exchange between the D pores and other pores to produce peaks of strong enough intensity to be resolved by the 2D ILT. Because of the short T_1 times of the sample, we cannot go to very long mixing times where we might be able to see exchange between the D peak and other peaks. The exchange times between the other pores were $\tau_{AB} = 17 ms$, $\tau_{AC} = 24 ms$, and $\tau_{BC} = 48 ms$. Approximately 30% of the fluid molecules in the Castlegate sample had changed environments at the longest mixing time of 160 ms.



Figure 7.5: Fontainebleau T_2 exchange spectra for a) 50 ms b) 200 ms c) 400 ms and d) 550 ms

2 Fontainebleau

The Fontainebleau inverse spectrum has two peaks appearing at approximately 20 ms and 100 ms. The small number of peaks is indicative of the very homogeneous nature of the pore space compared to the other samples. The Fontainebleau sample showed strong asymmetry in the resulting cross



Figure 7.6: Fontainebleau peak intensities as a function of mixing time a) Offdiagonal intensity and b) Diagonal Intensity

peaks. Regardless of experimental modifications we attempted, we could not get symmetric peaks from the Fontainebleau sample at short mixing times.

The exchange in the Fontainebleau sample was limited. In our fit of the exchange, we decided to consider the data points from the first few τ_m times to be outliers. This is because we suspect the zero and low values at the short mixing times are erroneously low as a side effect of the peak budding. The exchange time between the A and B pores was found to be $\tau_{AB} = 833 \, ms$. Only about 11% of the signal in the Fontainebleau sample had changed environment at the longest mixing time.

3 Mt Gambier limestone

The Mt. Gambier sample resulted in three exchange peaks at 5 ms, 20 ms, and 63 ms. It proved to be the most unreliable of the four samples, reflected in the error bars. The Mt. Gambier sample only produced reliable spectra



Figure 7.7: Mt. Gambier T_2 exchange spectra for a) 50 ms b) 200 ms and c)400 ms

up to $400 \, ms$. In a personal correspondence with our collaborators at ANU, it was mentioned that simulation of molecular walkers in the sample showed that a fluid molecule could inhabit up to thirty different pores in the space of a second. We speculate that the rapid exchange between the various pores may lead to more averaged T_2 values over the pore space. This means that



Figure 7.8: Mt. Gambier peak intensities as a function of mixing time a) Offdiagonal intensity and b) Diagonal Intensity

instead of only experiencing only one pore during the T_2 encode interval, the fluid molecules may inhabit two or more pores. This could lead to the uncertainty seen in the Mt. Gambier inversions.

The Mt. Gambier sample showed fairly quick and extensive exchange. As the limestone is a very porous material, this is to be expected. Nearly 50% of the signal intensity had changed T_2 environment by the longest mixing time. The exchange times between the different pores were $\tau_{AB} = 333 \, ms$, $\tau_{AC} = 80 \, ms$, and $\tau_{BC} = 625 \, ms$. The AC peak proved very unreliable. We estimated a characteristic time for this peak, but we are not confident in the accuracy of the value. While integrated intensity of the peak from repeated experiments would generally produce similar results, its value as a function of mixing time would fluctuate up and down significantly. The repeatability in these fluctuations leads us to believe this is an effect of the inverse Laplace transform. This underscores the caution we must take when interpreting from the intensities of the inverse Laplace spectra.



4 Quartz Sand

Figure 7.9: Quartz Sand T_2 exchange spectra for a) 50 ms b) 200 ms and c)400 ms d) 500 ms

The quartz sand spectra produced three diagonal peaks at 11 ms, 32 ms, and 71 ms. As with the Fontainebleau sample, we decided to lay emphasis on a better fit for the end of the data for the *BC* peak. The exchange times between the different pores were $\tau_{AB} = 142 ms$, $\tau_{AC} = 370 ms$, and



Figure 7.10: Quartz Sand peak intensities as a function of mixing time a) Offdiagonal intensity and b) Diagonal Intensity

 $\tau_{BC} = 589 \, ms$. Approximately 36% of the fluid molecules had changed T_2 environments by the longest mixing time.

VI Comparison between samples

	$ au_{AB}$	$ au_{AC}$	$ au_{BC}$
Castlegate	17	24	48
Fontainebleau	833	N/A	N/A
Mt. Gambier	333	80	625
Quartz Sand	142	370	589

Table 7.1: Pore Characteristic times (ms)

As discussed in Chapter 4, the porosity of a sample is linked with permeability, which will influence the ease with which fluid will travel through the medium. In addition, the rate of exchange will be influenced by pore size and inter-pore spacing. From Appendix A, the porosities of the Castlegate, Mt. Gambier, quartz sand and Fontainebleau are approxiamtely 28%, 50%, 40% and 16%. The amount and rate of exchange corresponds well with the porosities for the Mt. Gambier, quartz sand and Fontainebleau sample; at 400 ms the samples respectively had 47%, 31% and 9% of their signal change T_2 environments. The less porous Fontainebleau sandstone shows much less exchange than the very porous Mt. Gambier limestone. The quartz sand, with its in between porosity, showed more exchange than the Fontainebleau, but less than the Mt. Gambier. Despite the difference in their porosities, the Mt. Gambier and quartz sand samples showed similar amounts of exchange at short mixing times. We speculate this may be caused by the fact that despite that the Mt. Gambier is more open: it has larger pores so the fluid molecules must travel larger distances to reach a pore of a different size.

The Castlegate sandstone, however, shows a significant amount of exchange occurring even at short intervals. The other three samples required much longer mixing times before the exchange peaks would appear to reach equilibrium. This is surprising because the pore size of the Castlegate is not significantly smaller than the other three samples while the average inter-pore spacing is larger than in the Mt. Gambier and the Fontainebleau. While we originally hypothesized that shortest peaks in the Castlegate spectra arose from water in pore throats, we suggest this intensity may instead come from water bound in clay. We see exchange peaks at even the shortest mixing times where the water molecules will not have the opportunity to diffuse a significant distance. In addition, the Castlegate sandstone contains nearly nine percent clay by weight, so this is a distinct possibility. This would also explain why we see so much exchange in the Castlegate despite the larger inter-pore spacings.

VII Conclusion

Our results suggest that tracking the intensity from multiple T_2 exchange experiments is a viable way to monitor molecular dynamics within a porous material. The exchange peaks only indicate a change of T_2 environment and not necessarily a change of pore, but we are cautiously optimistic because the peak intensities match well with theory. We also see differing exchange behaviour between the different samples which agrees with their morphology. Future work should include experiments upon many more samples to confirm this trend.

The T_2 exchange technique is a very important method because it has no other clear experimental analogue. While pore size and pore shape can be found in alternative ways, such as TEM or X-Ray CT, we have no other current method to track the movement of fluid inside a porous matrix. We also suggest quantitative analysis should be attempted with the diffusion exchange experiments(74). We anticipate the T_2 exchange technique may also be used to more accurately estimate the effective and ineffective porosity in samples than the general cutoff technique.

The technique developed here has already begun to see use in outside groups. The Gladden group at Cambridge University has performed T_2 exchange work with borosilicate glass spheres of known size. The measured exchange times were compared with exchange times calculated from simulation. The experimental results matched the simulated results well and are a very promising validation of the technique(89). Tentative progress has been seen with the T_2 exchange technique in porous materials of a non-geological nature, such as wood and micelles, though experiments in animal tissue have proved unsuccessful thus far.

While the T_2 exchange experiment gives us important information about the movement of fluid between differing environments, it still is a limited technique. In the following two chapters, we discuss modifications using pulsed field gradients to the T_2 exchange experiment to obtain more information about the pore space. In the next chapter, we alter the transverse relaxation exchange experiment to allow for discrimination of different fluids despite loss of spectral information due to internal gradients. In the following chapter, we add spatial information to the transverse relaxation exchange to track how far the molecules move during the mixing time. By this addition, we try to expand the technique such that we can observe exchange between pores of similar size.
Chapter 8

Diffusion Attenuated Transverse Relaxation Exchange

I Introduction

The T_2-T_2 exchange experiments to this point of the thesis have focused on porous media saturated only with water. There are many situations, however, where the porous media we want to examine is saturated with two or more immiscible fluids. A common situation encountered is in rocks saturated with both oil and water. While bulk oil and water could easily be separated by their differing chemical shifts, the internal gradients within our porous samples make the linewidth of the chemical spectrum so broad that distinguishing between oil and water in the spectral domain is impossible. In these cases, diffusion attenuation(90; 54) is a possible solution to isolate the signals from the two components.

As discussed in the pulse sequence chapter, when a field gradient is applied

to a system, the dephasing of the spins is enhanced as the molecules diffuse through the gradient. The attenuation effect on the signal is described by the equation 3.17. Because molecules of oil are larger than molecules of water, they will have a slower diffusion coefficient and therefore their signal will be less affected by the applied gradient than that of the water. For strong enough gradients, the signal from the faster diffusing component will be attenuated more rapidly than the signal from the slower diffusing component such that only this latter signal will remain. This slowly decaying signal can then be corrected back to the zero gradient value and subtracted from the total unattenuated signal, at g = 0, to obtain the amplitude of the signal from the fast diffusing component. This technique was previously used by Seland et al. to separate oil and water signals in T_2 -g experiments(54). We easily adapt this technique to our T_2 exchange experiment, as the mixing period along with applied gradients can be used to attenuate the slower diffusing component. The magnetisation behaviour of this experiment is described by

$$M(-q, \delta, \Delta, t_1, t_2) = \exp\left(-q^2 D\left(\Delta - \frac{\delta}{3}\right)\right) \iint \exp\left(-\frac{t_1}{T_2^1}\right) \exp\left(-\frac{t_2}{T_2^2}\right) \\ \times F(T_2^1, T_2^2) dT_2^1 dT_2^2 + \epsilon(t_1, t_2)$$
(8.1)

where T_2^1 and T_2^2 are the measured T_2 times of the first and second encode intervals respectively and $F(T_2^1, T_2^2)$ the joint probability density. Unlike diffusion measurements which have a range of gradient intensities, the diffusion attenuation only uses one gradient strength for the experiment.

II Sample Preparation

The porous systems were created using glass microspheres (Duke Scientific) with a range of diameters from $5 - 50 \,\mu\text{m}$. The estimated porosity of the systems is approximately 20%. The glass spheres are originally water-wet.



Figure 8.1: Diffusion attenuated T_2 exchange pulse sequence

Some of the microspheres were chemically treated to make their surfaces oilwet. These spheres were treated with an excess of chlorotrimethylsilane in a mixed solvent pair of toluene and pyridine under an argon atmosphere. Water had been removed from the solvents used. The spheres were then separated from the solution, washed with dichloromethane, and dried under vacuum at 55° C. The water used for experimentation was distilled and deionised. The oil used in the study was hexadecane. 1.4 g of either water-wet or oil-wet glass beads were added to a 10 mm test tube. For the two-phase systems, $200 \,\mu$ l of both oil and water were added. One-phase systems consisting of $400 \,\mu$ l of oil or water and glass beads were also created for calibration. The samples were then set in an ultrasonic bath for several hours to ensure proper mixing. The samples were kept at 25° C for the duration of experimentation.

III Pulse Sequence

The pulse sequence used for our experiments can be seen in Figure 8.1. The system is excited with a hard 90° pulse. The first T_2 encoding is performed in the interval labeled "n". We perform the T_2 measurement using a fixed echo spacing and varying the number of refocusing pulses to avoid possible

influence by internal gradients. We used echo spacings t_E of $100 \,\mu$ s, which were determined through an internal gradient encoding experiment to be sufficiently short to avoid effects of internal gradients in this system.

After the first T_2 encoding interval, the first set of applied gradients provides the diffusion attenuation. If we want to acquire the signal from both oil and water, we simply do not turn on these gradients. In our experiment, we use uneven bipolar gradients for the diffusion attenuation. These, along with proper phase cycling, have been shown to cancel out unwanted coherence pathways between the applied gradients and internal gradients. After the first set of applied gradients, another 90° pulse stores the magnetisation along the z-axis for a mixing time τ_m . After the mixing time, the magnetisation was returned to the transverse plane by a third 90° pulse and the second set of bipolar gradients was applied to complete the diffusion attenuation. Lastly, the second T_2 encoding interval was performed simultaneously as acquisition.

To determine the duration and strength of gradients necessary for our experiments, we prepared samples of water in both water-wet and oil-wet spheres. We then ran the experiments to determine the minimum gradient length and intensity necessary to completely attenuate the water signal. At $\tau_m = 20$ ms, The resulting lengths of our gradients were 750 μ s and the bipolar gradient strengths for the shortest mixing time were 70 G/cm and 52.5 G/cm respectively. As the mixing time grows longer, we must compensate by lowering the strength of the gradients to keep the attenuation effect constant on the oil signal between the experiments. While the water is most strongly affected by the diffusion attenuation, the oil signal is also reduced. To correct for this, we performed the experiments on a system of only oil in the water-wet and oil-wet glass beads with and without the applied gradients

to determine the attenuation correction factor.

Experiments were performed with the mixing times 20 ms, 40 ms, 60 ms, 80 ms, 120 ms, 160 ms, 200 ms, 240 ms, 280 ms, 320 ms, 360 ms, 400 ms. Our phase cycling ensured all acquired magnetisation derived only from the first 90° pulse. The 2D inverse Laplace transform is then applied to the data to produce a 40 × 40 2D distribution of the T_2 values. As with the regular transverse relaxation exchange experiment, spin bearing fluid molecules that have remained in the same T_2 environment will appear along the diagonal in the 2D spectrum while the fluid molecules that have changed environments will have coordinates that are a combination of the two environments and will appear on the off diagonal.

IV Results

The influence of wettability on the rate and extent of fluid movement can be seen by comparison of the inverted spectra from the oil-wet and waterwet systems, even without separation of the two fluid components; distinctly different exchange patterns appear between the two wettability cases. We encountered difficulty with reproducibility of the data, particularly in the oilwet situation. The effect of treating the spheres with trichlorotrimethylsilane only temporarily makes the surface oil-wet, and we believe that the gradual loss of their oil-wet state led to the problems of experimental reproducibility. Unfortunately, these issues hindered a thorough quantitative analysis of the relative fluid movement in the oil-wet and water-wet spheres, though we do a general comparison of peak intensities.

Comparing Figure 8.2 and Figure 8.3, we note much faster exchange behaviour in the oil-wet system. The spectra from the oil-wet system shows



Figure 8.2: T_2 exchange spectra for water and oil in water-wet spheres for a) $\tau_m = 20 \,\mu\text{s}$, b) $\tau_m = 60 \,\mu\text{s}$, c) $\tau_m = 160 \,\mu\text{s}$, d) $\tau_m = 400 \,\mu\text{s}$

more cross peaks with greater intensity at short mixing time than the waterwet system. We speculate that this stems from the fact that the oil, the slower diffusing component, is constrained while the water is now free to exchange. In the water-wet system, the water, the fast diffusing component, may be constrained by its proximity to the pore walls.

We next look at the individual components for the differing systems. It



Figure 8.3: T_2 exchange spectra for water and oil in oil-wet spheres for a) $\tau_m = 20 \,\mu\text{s}$, b) $\tau_m = 160 \,\mu\text{s}$, c) $\tau_m = 320 \,\mu\text{s}$, d) $\tau_m = 360 \,\mu\text{s}$

should be pointed out that even though the water tends to appear at the shorter T_2 times and the oil signal at the longer T_2 times, this does not necessarily mean that all the water is in small pores and all the oil in larger pores. Equation 4.2 contains the dependence on surface relaxivity and oil is known to have a much smaller interaction with surfaces than water. Better correlations are necessary to make definitive statements about the location

$ au_m$	$20 \mathrm{ms}$	400ms
Water in Water-wet	0%	70%
Oil in Water-wet	12%	25%
Water in Oil-wet	30%	50%
Oil in Oil-wet	4%	12%

Table 8.1: Fluid exchange

of the fluid in the pore space and this is discussed further in Chapter 10.

For the oil in the water-wet system, we begin to see weak exchange peaks even at $20 \, ms$. We estimate that after $400 \, ms$ around 25% of the oil has shifted location, though we are somewhat unsure in this measurement due to the strong asymmetry seen in the data. Unlike the oil, which already shows weak exchange, the water in the water-wet system (Figure 8.4) appears to show no exchange at all at 20ms. Around 60ms exchange peaks begin to form. Despite the longer exchange time, more of the water changes environments. Around 70% of the water appears to have shifted location after the longest mixing time. This suggests that while the water exchange rate is slowed by the wettability of the pore surfaces, it still has opportunity to shift to other environments. The oil, while less constrained, may be caught in the middle of pores and unable move to others as easily as the water. From this we can see that even when the water is constrained due to surface wettability, it still has far greater mobility than even the unconstrained oil.

The oil in the oil-wet system, Figure 8.7, shows highly constrained behaviour. Only at the longest mixing times do we begin to see exchange peaks forming. We estimate at the longest mixing time, only 12% of the oil has shifted location. Compared to the 25% exchange observed for oil in



Figure 8.4: T_2 exchange spectra for water in water-wet spheres for a) $\tau_m = 20 \,\mu\text{s}$, b) $\tau_m = 160 \,\mu\text{s}$, c) $\tau_m = 320 \,\mu\text{s}$, d) $\tau_m = 360 \,\mu\text{s}$



Figure 8.5: T_2 exchange spectra for oil in water-wet spheres for a) $\tau_m = 20 \,\mu s$, b) $\tau_m = 160 \,\mu s$, c) $\tau_m = 320 \,\mu s$, d) $\tau_m = 360 \,\mu s$

the water-wet system, we see evidence that the wettability of the medium is limiting the exchange of the oil. As opposed to the water in the water-wet case, there appears to be rapid exchange occurring among the water in the oil-wet system. Approximately 30% of the molecules already changed their environment after 20 ms. Unfortunately, due to gradient limitations, mixing times shorter than this were unable to be investigated. By 280 ms, a steady state appears to have been reached, with approximately 50% of the water having shifted its environment. This appears to be similar behaviour to that of the oil in the water-wet system. While the non-wetting component is able to exchange more quickly than the wetting component, it is limited in the extent of exchange that can occur.

V Conclusions

We can conclude that the wettability has a definite influence on the selfdiffusion of fluid between pores in partially saturated systems. We also show that the diffusion attenuation can be used to separate components for T_2 exchange experiments in situations where the linewidth is too broad to allow the determination of the components in the spectra dimension. Our results show that the movement of the wetting phase appears to be constrained in two-phase systems, with oil more greatly affected.

The chlorotrimethylsilane seems to only temporarily impart a wettability change upon the surface of the spheres, leading to issues with reproducibility. Despite this setback, the diffusion attenuated transverse relaxation exchange experiment shows potential for tracking different types of fluid molecules through porous media. Our collaborators at the Australian National University are currently working to create a more stable means of controlling



Figure 8.6: T_2 exchange spectra for water in oil-wet spheres for a) $\tau_m = 20 \,\mu s$, b) $\tau_m = 160 \,\mu s$, c) $\tau_m = 320 \,\mu s$, d) $\tau_m = 360 \,\mu s$



Figure 8.7: T_2 exchange spectra for oil in oil-wet spheres for a) $\tau_m = 20 \,\mu\text{s}$, b) $\tau_m = 160 \,\mu\text{s}$, c) $\tau_m = 320 \,\mu\text{s}$, d) $\tau_m = 360 \,\mu\text{s}$

a surface's wettability. We anticipate completion of this project will finally enable a more thorough quantitative analysis through better reproducibility.

Chapter 9

Propagator Resolved Transverse Relaxation Exchange

I Introduction

While the T_2-T_2 exchange experiment gives us important information regarding the movement of fluid between pores of different sizes, it is limited in that it cannot differentiate between signals that come from spin-bearing molecules remaining in their original pore and molecules that have diffused to a pore of similar size. Another concern with the T_2-T_2 exchange experiment is that we assumed a change of T_2 during the mixing time, τ_m , indicated that molecules had changed pores. While this appears to be a reasonable assumption because the peak intensity reflects the theoretical exchange equations, we seek further evidence to support this assumption.

In this chapter, we expand upon the diffusion attenuation concept to produce a true three dimensional experiment. Instead of applying a single strength gradient to remove the signal contribution from one system component, we use a range of gradients to determine how far the fluid molecules move during the mixing period. We limit ourselves here to a single fluid phase, water, to show the underlying concept is sound, but future work with multiphase systems is planned.

NMR experiments that combine a single inverse Laplace dimension with a Fourier dimension are well known. The DOSY(91) and CORE(92) experiments combine spectral resolution in the chemical shift domain with a measurement of diffusion coefficients. Other researchers have correlated a T_2 measurement with fluid propagators(93). The technique we develop here, the propagator resolved T_2 exchange experiment, is the first NMR technique to combine two inverse Laplace dimensions with a Fourier dimension. The added third dimension is used to measure how far the molecules move during τ_m and allows us to estimate the movement of fluid between pores of similar size. By observing how the molecules move between pores of similar and different sizes, as well as look at the distances they move, we gain a better understanding of the pore space and the fluid dynamics therein.

II Experimental

1 Preparation

Experiments were carried out with the quartz sand, the Fontainebleau sandstone, and the Mt. Gambier limestone. Unfortunately the T_2 exchange propagator experiment could not be completed with the Castlegate sandstone because of gradient limitations. The length of the required gradients for diffusion encoding in the Castlegate sample were such that between the internal gradients and short T_2 times of the sample, significant loss of signal occured.



Figure 9.1: Propagator resolved transverse relaxation exchange pulse sequence

This made the resulting T_2 spectra of the Castlegate too T_1 weighted for accurate analysis.

The sand was tight-packed and then saturated with distilled water. The rock cores were saturated with distilled water and excess surface water removed, but no other specific preparations were undertaken. All samples were held at 25°C for the duration of experimentation.

2 Pulse Sequence

After the initial 90° excitation pulse, the experiment begins with a T_2 encoding interval. To avoid influence from internal gradients, we measure for T_2 by keeping our echo spacing fixed at $150 \,\mu$ s, and varying the number of 180° refocusing pulses. We use only an even number of echoes to avoid the odd-even echo effect. After the first T_2 encode, we apply the gradients for the diffusion measurement, using bipolar-pulsed field gradients sandwiched with a 180° refocusing RF pulse to prevent possible interference of internal gradients with the diffusion measurement. A subsequent 90° pulse stores the magnetisation along the z-axis for the mixing interval τ_m , where it does not experience T_2 relaxation, but only the longer T_1 relaxation. We used mixing times ranging from 50 ms to 550 ms in increments of 50 ms. After the mixing interval, another 90° pulse returns the magnetisation to the transverse plane. The complementing pair of bipolar gradients completes the measurement of the molecular diffusion during the mixing time. Finally, we perform our second T_2 encode simultaneously as acquisition, sampling the top of each echo in the CPMG train.

For our experiments, we acquired 4096×66 points in the T_2 dimensions and 32 points in the diffusion dimension. Each experiment required approximately 7 hours to complete. Our phase cycling ensured that all the measured signal derived solely from the first, initial excitation pulse. The 3D data was zero filled in the q-dimension to 64 points for fast Fourier transform (FFT), the equivalent of smooth interpolation in the spatial domain and then Fourier transformed along the diffusion axis to give the diffusion propagator. Planes of T_2-T_2 exchange data were taken from along the propagator. For each plane, we select the 'm' encoding times that corresponded to the 'n' encoding times used to produce a symmetric 62×62 matrix. The first four acquired points are not used due to oscillatory transients in the signal decay. For our transverse relaxation exchange experiment, the equation describing the magnetisation is given by

$$M(\tau_n, \tau_m) = \iint k_1(\tau_n, T_2^1) k_2(\tau_n, T_2^2) F(T_2^1, T_2^2) dT_2^1 dT_2^2 + \epsilon(\tau_n, \tau_m) , \qquad (9.1)$$

where k_1 and k_2 are the kernels relating the experimental parameters to possible T_2 times, $F(T_2^1, T_2^2)$ is the joint probability density, and T_2^1 and T_2^2 are the measured T_2 values from the first and second encoding intervals respectively. The planes of T_2 - T_2 exchange data are then transformed using a 2D inverse Laplace algorithm to a 40 × 40 matrix.

3 Regularisation

A major point of deliberation for our experiments concerned consistency of the inverse Laplace regularisation. As mentioned in Chapter 5, the Non-Negative Least Squares algorithm (NNLS) used in the inverse Laplace transform tends to return solutions consisting of numerous sharp peaks. The regularisation parameter α is used to force the algorithm to return solutions that have a smooth spectrum. In most situations, the value of α would be adjusted to just minimise χ^2 (and no further) for each spectrum. However, as we are tracking integrated peak intensities over numerous spectra, a single common value of α is chosen for consistency. The use of a common α value for all the spectra is not expected to have a significant impact on the results, as the differences in individually optimised α values were slight.

III Analysis

Figures 9.2, 9.3, and 9.4 show the exchange spectra for the Quartz Sand, Fontainebleau, and Mt. Gambier limestone respectively. The resulting T_2 times of the peaks compare well with the T_2 times measured in the regular T_2 exchange experiments. The shortest T_2 peak in the Fontainebleau and Mt. Gambier spectra appears at a slightly longer T_2 time, however. This is most likely the result of some of the shortest T_2 components in the spectra relaxing during the additional time taken for diffusion encoding in the propagator resolved version of the experiment.

The T_2 - T_2 exchange spectra exhibit remarkable differences depending on mixing time and displacement. All three samples show similar types of behaviour, though at different rates. For short mixing times, the signal mainly lies along the diagonal, indicating that the spin-bearing fluid molecules are



Figure 9.2: Quartz sand exchange spectra a) 100 ms exchange time, 0 μ m displacement b) 100 ms exchange time, 30 μ m displacement c) 250 ms exchange time, 0 μ m displacement d) 250 ms exchange time, 30 μ m displacement e) 250 ms exchange time, 45 μ m displacement f) 500 ms exchange time, 0 μ m displacement g) 500 ms exchange time, 30 μ m displacement h) 500 ms exchange time, 45 μ m displacement.



Figure 9.3: Fontainebleau exchange spectra a) 100 ms exchange time, $0 \mu m$ displacement b) 100 ms exchange time, $30 \mu m$ displacement c) 250 ms exchange time, $0 \mu m$ displacement d) 250 ms exchange time, $30 \mu m$ displacement e) 250 ms exchange time, $50 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement g) 500 ms exchange time, $30 \mu m$ displacement h) 500 ms exchange time, $50 \mu m$ displacement f) 500 ms exchange time, $50 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement f) for $0 \mu m$ displacement f) for



Figure 9.4: Mt. Gambier exchange spectra a) 100 ms exchange time, $0 \mu m$ displacement b) 100 ms exchange time, $30 \mu m$ displacement c) 250 ms exchange time, $0 \mu m$ displacement d) 250 ms exchange time, $30 \mu m$ displacement e) 250 ms exchange time, $50 \mu m$ displacement f) 500 ms exchange time, $0 \mu m$ displacement g) 500 ms exchange time, $30 \mu m$ displacement h) 500 ms exchange time, $50 \mu m$ displacement f) for more time, $50 \mu m$ displacement f) for more time, $0 \mu m$ displacement f) for more time, for more time

still in their original environments. A slight skewing off the diagonal can be seen for the shortest T_2 peak for short mixing times and small displacement. We are uncertain as to the cause of this skewing effect. Poor tuning in the RF coil can lead to skewing in the resulting inverted spectra, but we do not believe this to be the factor here, as the tuning of the coil was carefully controlled. We speculate it may have to do with exchange peaks that have not been resolved by the transform. The inverse Laplace transform cannot yet resolve the two peaks individually, so the optimisation forces the location of the diagonal peak upward to account for the contribution of the unresolved cross-peak.

For the Mt. Gambier sample and the sand, the T_2 - T_2 exchange plots at these short mixing periods start to show evidence for pore-to-pore exchange for displacements of about 25-30 μ m. The Fontainebleau sample, however, shows no evidence of exchange at any displacement for the short mixing periods. As we move to longer mixing times, we see that the off-diagonal intensity increases, indicating that more fluid molecules have managed to shift T_2 environments. The Fontainebleau finally begins to show evidence of exchange at large displacements. We also start to see off-diagonal intensity arising at smaller displacements. By $\tau_m = 150 \, ms$ in Mt. Gambier and $\tau_m = 250 \, ms$ in the sand, we begin to see off-diagonal peaks form even at the smallest displacements. This at first seems contradictory, as molecules that have not moved should still be in their original T_2 environment. However, it is important to note that the porous medium is isotropic and we are encoding for movement in one direction only. Therefore, it is possible for molecules to move to a new environment perpendicular to the diffusion axis while having travelled very little distance along it.

An interesting effect is that the peaks become more discretised for both

large displacements and long mixing times, changing from a continuous signal along the diagonal into individual peaks. We speculate that this could be due to a T_1 averaging effect. For short times and displacements, the fluid molecules have only experienced a small portion of the pore surface. At longer displacements and times, molecules are likely to have experienced more of the pore surface, leading to a better averaged T_1 time, thus helping to discretise the peaks in the T_2 exchange spectrum.

We now turn to quantitative analysis of our NMR data. We integrate the different peak intensities for the various mixing times and displacements, combining intensities for the complementary (symmetric) exchange peaks. We then normalise the peak intensities as a function of the total integrated value at that mixing time so as to remove influence of T_1 relaxation. These normalised intensities are then plotted as a function of mixing time and displacement seen in Figures 9.5, 9.6, and 9.7. These intensities effectively represent probability distributions or propagators, $P^{\alpha\beta}$, that a molecule starting in pore α and ending in pore β has displaced a distance Z over the experimental mixing time.

IV Simulations of Inter-Pore Diffusion

To interpret our data, we require a representation of the pore hopping probability C_n to mimic the movement of fluid between pores. Two models were developed: an analytic model, which uses spreading Gaussians to determine pore occupancy, and a probabilistic hopping model, where molecules have a finite chance of moving to a new pore at each time step. Both sets of simulations were carried out in MATLAB, the computed probability first roughly fitted to the experimental data by hand, and then optimised using



Figure 9.5: Quartz sand normalised experimental intensity plots for propagators $P^{\alpha\alpha}$, $P^{\beta\beta}$, $P^{\gamma\gamma}$, $P^{\alpha\beta}$, $P^{\alpha\gamma}$, $P^{\beta\gamma}$ describing the probability that spin-bearing molecules migrate a distance Z along the magnetic field gradient direction in a time τ_m corresponding to the experimental mixing time.



Figure 9.6: Fontainebleau normalized experimental intensity plots propagators $P^{\alpha\alpha}$, $P^{\beta\beta}$, $P^{\alpha\beta}$, describing the probability that spin-bearing molecules migrate a distance Z along the magnetic field gradient direction in a time τ_m corresponding to the experimental mixing time.



Figure 9.7: Mt. Gambier normalized experimental intensity plots propagators $P^{\alpha\alpha}$, $P^{\beta\beta}$, $P^{\gamma\gamma}$, $P^{\alpha\beta}$, $P^{\alpha\gamma}$, $P^{\beta\gamma}$, describing the probability that spin-bearing molecules migrate a distance Z along the magnetic field gradient direction in a time τ_m corresponding to the experimental mixing time.

the Nelder-Mead Method. This technique serves to minimise a function of several variables, which in our case is a chi squared relation

$$\chi^2 = (P_{exp} - P_{sim})^2, \tag{9.2}$$

where χ^2 is the squared difference between the experimental and simulated results. For our model, the variables were the different pore sizes (r_{α}, r_{β}) , pore spacings $(b_{\alpha\alpha}, b_{\alpha\beta}, b_{\beta\beta})$, and inter-pore diffusion coefficients $(D_{\alpha\alpha}, D_{\alpha\beta}, D_{\beta\beta})$. To find our confidence intervals, we found the deviation from the optimised value needed to double χ^2 . The probabilistic nature of the pore-hopping simulations causes minor variations in χ^2 , even for identical starting parameters, such that calculation of precise error-bars was not possible.

The Fontainebleau is a straightforward two-pore system. We refer to the smaller pores as α pores and the larger pores as β pores. In an isotropic distribution around our starting α and β pores, there exist corresponding α and β pores. We refer to this first shell of pores as α' or β' pores. Around these pores there is yet another shell, α'' and β'' . We only consider the shells as far out as the second nearest neighbour since movement beyond the second pore is extremely unlikely at the time scales with which we are working. For our sand, we analyse our data in two different ways. For the first method, we assume a two-pore system reflecting the small number of peaks in the T_2 - T_2 spectra. We justify this assumption by noting that the signal intensity from the shortest T_2 peak comprises only a small percentage of total signal intensity. For the second method, we re-wrote the simulations to model for three pore exchange. We now have a system that consists of $\alpha,\,\beta,$ and γ pores. Like the two pore system, there exist shells of $\alpha',\,\beta',\,\gamma'$ and α'' , β'' , γ'' . Due to memory constraints, we were only able to perform this simulation analytically. The probabilistic simulations need a certain number of molecular walkers to produce statistically averaged results, and

the number required in the three pore system were beyond the computer system's capabilities. Unlike the sand sample, the shortest peak in the Mt. Gambier inverse Laplace spectra was not weak enough to allow us to assume a two pore system, so we only analysed this sample using the three pore exchange model.

1 Pore Glass

The porous systems we work with are classified as porous glasses. There is randomness to the spacing and orientation of their pores. We idealised these systems as rapid fluid diffusion within discrete classes of pores labelled by their local surface to volume ratio, and hence T_2 value, using an exponent α,β , etc., with slower diffusion between pores, over the time scale Δ . The fast intra-pore diffusion assumption will require pores to have dimensions on the order of or smaller than $D_0\Delta$ where D_0 is the free molecular self-diffusion coefficient. The advantage of this assumption is that the echo attenuation may be reduced to a simple product of a pore structure factor $|S_0^{\alpha}(q)|^2$ and the Fourier transform of the propagator $P_{pore-to-pore}(Z, \Delta)$ representing displacements between pores. Obviously $|S_0^{\alpha}(q)|^2$ will depend on the pore size, while $P_{pore-to-pore}(Z, \Delta)$ will depend on the occupancies of the various pores to which molecules migrate from the starting pore, and the displacements of those pores from the origin. Different values of $P_{pore-to-pore}(Z, \tau_m)$ apply depending on whether the exchange is between pores of similar size or differing size.

2 Exchange between similar size pores

We start by considering hopping between pores of the same class, which have the same T_2 value. We shall further assume an orientationally disordered pore glass, for which displacements have a mean length b but no orientational order. The diffusion echo attenuation is described by

$$M^{\alpha\alpha}(q,\Delta) = |S_0^{\alpha}(q)|^2 \sum_n C_n \Im \{H(Z,b)\},, \qquad (9.3)$$

where C_n is the probability of hopping to the n^{th} neighbour shell, \Im is the Fourier transform, and b the pore spacing. H is the probability distribution of pore centers for the n^{th} pore shell along Z. As we assume an isotropic medium, this distribution will be uniform across a range of -nb < Z < +nb and can be modeled as a hat function. Evaluation of the Fourier Transform in equation 9.3 gives :

$$M^{\alpha\alpha}(q,\Delta) = |S_0^{\alpha}(q)|^2 \sum_n C_n \frac{\sin(2\pi qb)}{2\pi qb}$$
(9.4)

Because the signal from molecules in their original pores and the signal from molecules that have exchanged with pores of the same class both lie upon the diagonal in the T_2 - T_2 plane, we will have an initial starting intensity. We must then separate the case of n=0 because the two types of signal will behave differently. Separation of the contribution to the magnetisation from the molecules in their original pores from the signal of molecules that have shifted environments gives us:

$$M^{\alpha\alpha}(q,\Delta) = |S_0^{\alpha}(q)|^2 \left[C_0^{\alpha} + \sum_n C_n^{\alpha\alpha} \frac{\sin(2\pi q b_{\alpha\alpha})}{2\pi q b} \right]$$
(9.5)

The form factor, $|S_0^{\alpha}(q)|^2$ is the squared Fourier transform of the density function, which makes it dependent upon not only pore size, but pore shape as well. We assume for simplicity spherical pores. The density function of a sphere projected along a one dimensional axis of radius r is described by:

$$\rho(z) = \left(\frac{3}{4r^3}\right)\left(r^2 - z^2\right)\tag{9.6}$$

for -r < z < r. The measured signal in an experiment would be the Fourier transform of this distribution, given by

$$S(q) = \int_{-r}^{2} \left(\frac{3}{4r^{3}}\right) \left(r^{2} - z^{2}\right) \exp(2\pi i q z) dz = \frac{3\left[\sin(2\pi q r) - (2\pi q r)\cos(2\pi q r)\right]}{(2\pi q r)^{3}}$$
$$|S_{0}^{\alpha}(q)|^{2} = \exp(-\frac{1}{5}(2\pi q)^{2}r^{2}) \tag{9.7}$$

We rewrite this equation in terms of $\sigma = \frac{2}{5}r^2$ to obtain:

$$|S_0^{\alpha}(q)|^2 = \exp(-\frac{1}{2}(2\pi q)^2 \sigma^2)$$
(9.8)

This form of the equation will simplify later Fourier transform calculations. We then substitute equation 9.8 into equation 9.5 to obtain the equation:

$$M^{\alpha\alpha}(q,\Delta) = \exp(-\frac{1}{2}(2\pi q)^2 \sigma^2) \left[C_0^{\alpha} + \sum_n C_n^{\alpha\alpha} \frac{\sin(2\pi q b_{\alpha\alpha})}{2\pi q b} \right]$$
(9.9)

We take the Fourier transform of equation 9.9 with respect to q to obtain the propagator P(Z):

$$P^{\alpha\alpha}(Z,\Delta) = C_0^{\alpha}\rho_0^{\alpha}(Z) * \rho_0^{\alpha}(Z) + \sum_n C_n^{\alpha\alpha} \left[\rho_0^{\alpha}(Z) * \rho_0^{\alpha}(Z)\right] \bigotimes H(Z, nb_{\alpha\alpha})$$
(9.10)

where * denotes a spatial correlation function and \bigotimes denotes a spatial convolution. $P^{\alpha\alpha}$ gives us the distribution of molecular movement as determined by the restrictions in the sample due to pore configuration. For molecules in their original pores, this is simply the pore occupancy multiplied by the density function. For molecules that have moved to a new pore, the distribution of pores also plays a part. We now need to solve for this convolution of density function with the hat function in terms of inter-pore spacing and pore size:

$$\left[\rho_0^{\alpha}(Z) * \rho_0^{\alpha}(Z)\right] \bigotimes H(Z, nb_{\alpha\alpha}) = (2\pi\sigma^2)^{\frac{1}{2}} \frac{\sqrt{2\pi\sigma^2}}{4nb_{\alpha\alpha}} \times \left[erf\left[\frac{Z+nb_{\alpha\alpha}}{\sqrt{2}\sigma_{\alpha\alpha}}\right] \pm erf\left[\frac{Z-nb_{\alpha\alpha}}{\sqrt{2}\sigma_{\alpha\alpha}}\right]\right]$$
(9.11)

equation 9.11 simplifies to one of two equations depending whether Z is larger or smaller than the pore. For the case of Z < nb:

$$\left[\rho_0^{\alpha}(Z) * \rho_0^{\alpha}(Z)\right] \bigotimes H(Z, nb_{\alpha\alpha}) = \frac{1}{4nb_{\alpha\alpha}} \left[erf\left[\frac{Z + nb_{\alpha\alpha}}{\sqrt{2}\sigma_{\alpha\alpha}}\right] + erf\left[\frac{Z - nb_{\alpha\alpha}}{\sqrt{2}\sigma_{\alpha\alpha}}\right] \right]$$

and for the case of $Z > nb$:

$$\left[\rho_0^{\alpha}(Z) * \rho_0^{\alpha}(Z)\right] \bigotimes H(Z, nb_{\alpha\alpha}) = \frac{1}{4nb_{\alpha\alpha}} \left[erf\left[\frac{Z + nb_{\alpha\alpha}}{\sqrt{2}\sigma_{\alpha\alpha}}\right] - erf\left[\frac{Z - nb_{\alpha\alpha}}{\sqrt{2}\sigma_{\alpha\alpha}}\right] \right]$$
(9.12)

Note that equation 9.10 only holds true in the fast diffusion limit, where all the molecules have diffused the distance length of the pore. If the fast diffusion limit has not been reached, equation 9.10 must be modified. For these cases, one method to deal with this situation is to multiply the pore density function by the diffusive envelope:

$$\frac{1}{\sqrt{4\pi D_0 \Delta}} \exp\left[\frac{-Z^2}{4D_0 \Delta}\right] \tag{9.13}$$

We multiply equation 9.10 by this function. We take as D_0 the diffusion coefficient of water at room temperature, which is $2.3 \times 10^{-9} \frac{m^2}{s}$ in the present context. This becomes a constant multiplier once the fast diffusion limit is reached.

3 Exchange between different size pores

We begin with equation 9.4. Unlike with movement between similar size pores, we have no starting intensity. For this case, the echo attenuation can simply be described by:

$$M^{\alpha\beta}(q,\Delta) = |S_0^{\alpha}(q)| \left| S_0^{\beta}(q) \right| \left[\sum_n C_n^{\alpha\beta} \frac{\sin(2\pi q b_{\alpha\beta})}{2\pi q b} \right]$$
(9.14)

Between pores of differing sizes, the form factor is a combination of both pore sizes. Again, we assume the case of spherical pores.

$$S_0^{\alpha}(q)S_0^{\beta}(q)^* \approx \exp\left(-\frac{1}{5}(2\pi q)^2 \frac{1}{2}(r_{\alpha}^2 + r_{\beta}^2)\right)$$
(9.15)

To simplify the Fourier transform, we rewrite equation 9.15 as a function of $\sigma_{\alpha\beta}^2 = \frac{1}{5}(r_{\alpha}^2 + r_{\beta}^2)$. The echo attenuation can be rewritten as:

$$M^{\alpha\beta}(q,\Delta) = \exp\left(-\frac{1}{2}(2\pi q)^2 \sigma_{\alpha\beta}^2\right) \left[\sum_n C_n^{\alpha\beta} \frac{\sin(2\pi q b_{\alpha\beta})}{2\pi q b}\right]$$
(9.16)

We Fourier transform equation 9.16 to obtain the average propagator. For Z < nb:

$$P^{\alpha\beta}(Z,\Delta) = \sum_{n+1} C_n^{\alpha\beta} \frac{1}{4nb_{\alpha\beta}} \times \left[erf\left[\frac{Z+nb_{\alpha\beta}}{\sqrt{2}\sigma_{\alpha\beta}}\right] + erf\left[\frac{Z-nb_{\alpha\beta}}{\sqrt{2}\sigma_{\alpha\beta}}\right] \right] \quad (9.17)$$

if Z > nb:

$$P^{\alpha\beta}(Z,\Delta) = \sum_{n+1} C_n^{\alpha\beta} \frac{1}{4nb_{\alpha\beta}} \times \left[erf\left[\frac{Z+nb_{\alpha\beta}}{\sqrt{2}\sigma_{\alpha\beta}}\right] - erf\left[\frac{Z-nb_{\alpha\beta}}{\sqrt{2}\sigma_{\alpha\beta}}\right] \right] \quad (9.18)$$

Once again, we need to multiply the result by the diffusive envelope of equation 9.13 to account for the fact we are not in the fast diffusion limit at short mixing times.

4 Analytic simulation

A simplistic approach to representing the inter-pore occupancies C_n is to use a simple diffusive envelope, where the relevant diffusion coefficient is the time for inter-pore migration. For the case of movement between pores of the same class, this probability is represented as a spreading Gaussian

$$C_n^{\alpha\alpha} = \frac{4\pi (nb_{\alpha\alpha})^2 b_{\alpha\alpha}}{(4\pi D_p^{\alpha\alpha} \Delta)^{\frac{3}{2}}} \exp\left(-\frac{n^2 b_{\alpha\alpha}^2}{4D_p^{\alpha\alpha} \Delta}\right), \qquad (9.19)$$

where n is the pore shell, b is the mean pore spacing, and D_p the inter-pore diffusion coefficient. The equation for the case of exchange between pores of differing sizes is similar, except it now uses the mean pore spacing and inter-pore diffusion coefficient between pores of different classes

$$C_n^{\alpha\beta} = \frac{4\pi (nb_{\alpha\beta})^2 b_{\alpha\beta}}{(4\pi D_p^{\alpha\beta} \Delta)^{\frac{3}{2}}} \exp\left(-\frac{n^2 b_{\alpha\beta}^2}{4D_p^{\alpha\beta} \Delta}\right).$$
(9.20)

Unlike the other two occupancies, which will grow with time, the occupancy of the origin pores will decrease. To calculate the residency in the original pore, we subtract the two inter-pore occupancies

$$C_0^{\alpha} \approx 1 - \sum_{n=1} C_n^{\alpha \alpha} - \sum_{n=1} C_n^{\alpha \beta}.$$
(9.21)

5 Probabilistic simulation

For our probabilistic simulations, we fill the pores and pore shells with molecular walkers. At the end of the simulation, though, we will only consider the movement of molecules starting from α or β pores, which we consider origin pores. For each time step in the simulation, a molecule has a certain likelihood that it will jump from the pore it is in to a neighbouring pore. The balance of mass must be maintained as our system is fully saturated. To do this, a molecule in the new pore must exchange with the hopping molecule. The program randomly searches for a molecule in the new pore to place into the hopping molecule's original pore. At the end of the experiment, we tally the locations of molecules from the original α and β pores for each time step. The number of molecules in each location is then substituted for C_n in the propagator equation in our pore-hopping simulation. We can then apply these occupancies in a simulation which solves the average propagator equation to find the fluid movement within the sample over time.

V Results

On suitable variation of the fitting parameters, the simulated results, shown in Figures 9.9, 9.10, 9.11, and 9.12, show agreement with the experimental data, with the poorest results being for exchange between pores of differing size (off-diagonal peaks) at short mixing times and displacements. We believe that this discrepancy at short mixing times and displacements between the simulated and experimental data for exchange between pores of differing size arises from resolution problems in the inverse Laplace transform where the off-diagonal peak is of weak intensity. In the presence of a peak of much greater intensity, the inverse Laplace transform often cannot resolve a weak intensity peak. Therefore, until the weaker peak has reached a sufficient intensity compared to the greater peak, the transform cannot resolve it. The Mt. Gambier, which has the most exchange, has cross peak intensity plots that best resemble the simulated exchange plots while the Fontainebleau, which has the least exchange, has a poorly developed exchange plot for the off diagonal peaks. As our simulations require matching of intensities, this discrepancy has led to some uncertainty in some of the values of the interpore spacing and inter-pore diffusion coefficient between α , β , and in some cases γ pores.



1 Diagram Interpretation

Figure 9.8: Annotated peak intensity diagram. The τ_m -axis is increasing mixing time, the *P*-axis is increasing displacement, and the *Z*-axis is the normalised intensity.

The fitting process was based on a least-squares minimisation right across the (Z, τ_m) plane of peak intensity. However, specific parameters of the fit influence different features of the distributions, thus simplifying the search for suitable initial parameters in the multi-dimensional parameter space, and thus assisting in the search for a global minimum. Figure 9.8 gives an annotated peak intensity diagram that shows how to interpret the plots. The vertical axis is the normalised peak intensity. The displacement axis (Z)shows how the intensity of a peak evolves depending on distance. The mixing time axis (τ_m) shows how the peak intensity behaves as a function of time. At small displacements, the decrease in signal intensity along the mixing time axis, or increase for exchange between unlike pores, is governed by inter-pore diffusion. For short mixing times, the signal intensity along the displacement axis is influenced mostly by pore radius. For longer mixing times and finite displacements, the spread of intensity is governed by the inter-pore spacing.

2 Pore Radii

Provided the amount of exchange is small, pore radii for pores smaller than the maximum displacement Z measured by the experiment can almost be read directly from the experimental results at small values of τ_m . The intensity will temporarily stop advancing along the displacement axis with increased mixing time once τ_m is sufficiently large that the molecules have collided with the starting pore surface, which is displaced on the order of the pore radius. For pore radii larger than the maximum measured displacement of the experiment, such simple manifestation of the pore size is not apparent at short τ_m . Here we must analyse our distributions across the (Z, τ_m) plane by looking at how pore size affects the spread of intensity. The more quickly the intensity continues to spread, the larger the pore size.
3 Inter-Pore Spacing

The effects of inter-pore spacing are subtle in the case of exchange between like pores, except in the situation of very fast diffusion. The inter-pore spacing strongly influences the intensity at long mixing times, where signal has begun to spread beyond the distance of the estimated starting pore space. The further the intensity distribution spreads along the Z axis, the larger the inter-pore distance. The inter-pore spacing also has an influence on the rate of intensity decay. If the pores are very far apart, the likelihood of moving from one pore to another is less, so the signal decays more slowly. Clearly the interplay between decay along the τ_m and Z axes is sensitive to both inter-pore spacing and inter-pore diffusion rate. Note that, in principle, it is possible to estimate pore spacings greater than the molecular diffusion distance because of this interplay, though accuracy may be impeded.

Finding the inter-pore spacing between unlike pores is similar to finding the pore radius. For pore spacings less than the maximum diffusion distance measured by the experiment, the signal will stop advancing at approximately the inter-pore spacing. For pore-spacing larger than the diffusion resolution, we look at how the signal advances. Unfortunately, due to previously discussed resolution issues of the inverse Laplace transform, we need to be cautious with regard to the accuracy of the average inter-pore spacing between unlike pores.

The optimisation for exchange between pores of a similar class returned interesting behaviour. Above certain inter-pore spacings, χ^2 would reach a minimum, but in a broad valley where the value of χ^2 was constant extending to large values of $b_{\alpha\alpha}$, $b_{\beta\beta}$, and $b_{\gamma\gamma}$. We believe this behaviour can give an estimate of the possible minimum inter-pore spacing, but we are unsure as to the upper limits of the fit. While the inter-pore spacings we calculate are consistent with the interpore spacings seen in the X-ray CT data, that data suggests that there also exist many pores with connection distances larger than those found with our data. Because we are limited by the diffusion distance of the molecules, the nearest neighbour pores at the longer distances may not be adequately probed. We believe the wide valleys in our simulated fits reflect our inability to investigate these longer length scales. We anticipate that driven fluid flow through the sand will increase the number of molecules exchanging pores, allowing the exchange peaks to be better resolved by the inverse Laplace transform and giving them stronger intensity in the exchange plots, and thus allow us to more accurately determine inter-pore spacing.

4 Rate of exchange between pores

The rate at which intensity decays along the Z-axis for the pore-hopping simulations reflects how quickly fluid moves between pores. This characteristic rate is controlled by the likelihood of hopping in the probabilistic simulation. For the analytic simulation, the inter-pore diffusion rate is the main factor affecting intensity decay while inter-pore spacing has a minor influence. For the probabilistic simulation, the characteristic time between pores can be found by

$$\lambda = \frac{\Delta t}{P} , \qquad (9.22)$$

where λ is the characteristic time, Δt is the time step, and P is the probability of hopping during that time step. λ can be simply related to the inter-pore diffusion coefficient by

$$\lambda = \frac{b^2}{6D_p} \,, \tag{9.23}$$

where b is the inter-pore spacing.

5 Tortuosity

Now that we have calculated inter-pore spacings and characteristic times, we can then find the tortuosity between the pores of like and unlike classes. Tortuosity is a measure of how convoluted a path is and is defined as the length of a curve divided by the distance between its end points. In the case of a pore space, we can approximate this as the free diffusion coefficient divided by the inter-pore diffusion coefficient

$$T = \frac{D_0}{D_p} \,. \tag{9.24}$$

This is straight forward to calculate from the data using the analytic model as D_p is a fitting parameter. For the pore-hopping model, the inter-pore diffusion rate can be calculated from the characteristic time and the pore spacing such that

$$D_p = \frac{b^2}{6\lambda} , \qquad (9.25)$$

where λ is the characteristic time, and b is the inter-pore spacing, either between like or unlike pores. This can be rewritten in terms of tortuosity to give

$$T = \frac{6D_0\lambda}{b^2} \,. \tag{9.26}$$

VI Quartz sand two pore model

1 Pore Radii

From our probabilistic simulations, we estimate that the pore radius size for the smaller βT_2 peak is on the order of 24 μ m. The analytic simulations agree with this value, producing a pore radius size of 25 μ m. By matching our simulated intensity spreads we were able to estimate our γ pore sizes.

T_2	eta(ms)	$\gamma(ms)$
	38	79
Pore radius	$r_{eta}~(\mu{ m m})$	$r_{\gamma}~(\mu m)$
Analytic	25 ± 3	52 ± 13
Probabilistic	24	49

Table 9.1: Quartz sand pore properties.

Table 9.2: Quartz sand inter-pore properties.

Inter-pore spacing	$b_{etaeta}(\mu m)$	$b_{\gamma\gamma}(\mu m)$	$b_{\beta\gamma}(\mu m)(\mathbf{s})$
Analytic	51 ± 9	134 ± 37	83 ± 15
Probabilistic	56	108	76
Characteric times	$\lambda_{etaeta}(\mathrm{s})$	$\lambda_{\gamma\gamma}(\mathrm{s})$	$\lambda_{eta\gamma}({ m s})$
Analytic	1.35	3.2	0.63
Probabilistic	2.63	2.38	0.71
D _p	$D_{\beta\beta}(\frac{m^2}{s})$	$D_{\gamma\gamma}(\frac{m^2}{s})$	$D_{\beta\gamma}(\frac{m^2}{s})$
Analytic	3.2×10^{-10}	9.3×10^{-10}	18.0×10^{-10}
Probabilistic	1.9×10^{-10}	10.8×10^{-10}	$13.6\!\times\!10^{-10}$
Tortuosity	T_{etaeta}	$T_{\gamma\gamma}$	$T_{eta\gamma}$
Analytic	7.1	2.5	1.3
Probabilistic	11.5	2.1	1.8



Figure 9.9: Quartz sand two pore model peak intensity plots for a) Analytic simulation b) Probabilistic Simulations. Experimental peaks shown in Figure 9.5

The probabilistic and analytic simulations gave γ pore sizes of around 49 μ m and 52 μ m respectively. These calculated values of β and γ are consistent with the pore size distribution obtained from the X-ray CT data.

2 Inter-pore spacing

Between unlike pores, the pore hopping model fit found a distance of $b_{\beta\gamma} = 76 \,\mu\text{m}$ while the analytic model had a larger spacing of $b_{\beta\gamma} = 83 \,\mu\text{m}$. We estimate the minimum inter-pore spacing between β pores to be $b_{\beta\beta} = 56 \,\mu\text{m}$ from our pore hopping model and $b_{\beta\beta} = 51 \,\mu\text{m}$ from our analytic model. The probabilistic model returned a minimum value of $b_{\gamma\gamma} = 108 \,\mu\text{m}$ and the analytic model $b_{\gamma\gamma} = 134 \,\mu\text{m}$. These minimum values are later used for calculations of other pore characteristics. While the inter-pore spacings we calculate are consistent with the inter-pore spacings seen in the X-Ray CT data, there exist many pores with connection distances larger than those found with our data.

3 Rate of exchange between pores

For the probabilistic simulations, using equation 9.22 with our simulation probabilities, the characteristic times for the pores are estimated to be $\lambda_{\beta\beta} =$ 2.63 s between β pores, $\lambda_{\gamma\gamma} = 2.38$ s between γ pores and $\lambda_{\beta\gamma} = 0.71$ s between β and γ pores. From this, we calculate $D_{\beta\beta} = 1.9 \times 10^{-10} m^2 s^{-1}$, $D_{\gamma\gamma} = 10.8 \times 10^{-10} m^2 s^{-1}$, $D_{\beta\gamma} = 13.6 \times 10^{-10} m^2 s^{-1}$

Our inter-pore diffusion rates for the analytic simulations were $D_{\beta\beta} = 3.2 \times 10^{-10} m^2 s^{-1}$, $D_{\gamma\gamma} = 9.3 \times 10^{-10} m^2 s^{-1}$, $D_{\beta\gamma} = 18.0 \times 10^{-10} m^2 s^{-1}$ from which we calculate $\lambda_{\beta\beta} = 1.35$ s, $\lambda_{\gamma\gamma} = 3.2$ s, $\lambda_{\beta\gamma} = 0.63$ s. Both of the analytic and probalistic model indicate faster exchange between unlike pores than between like pores. The diffusion coefficient between β pores indicates a significant restricted diffusion.

4 Tortuosity

Using the inter-pore diffusion coefficients of our analytic model, we obtain tortuosity values of $T_{\beta\beta} = 7.1$, $T_{\gamma\gamma} = 2.5$, $T_{\beta\gamma} = 1.3$. We then use our values of pore spacing and characteristic time to estimate the probabilistic model tortuosities of $T_{\beta\beta} = 11.5$, $T_{\gamma\gamma} = 2.1$, $T_{\beta\gamma} = 1.8$.

The values of tortuosities found for exchange between γ pores and between β and γ pores seem to agree with the calculated tortuosity from electrical conductivity simulations. Curiously, the tortuosity between β pores is larger than between other two types. While tortuosity tends to be higher in general for small pores, our values appear quite high.

VII Quartz sand three pore model

T_2	$\alpha(ms)$	$\beta(ms)$	$\gamma(ms)$
	12	38	79
Pore radius	$r_{\alpha} \; (\mu { m m})$	$r_{eta} \; (\mu m)$	$r_{\gamma}~(\mu m)$

Table 9.3: Quartz sand three pore properties

1 Pore Radii

The pore radii found for the quartz sand sample using the three pore exchange method were estimated to be $r_{\alpha} = 16 \,\mu\text{m}$, $r_{\beta} = 31 \,\mu\text{m}$, and $r_{\gamma} = 54 \,\mu\text{m}$. These results are also consistent with the x-ray CT results. The values from the three pore model are bit a larger than those found using both methods of the two pore model, but are still of similar size.



Figure 9.10: Quartz sand three pore model simulated peak intensity plots. Experimental peaks shown in Figure 9.5

b	$b_{lphalpha}(\mu m)$	$b_{etaeta}(\mu m)$	$b_{\gamma\gamma}(\mu m)$	$b_{lphaeta}(\mu m)$	$b_{lpha\gamma}(\mu m)$	$b_{eta\gamma}(\mu m)$
Analytic	35 ± 6	64 ± 12	142 ± 53	39 ± 18	65 ± 44	73 ± 29
λ	$\lambda_{lpha lpha}({ m s})$	$\lambda_{etaeta}(\mathrm{s})$	$\lambda_{\gamma\gamma}(\mathrm{s})$	$\lambda_{lphaeta}({ m s})$	$\lambda_{lpha\gamma}({ m s})$	$\lambda_{eta\gamma}(\mathrm{s})$
Analytic	0.2	1.4	3.9	0.15	0.42	0.51
Dp	$D_{\alpha\alpha}(\frac{m^2}{s})$	$D_{\beta\beta}(\frac{m^2}{s})$	$D_{\gamma\gamma}(\frac{m^2}{s})$	$D_{\alpha\beta}(\frac{m^2}{s})$	$D_{\alpha\gamma}(\frac{m^2}{s})$	$D_{\beta\gamma}(\frac{m^2}{s})$
Analytic	10.1×10^{-10}	$4.9\!\times\!10^{-10}$	$8.5 imes 10^{-10}$	16.7×10^{-10}	16.8×10^{-10}	17.3×10^{-10}
Tortuosity	$T_{lpha lpha}$	$T_{\beta\beta}$	$T_{\gamma\gamma}$	$T_{lphaeta}$	$T_{lpha\gamma}$	$T_{\beta\gamma}$
Analytic	2.3	4.7	2.7	1.4	1.4	1.3

Table 9.4: Quartz sand inter-pore properties.

2 Inter-pore spacing

The inter-pore spacing between like pores is $b_{\alpha\alpha} = 35 \,\mu\text{m}$, $b_{\beta\beta} = 64 \,\mu\text{m}$, and $b_{\gamma\gamma} = 142 \,\mu\text{m}$. The inter-pore spacing between unlike pores is $b_{\alpha\beta} = 39 \,\mu\text{m}$, $b_{\alpha\gamma} = 65 \,\mu\text{m}$, and $b_{\beta\gamma} = 73 \,\mu\text{m}$. The three-pore model produces inter-pore spacings between like pores that are slightly larger than those seen in the two-pore models while the unlike pores have a slightly smaller value. Again, due to diffusion limitations we seem unable to probe the longer distances between a significant number of pores.

3 Rate of exchange between pores

Our inter-pore diffusion rates for the analytic simulations were $D_{\alpha\alpha} = 10.1 \times 10^{-10} m^2 s^{-1}$, $D_{\beta\beta} = 4.9 \times 10^{-10} m^2 s^{-1}$, and $D_{\gamma\gamma} = 8.5 \times 10^{-10} m^2 s^{-1}$ between like pores. For unlike pores, the diffusion rates were $D_{\alpha\beta} = 16.7 \times 10^{-10} m^2 s^{-1}$, $D_{\alpha\gamma} = 16.8 \times 10^{-10} m^2 s^{-1}$, and $D_{\beta\gamma} = 17.3 \times 10^{-10} m^2 s^{-1}$.

From these values, the characteristic times for the pores are estimated to be $\lambda_{\alpha\alpha} = 0.2$ s between α pores, $\lambda_{\beta\beta} = 1.4$ s between β pores, and $\lambda_{\gamma\gamma} = 3.9$ s between γ pores. The characteristic times between unlike pores were $\lambda_{\alpha\beta} = 0.15$ s between α and β pores, $\lambda_{\alpha\gamma} = 0.42$ s between α and γ pores, and $\lambda_{\alpha\beta} = 0.51$ s between β and γ pores.

4 Tortuosity

Using the inter-pore diffusion coefficients we obtain tortuosity values between like pores of $T_{\alpha\alpha} = 2.3$, $T_{\beta\beta} = 4.7$, $T_{\gamma\gamma} = 2.7$ and $T_{\alpha\beta} = 1.4$, $T_{\alpha\gamma} = 1.4$, $T_{\beta\gamma} = 1.3$ between unlike pores. Most of the tortuosities are consistent with those calculated from X-Ray CT images. While more reasonable, the tortuosity for exchange between β pores still seems a bit high.

VIII Fontainebleau

T_2	lpha(ms)	eta(ms)
	25	100
Pore radius	$r_{lpha}~(\mu{ m m})$	$r_{eta} \; (\mu m)$
Analytic	33 ± 4	64 ± 15
Probabilistic	30	59

Table 9.5: Fontainebleau pore properties

1 Pore Radii

The pore radii of the Fontainebleau sample were estimated to be $r_{\alpha} = 33 \,\mu\text{m}$ and $r_{\beta} = 64 \,\mu\text{m}$. Using the probabilistic model, the pore radii of the Fontainebleau sample were estimated to be $r_{\alpha} = 30 \,\mu\text{m}$ and $r_{\beta} = 59 \,\mu\text{m}$.



Figure 9.11: Fontainebleau peak intensity plots for a) analytic simulation b) probabilistic simulations. Experimental peaks are shown in Figure 9.6

Inter-pore spacing	$b_{lphalpha}(\mu m)$	$b_{\beta\beta}(\mu m)$	$b_{lphaeta}(\mu m)$
Analytic	71 ± 12	129 ± 36	90 ± 41
Probabilistic	80	131	99
Characteric times	$\lambda_{lpha lpha}({ m s})$	$\lambda_{etaeta}(\mathrm{s})$	$\lambda_{lphaeta}({ m s})$
Analytic	1.4	4.5	0.9
Probabilistic	1.4	5.0	2.5
D _p	$D_{\alpha\alpha}(\frac{m^2}{s})$	$D_{\beta\beta}(\frac{m^2}{s})$	$D_{\alpha\beta}(\frac{m^2}{s})$
Analytic	5.9×10^{-10}	6.1×10^{-10}	15.0×10^{-10}
Probabilistic	$7.5\!\times\!10^{-10}$	$5.7\!\times\!10^{-10}$	$6.5 imes 10^{-10}$
Tortuosity	$T_{lpha lpha}$	T_{etaeta}	$T_{lphaeta}$
Analytic	3.9	3.8	1.5
Probabilistic	3.0	4.0	3.5

Table 9.6: Fontainebleau inter-pore properties.

These estimated values are consistent with the values from the X-Ray CT analysis.

2 Inter-pore spacing

From the analytic model, the inter-pore spacing is $b_{\alpha\alpha} = 71 \,\mu\text{m}$, $b_{\beta\beta} = 129 \,\mu\text{m}$ and $b_{\alpha\beta} = 90 \,\mu\text{m}$. The probabilistic model gave good agreement, though a bit higher values. $b_{\alpha\alpha} = 80 \,\mu\text{m}$, $b_{\beta\beta} = 131 \,\mu\text{m}$ and $b_{\alpha\beta} = 99 \,\mu\text{m}$. For the Fontainebleau, the calculated inter-pore spacing agreed well with the interpore spacings calculated from the X-Ray CT data. As the Fontainebleau has smaller inter-pore spacings than the other samples, the distribution of pore spacings could be better sampled.

3 Rate of exchange between pores

The probabilistic characteristic times for the pores are estimated to be $\lambda_{\alpha\alpha} = 1.4$ s between α pores, $\lambda_{\beta\beta} = 5.0$ s between β pores and $\lambda_{\alpha\beta} = 2.5$ s between α and β pores. Our calculated inter-pore diffusion rates from the probabilistic model were $D_{\alpha\alpha} = 7.5 \times 10^{-10} m^2 s^{-1}$, $D_{\beta\beta} = 5.7 \times 10^{-10} m^2 s^{-1}$, $D_{\alpha\beta} = 6.5 \times 10^{-10} m^2 s^{-1}$ from which we calculate $\lambda_{\alpha\alpha} = 1.42$ s between α pores, $\lambda_{\beta\beta} = 5.0$ s between β pores and $\lambda_{\alpha\beta} = 0.9$ s between α and β pores.

Our inter-pore diffusion rates for the analytic simulations were $D_{\alpha\alpha} = 5.9 \times 10^{-10} m^2 s^{-1}$, $D_{\beta\beta} = 6.1 \times 10^{-10} m^2 s^{-1}$, $D_{\alpha\beta} = 15.0 \times 10^{-10} m^2 s^{-1}$ from which we calculate $\lambda_{\alpha\alpha} = 1.4$ s between α pores, $\lambda_{\beta\beta} = 4.5$ s between β pores and $\lambda_{\alpha\beta} = 0.9$ s between α and β pores. There is good agreement between the two types of simulations.

4 Tortuosity

Using the inter-pore diffusion coefficients of our analytic model, we obtain tortuosity values of $T_{\alpha\alpha} = 3.9$, $T_{\beta\beta} = 3.8$, $T_{\alpha\beta} = 1.5$. We then use our values of pore spacing and characteristic time to estimate $T_{\alpha\alpha} = 3.0$, $T_{\beta\beta} = 4.0$, $T_{\alpha\beta} = 3.5$ for the probabilistic models. The tortuosity between the α and β pores is a bit low for the analytic model compared to the results from the X-Ray CT data. Considering the incompleteness of the cross peak intensity plot, the deviation is not surprising.



Figure 9.12: Mt. Gambier simulated peak intensity plots. Experimental peaks shown in Figure 9.7

T_2	lpha(ms)	eta(ms)	$\gamma(ms)$
	8	20	63
Pore radius	$r_{lpha} \; (\mu { m m})$	$r_{eta} \; (\mu m)$	$r_{\gamma}~(\mu m)$
Analytic	17 ± 4	44 ± 11	74 ± 27

Table 9.7: Mt. Gambier pore properties

Table 9.8: Mt. Gambier inter-pore properties.

b	$b_{lphalpha}(\mu m)$	$b_{etaeta}(\mu m)$	$b_{\gamma\gamma}(\mu m)$	$b_{lphaeta}(\mu m)$	$b_{lpha\gamma}(\mu m)$	$b_{eta\gamma}(\mu m)$
Analytic	33 ± 5	73 ± 14	151 ± 81	61 ± 23	66 ± 32	74 ± 24
λ	$\lambda_{lpha lpha}({ m s})$	$\lambda_{\beta\beta}(s)$	$\lambda_{\gamma\gamma}(s)$	$\lambda_{lphaeta}({ m s})$	$\lambda_{lpha\gamma}({ m s})$	$\lambda_{eta\gamma}({ m s})$
Analytic	0.2	1.0	4.0	0.41	0.57	0.69
D _p	$D_{\alpha\alpha}(\frac{m^2}{s})$	$D_{\beta\beta}(\frac{m^2}{s})$	$D_{\gamma\gamma}(\frac{m^2}{s})$	$D_{\alpha\beta}(\frac{m^2}{s})$	$D_{\alpha\gamma}(\frac{m^2}{s})$	$D_{\beta\gamma}(\frac{m^2}{s})$
Analytic	9.2×10^{-10}	8.8×10^{-10}	9.4×10^{-10}	$15.2\!\times\!10^{-10}$	12.7×10^{-10}	13.3×10^{-10}
Tortuosity	$T_{lpha lpha}$	$T_{\beta\beta}$	$T_{\gamma\gamma}$	$T_{lphaeta}$	$T_{lpha\gamma}$	$T_{eta\gamma}$
Analytic	2.5	2.6	2.5	1.5	1.8	1.7

IX Mt. Gambier

1 Pore Radii

The pore radii of the Mt. Gambier sample were estimated to be $r_{\alpha} = 17 \,\mu\text{m}$, $r_{\beta} = 44 \,\mu\text{m}$, and $r_{\gamma} = 74 \,\mu\text{m}$. These distributions agree well with the pore size distributions found from the X-Ray CT results.

2 Inter-pore spacing

The inter-pore spacing between like pores is $b_{\alpha\alpha} = 33 \,\mu\text{m}$, $b_{\beta\beta} = 73 \,\mu\text{m}$, and $b_{\gamma\gamma} = 151 \,\mu\text{m}$. The inter-pore spacing between unlike pores is $b_{\alpha\beta} = 61 \,\mu\text{m}$, $b_{\alpha\gamma} = 66 \,\mu\text{m}$, and $b_{\beta\gamma} = 74 \,\mu\text{m}$. The inter-pore spacings between unlike pores seems remarkably low considering the estimated pore size. However, the distribution agrees well with the calculated distribution from X-Ray CT, though some of the larger inter-pore spacings are not probed.

3 Rate of exchange between pores

In the β and γ peak decays, we note that instead of having a smooth decay, there are humps in the intensity along the mixing time axis. We believe that this arises from the budding behaviour of the spectra. Intensity that in actuality belongs to the off-diagonal peaks remains in the on diagonal peaks until the cross peaks finally resolve themselves, which then leads to the sudden dip of intensity seen once the off-diagonal peaks arise.

Our inter-pore diffusion rates were $D_{\alpha\alpha} = 9.2 \times 10^{-10} m^2 s^{-1}$, $D_{\beta\beta} = 8.8 \times 10^{-10} m^2 s^{-1}$, and $D_{\gamma\gamma} = 9.4 \times 10^{-10} m^2 s^{-1}$ between like pores. For unlike pores, the diffusions rates were $D_{\alpha\beta} = 15.2 \times 10^{-10} m^2 s^{-1}$, $D_{\alpha\gamma} = 12.7 \times 10^{-10} m^2 s^{-1}$, and $D_{\beta\gamma} = 13.3 \times 10^{-10} m^2 s^{-1}$.

The characteristic times for the pores are estimated to be $\lambda_{\alpha\alpha} = 0.2$ s between α pores, $\lambda_{\beta\beta} = 1.0$ s between β pores, $\lambda_{\gamma\gamma} = 4.0$ s between γ pores. The characteristic times between unlike pores were $\lambda_{\alpha\beta} = 0.41$ s between α and β pores, $\lambda_{\alpha\gamma} = 0.57$ s between α and γ pores, $\lambda_{\beta\gamma} = 0.69$ s between β and γ pores.

4 Tortuosity

Using the inter-pore diffusion coefficients we obtain tortuosity values between like pores of $T_{\alpha\alpha} = 2.5$, $T_{\beta\beta} = 2.6$, $T_{\gamma\gamma} = 2.5$ and $T_{\alpha\beta} = 1.5$, $T_{\alpha\gamma} = 1.8$, $T_{\beta\gamma} = 1.7$ between unlike pores. Again, the tortuosity between like pores shows correspondence with the tortuosity calculated from the X-Ray CT data but the tortuosity between unlike pores is rather low.

X Discussion

Our results for the quartz sand show a rather unusual behaviour. The intensity for the $\beta\beta$ peak spreads very little beyond the pore radius, even at long mixing times. If the inter-pore spacing between β pores is only approximately $50\mu m$, coupled with the spuriously high tortuosity, this seems remarkably incongruous, especially considering that there appears to be significant exchange between the β and γ pores at larger distances. We suggest possible solutions. First, the smaller β pores may be nestled in the gaps between the larger pores such that molecules need to diffuse through a larger pore before reaching another small pore, producing little direct exchange between the smaller pores. Second, the β pores may not be true pores. Porous media research tends to idealise pore-systems into regular shapes, often spheres. However, from the X-ray CT, one can see that the pores of our sand system are more like spheres with trumpets attached. A possibility is that the β pores are the "trumpets" and the modelled β pores the effective spherical centre of the pore. This theory is supported by the fact the quartz sand had calculated X-Ray CT spacings much larger than the other samples despite the pore sizes not being significantly larger than the other samples. Despite the anisotropic shape of these trumpets, their isotropic distribution will produce an averaged spherical density. Therefore if this is the case, our spherical form factor assumption still holds true, though we are only finding the radius of this averaged spherical density. Further experimentation would be necessary to determine the precise dimensions of the conical pores from the apparent radius.

For both situations, the fluid molecules would need to travel through a γ pore before they came to another β pore, leading to the high tortuosity. A third explanation is that the structure of the small pores is such that it is simply unlikely for molecules to exchange between small pores. Finally, we note that the tortuosity calculation is dependent on inter-pore spacing to convert a rate into a diffusion coefficient. Consequently, the abnormally high $T^{\beta\beta}$ may simply be an artefact of underestimated inter-pore spacings. Despite this anomaly, the values of $T^{\gamma\gamma}$ and $T^{\beta\gamma}$ for the quartz sand appear reasonable.

For almost all the results, the diffusion rate between pores seems to be significantly higher between unlike pores than between like pores. This in turn leads to smaller tortuosities. We suspect this stems from the poor resolution of the cross peak intensities. In addition, the diffusion coefficients calculated from the analytic model tended to be relatively insensitive; large changes in the diffusion coefficient were often required to produce a significant change in the resulting intensity plot. We also note that the confidence intervals tend to be much larger for the fits for the cross peaks than the diagonal peaks. The confidence intervals tended to be much larger for the largest inter-pore spacings, as well. This is to be expected, as these are calculated from indirect behaviour in the peak intensities.

Only in the Mt. Gambier sample did the off-diagonal peak intensities bear good resemblance to the expected theoretical behaviour. This is, no doubt, due to the high amount of exchange that occurs in the Mt. Gambier sample, allowing us to resolve the off diagonal peaks at short mixing times and short displacements. Despite the high exchange in Mt. Gambier compared to the other samples, the spectra still seem to experience problems with resolution of the inverse Laplace transform.

As with the regular T_2 exchange experiments, the amount of exchange seen in the differing samples reflects well the connectivity: Fontainebleau exhibits the least amount of exchange, Mt. Gambier the most, and the tightpacked quartz sand in between. In the exchange plots shown in Figure 9.5 and 9.7, the quartz sand appeared to show more exchange at short τ_m than the Mt. Gambier. Considering that Mt. Gambier sample is much more porous than the sand, this was a surprising behaviour. However, considering the difference in pore sizes between the two samples, the result is sensible. Despite the openness of the Mt. Gambier, the pores are further apart than the pores of the sand. During the short mixing times, enough molecules could move between the pores in the sand for the inverse transform to resolve the cross peaks, but not enough molecules moved the distance between pores in the Mt. Gambier sample.

Comparison between the measured T_2 values of the samples and the estimated pore radius shows the problems with trying to estimate T_2 using size alone. For example, the T_2 peak at 79 ms in the sand appears comes from around pores of approximately 50 μm in radius while the 64 ms T_2 peak in the Mt. Gambier sample appears to arise from pores approximately 75 μm in size.

XI Comparison between the T_2 exchange and propagator resolved T_2 exchange experiments

	$ au_{AB}$	$ au_{AC}$	$ au_{BC}$
Fontainebleau	833	N/A	N/A
Mt. Gambier	333	80	625
Quartz Sand	142	370	589

Table 9.9: T_2 exchange pore characteristic times (ms)

Table 9.10: Propagator resolved T_2 exchange pore characteristic times (ms)

	$ au_{AB}$	$ au_{AC}$	$ au_{BC}$
Fontainebleau Analytic	900	N/A	N/A
Fontainebleau Probabilistic	2500	N/A	N/A
Three pore Mt. Gambier	410	570	690
Quartz Sand Analytic	N/A	N/A	630
Quartz Sand Probabilistic	N/A	N/A	710
Three pore Quartz Sand	150	420	510

We see decent consistency between the estimated exchange times found by the normal T_2 exchange experiments and those from the propagator resolved version. One of the notable exceptions is that the exchange peaks begin to arise in the spectra at much earlier mixing times in the T_2 exchange experiment than in the T_2 -propagator experiment. This is most likely a resolution issue of the inverse Laplace transform. When we separate out the signal by displacement, the off-diagonal peaks at short mixing times and low displacements are too weak to be resolved from the strong intensity diagonal peaks. Once we go to longer displacements or longer mixing times, the peaks begin to be resolved. For the regular T_2 exchange experiment, the combined intensity of the off diagonal peaks at all displacements appears to be strong enough compared to the diagonal peaks so that it can be resolved by the inverse transform. This indicates that the propagator resolved experiment is a supplement to the regular T_2 exchange experiment, and not a replacement for it.

XII Conclusions

We presented in this chapter the novel technique of propagator resolved transverse relaxation exchange, the first NMR experiment to combine two inverse Laplace dimensions with a Fourier dimension. We used pulsed field gradients to encode for molecular movement during the mixing time τ_m of the transverse relaxation exchange experiment. The resulting two dimensional T_2 exchange spectra show significant dependence upon both mixing time and displacement. Short mixing times and displacements produce T_2 plots with signal mostly along the diagonal. Longer mixing times and displacements result in plots with exchange peaks.

We then integrated the different peak intensities and plotted them as a function of mixing time and displacement. We ran analytic and probabilistic simulations where we minimised the difference between the simulated and experimental peak intensities to try to match the measured behaviour we see in the theory. From this, we are able to estimate exchange times between like and unlike pores, inter-pore spacing, inter-pore diffusion coefficients, pore radii and tortuosity between pores. We see decent agreement between the exchange time parameters found in the regular two dimensional T_2 exchange experiment. This technique has the potential to provide vital information about the pore space, though further validation of the results for a wider range of samples is necessary. Future work involving flow will hopefully allow us to better resolve the behaviour between unlike pores. By driving fluid flow through the system, we will increase the amount of exchange occurring between pores. This should allow the inverse Laplace transform to more readily resolve the exchange peaks, giving us more reliable plots for them. Flow will also mean the fluid molecules will travel longer distances, so that we might be able to better determine inter-pore spacing and possibly determine the permeability.

Chapter 10

Multidimensional Inverse Laplace

I Introduction

The work of this thesis thus far has mostly dealt with two dimensional inverse Laplace techniques. While these methods can be very useful to help characterise porous systems, many real world systems push the limits of the two dimensional experiments. In the previous chapter, we remarked on the uncertainty in whether some of the shortest T_2 peaks in the T_2-T_2 exchange spectra arose from small spherical pores or from the "trumpets" attached to larger spherical pores. The DDCOSY experiment(75) would be a excellent technique to determine which scenario was correct. This two dimensional inverse Laplace transform technique correlates the diffusion coefficient in two different directions. The DDCOSY method can be used to find local anisotropy in the presence of global isotropy, which would occur if the shortest T_2 peaks arose from trumpets. However, the contribution to the diffusion coefficient from the roughly spherical, larger pores would confound the results. Therefore we would need to separate the DDCOSY spectra in the T_2 dimension. This would require a third inverse Laplace transform dimension.

A three dimensional inverse Laplace transform experiment would also be helpful when working with multi-phase systems. Identification of features of the porous system and saturating fluid can be straightforward when there is only one fluid present, but becomes more difficult when the porous material is saturated with multiple fluids, as seen in the diffusion attenuation work of Chapter 7. To complicate matters further, mixed wettability systems lead to additional ambiguity in the interpretation of the results as well(94; 95). For these cases, individual components cannot be resolved with only two dimensions, so we need more correlations to make reliable identifications. By moving to higher dimensions, we can reduce ambiguity in our results.

Because of the immense usefulness of the ability to correlate three inverse Laplace parameters, there have been previous attempts at three dimensional inverse Laplace transformations. Unfortunately, the memory issues with the two dimensional techniques mentioned in Chapter 5 become even more problematic with the larger matrices of three dimensional experiments. Sun and Dunn (96) attempted a three dimensional inverse Laplace experiment correlating T_1 – T_2 –D. To overcome the memory issues, their inversion was performed with extremely small matrix sizes, such that the number of points measured could not adequately capture the extent of variability in the pore space.

We undertake a more thorough attempt at a three dimensional Laplace inversion. We attempt a simple correlation between T_2 -D-g using the Castlegate and Mt. Gambier samples. This three dimensional technique was first proposed by Seland et al.(54), but was evaluated only as a diffusion attenuation experiment, as computational techniques for a full three dimensional



Figure 10.1: T_2 -D-g correlation pulse sequence

inversion were not available. The work presented in this chapter has been performed in close collaboration with Christoph Arns at the Australian National University in Canberra. The development of the multidimensional Laplace inversion algorithm and execution of the inversions were performed by Christoph Arns in Canberra. The experimental NMR work was performed in Wellington as part of this thesis.

II Pulse Sequence

The pulse sequence begins with a 90° excitation pulse followed by the diffusion encoding. Due to the gradient limitation of our system, we used a pulsed field gradient stimulated echo instead of a pulsed field gradient spin echo; we compensate for our relatively weak gradient strength by having a long Δ interval. A unipolar gradient of duration δ is applied to impart a phase shift to the spins and then the magnetisation stored along the z-axis using a 90° pulse. After a time Δ , the magnetisation is returned to the transverse plane using a third 90° pulse and the second complimentary unipolar gradient is applied to complete the diffusion measurement. After the diffusion measurement, the pulse sequence then encodes for internal gradients. During the time t_0 , the number of applied 180° pulses is varied to change τ_n , the time the molecules can diffuse through internal gradients before refocusing. Finally, the T_2 encoding is performed simultaneously as acquisition using a fixed echo CPMG train, where the maximum amplitude of each echo is measured. The phase cycle ensured that all measured magnetisation derived solely from the initial 90° excitation pulse.

The magnetisation measured by the experiment is described by the relation

$$M(q, \tau_n, \tau) \approx \iiint F(D, DG_0^2, T_2) \exp\left(-q^2 D\Delta\right)$$
$$\times \exp\left(\frac{1}{3}DG_0^2\left[\tau'^2(2\tau') + \tau_n^2(2n\tau_n)\right]\right)$$
$$\times \exp\left(\frac{2\tau' + 2n\tau_n + 2n\tau}{T_2}\right) dDdT_2 dDG_0^2(10.1)$$

where $F(D, DG_0^2, T_2)$ is the joint probability density, D is the diffusion coefficient, G_0^2 is the magnitude of the internal gradients, τ' is the time between the gradient pulse and the 90° storage pulse, τ_n is the echo spacing for internal gradient encoding and τ is the echo spacing of the CPMG train used for T_2 encoding.

III Regularisation

Three different types of regularisation were considered for the processing of the three dimensional data: an SVD(64) with Tikhonov regularisation(68), an SVD with NNLS(66) and Tikhonov regularisation, and the Butler-Reeds-Dawson method(97). The SVD with NNLS and Tikhonov is the regularisation method used for the other inversions of this thesis. The SVD and Tikhonov is the same type of regularisation, but without non-negativity requirements.

Whereas the SVD with Tikhonov regularisation and SVD with NNLS and Tikhonov regularisation use the L-shaped curve of the minimised χ^2 to determine the optimised value of $\alpha(70)$, shown in Figure 5.2, the Butler-Reeds-Dawson method of regularisation uses an iterative process to arrive at an optimised α value for the inversion. A sub-optimal value of α is chosen and then the inversion performed. Another value of α is selected based on the results of the first inversion and the transform is performed again. This process is repeated until the algorithm converges to an optimised value of α for the inverse Laplace transform.

To assess the resolution capabilities of the different regularisation methods, a test two dimensional plot was created that consisted of two peaks, one sharp and one broad Gaussian peak, shown in Figures 10.2a and 10.2b. The exponential decays that would be produced by such a distribution, Figures 10.2c and 10.2d, were then simulated for a range of signal to noise values. The decays were then inverted with the different regularisation methods, with results shown in Figure 10.3, to see how the inverted plots compared to the original plots.

The inversions by the BRD method and the NNLS method produced similar solutions. The sharp Gaussian peak begins to be resolved using these



Figure 10.2: Figures a) and b) show the simulated Gaussian test peaks and c) and d) are the decays which would result from such a probability distribution



Figure 10.3: Inversion performance of the three inversion methods. The signal to noise ratios vary from top to bottom as [a-c], 100 for [d-f], 1000 for [g-I], and 10000 for [j-l]. The inversion method from left to right is: SVD and Tikhonov(left), SVD, NNLS and Tikhonov (middle) and Butler-Reeds-Dawson (right)

two methods at approximately 10^2 SNR. The SVD with Tikhonov alone only begins to resolve the peak at 10^4 SNR. The location of the peaks remains consistent regardless of inversion method or signal to noise. The NNLS and BRD methods clearly show superiority in the inversion process.

IV Experimental

For the diffusion encoding, the gradient strength of the encoding pulses ranged from $-90 G cm^{-1}$ to $90 G cm^{-1}$. The duration of the gradient pulses was $\delta = 2 m$ s plus the two 160μ s ramping times. The diffusion interval Δ was 10 ms. The total interval time for the internal gradient encoding was $t_0 = 16 m$ s. The time between refocusing pulses ranged from 160μ s to 8 ms. For the T_2 encoding, a τ spacing of 160μ s was determined to be sufficiently short to avoid influence from internal gradients. The cores were saturated with distilled de-ionised water with no other specific preparation. The rock cores were held at a temperature of 25° C for the experiments. The experiments required approximately eight hours to complete.

V Results and Discussion

Before inversion, the experimental data underwent pre-processing. The data was Fourier transformed into the spectral domain and the resulting peak symmetrised to provide phase correction. In addition, any spurious peaks in the spectral dimension were removed using a bandpass filter before a back transformation to the time domain.

The measured signal to noise ratio for the Mt. Gambier sample is approximately 500 while the signal to noise for the Castlegate sample is only

100. As we can see from Figure 10.3, the resolution at these signal to noise levels can only adequately recover the smaller peak for two of the attempted inversion techniques. Unfortunately, as mentioned in section 2.11.1, running multiple scans is governed by a law of diminishing returns. Obtaining an order of magnitude increase in the signal to noise in the samples would require over a week to acquire the data, which is becoming prohibitively long. While measures can be taken to prevent evaporation, for an experiment of that length there is a significant risk of the sample drying out in the time required for the experiment.

As the 3D inverse Laplace transform is already ill-conditioned, the probability densities were discretised onto a map of a hundred points each to prevent further ill-conditioning. For most situations this would be redundant, as we gain no additional information from the extra points in the resulting inverted spectra. However, it is possible that there may be peak positions that are most favourable for the inversion with the additional points where they could not be placed if the inverted spectra had fewer points, i.e. between points. With the experimental values chosen, this would produce a kernel of size $K \in \Re^{(8196 \times 32 \times 32) \times (100 \times 100 \times 100)}$. A full kernel of this size would require 60 terabytes of memory, far beyond our current technical capabilities. To overcome this, the kernel was compressed through several methods. First, the experimental data was compressed using a truncated SVD and choosing a rank of $r \approx 12$. The data was then compressed by choosing values from the SVD where the singular values obey the relation

$$\frac{\sigma_1^{max} \times \ldots \times \sigma_n^{max}}{\sigma_1^i \times \ldots \times \sigma_n^i} < C , \qquad (10.2)$$

where σ^{max} is the largest singular value of the matrix, σ_1^i is the i^{th} singular value of matrix K_1 and C is the condition number for the representation of the kernel. Lastly, the kernel was further compressed by only selecting the

rows and columns needed for the separable kernel structure. The separable structure assumes that the kernel for one parameter is independent from the other kernels. These compressions reduce the size of the kernel to approximately 2 GB, which is manageable with a desktop computer. To confirm the compressed kernel was an accurate representation of the original data, the magnetisation decay was back-projected. The back projection matched well with the original data, though the compressed data is significantly smoother, indicating some loss of the finer details of the data in the compression.

The inversions were attempted using a personal computer. Of the three methods considered for regularisation of the inversion, only the SVD with Tikhonov regularisation proved feasible. Unfortunately, in the three dimensions, the memory constraints of the solver for the NNLS technique exceeded the system's capabilities. While it was possible to attempt the inversion using the BRD algorithm, it never reached a solution which met the positivity constraints. The inversion using the SVD and Tikhonov regularisation took several minutes to complete. Figures 10.4 and 10.5 show the 3D inversions of the Mt. Gambier and the Castlegate. For ease of interpretation, several 2D planar projections are shown.

As mentioned previously, one of the issues with internal gradient encoding is that the result needs to be normalised by the diffusion coefficient. For the two dimensional experiments, how the diffusion coefficient varies in the different regions of the pore space is unknown, so a generalisation about the diffusion coefficient for the system is typically made. With the three dimensional correlation experiment, what diffusion coefficients are correlated with the different parameters is known, and so Dg^2 can be normalised with the true diffusion coefficients throughout the pore space to give a more accurate g value.



Figure 10.4: Three-dimensional T_2 -D- Dg_0^2 distribution function of Mt Gambier limestone a) and its projections onto 2D distributions. b)- d) are direct 2D projections, integrating along the remaining direction, while projections e) and f) were derived using the measured |g|-D dependence of d). D_{app} is the measured apparent diffusion coefficient.



Figure 10.5: Three-dimensional T_2 -D- Dg_0^2 distribution function of Castlegate sandstone a) and its projections onto 2D distributions. b)- d) are direct 2D projections, integrating along the remaining direction, while projections e) and f) were derived using the measured |g|-D dependence of d). D_{app} is the measured apparent diffusion coefficient.

The Castlegate system shows stronger internal gradients than the Mt. Gambier system, with maximum values of 10^2 to $10^3 \ Gcm^{-1}$ respectively. This is consistent with the smaller pore sizes found in the Castlegate sample, as well as the larger magnetic susceptibility difference. Figures 10.4f and 10.5f show the *g-D* relationships for the two samples where there exists a clear negative relationship. We attribute this effect to the reduction of *D* due to tortuosity and pore throat narrowing having a simultaneous influence in increasing *g* due to sharper edges and a dependence of internal gradient strength on pore size, where smaller pores typically exhibit larger internal gradients but diffusion is more restricted.

An assumption we made with regards to experiment design was that the applied gradients were much larger than the internal gradients present in the samples (20; 98). Analysis of the data shows that this assumption is not true, as the average internal gradients were on the order of $10^1 \, G \, cm^{-1}$ and our applied gradients only on the order of $10^2 G \, cm^{-1}$. Therefore, it is quite likely the cross term between the two gradients had a non-negligible effect upon the diffusion measurements. Future work should include bipolar gradients in order to avoid any interference between the applied and internal gradients. In addition, stronger gradients should be used so that a pulsed field gradient spin echo experiment can be used instead of the pulsed field gradient stimulated echo. A concern with the longer pulse sequences is that molecules will diffuse from one pore to another in the time required for all the encoding intervals. In this situation, the correlations would become meaningless, as one would be correlating characteristics between different pores as opposed to the characteristics of the individual pores. Performing a preliminary T_2 exchange experiment could help determine whether this is a potential concern for a given system.

There exist multiple islands of signal at diffusion values greater than that of water. As we have no reason to suspect anomalous diffusion in this system, the high values of diffusion are most likely an artefact of the inversion. One can see from Figure 10.3 that at low signal to noise, the SVD with Tikhonov regularisation method also has issues with the inverted plot giving values larger than the true values. The overestimation of the diffusion coefficient of water is unlikely to be an artefact from the interaction between the applied and internal gradients, as this interaction tends to underestimate diffusion coefficients. Similarly, the T_2 values above 1 s must be an artefact as well, as there is no physical basis for T_2 values that long in these systems.

VI 3D and 2D ILT Comparison

We now compare the results from the 3D experiments to results obtained from the 2D inverse Laplace experiments in Chapter 7 of this thesis. While the results are not directly comparable as the choice of parameters for encoding are different, we can get a general idea of how the characteristics found with the 3D ILT correspond to those found from the 2D ILT.

1 Signal to Noise

The signal to noise in the time domain from the 3D experiments are generally on the order of 10^2 whereas the 2D experiments often have signal to noise of 10^4 . Even the 3D transverse relaxation exchange propagator experiments usually have signal to noise on the order 10^4 . Considering our current inversion limitations, this is a serious detriment for the 3D methods compared to the 2D methods. A change to a pulsed field gradient experiment will provide a small improvement, as a factor of two will be gained in the SNR.
2 Transverse relaxation

We see a loss of some of the shorter T_2 components in the Castlegate sandstone. The T_2 exchange work in Chapter 7 shows that the Castlegate has T_2 components as short as $10^2 \,\mu$ s, which would decay away during the internal gradient and diffusion encoding before acquisition. Due to the lengths of the experimental intervals, any components under ~ 20 ms will not be measured during acquisition. Examination of the T_2 plots shows this to be the approximate lower limit in the T_2 resolution in the two samples.

3 Internal Gradients

Comparison of the internal gradient measurements between the 3D and 2D experiments shows decent agreement, though the weaker signal at higher internal gradients is lost. In the Mt. Gambier sandstone, the main portion of signal is seen between 10^0 to $10^2 Gcm^{-1}$, which compares well to the 2D experiments of Chapter 6. However, the signal from internal gradients ranging from 10^2 to $10^4 Gcm^{-1}$ does not appear. As the Castlegate is resolved to nearly $10^3 Gcm^{-1}$, we do not believe this is a limitation of our encoding for the Mt. Gambier sample, and most likely stems from the resolution of the inversion. In the case of the Castlegate, the loss of the shortest T_2 components. The pores which produce the strongest internal gradients most likely have the shortest T_2 times.

VII Conclusions

Algorithms capable of reliably performing a three dimensional inverse Laplace transform still require further development. Hopefully, as computational power improves, some of the current computational limits will no longer be obstacles to inversions. The artefacts in the spectra show that we must proceed with caution in interpreting data resulting from these inversions. In addition, further ways of improving signal to noise need to be investigated to avoid prohibitively long experiments. A possible solution is to move to a smaller sample size and make use of a cryoprobe. Improvements to the NNLS and BRD algorithms so that they could be used to invert the data would also lead to a significant increase of resolution and stability in the inverted spectra. Despite these impediments, the three dimensional inversions show potential to provide better correlations, particularly in the situation of finding the true internal gradients as opposed to gradients normalised by diffusion. Though there are inconsistencies between the values found by the 3D and the 2D transforms, there was general agreement between the two types of inversions. With improvement to the inversion, three dimensional Laplace inversion techniques will become a useful tool along with the array of 2D inverse Laplace methods in porous media characterisation.

Several 4D pulse sequences have been proposed as well, such as T_2-D and T_2-g exchange experiments or a T_1-T_2-D-g correlation experiment. While the NMR machine capability to perform these sequences currently exists, the current inversion stability and required computational time would not make these experiments practical. In addition, the expansion to the fourth dimension is likely to decrease the measured signal to noise.

Chapter 11

Conclusions

Multidimensional inverse Laplace spectroscopy techniques enable us to gain useful information regarding the behaviour of fluid imbibed in a porous matrix and the pore space itself. Several new NMR techniques and applications were presented in this thesis to help expand our knowledge of fluid behaviour within porous materials, as well as the limits of inverse Laplace spectroscopy techniques.

We began by presenting a new correlational two dimensional inverse Laplace technique that relates the longitudinal relaxation with the internal gradients in the sample. This technique is a useful alternative to other two dimensional inverse Laplace internal gradient techniques, as there is no concern that the T_1 relaxation will be influenced by the presence of internal gradients at high applied fields. We ran the experiment on samples over a wide range of field strengths. We found that even at an ultra-high applied field, there can exist signal at gradient strengths where techniques for suppressing the unwanted interaction between the applied and internal gradients can be used. We also provided experimental evidence for the theory of how the maximum effective gradients in porous materials scale as a function of pore size by tracking the peaks resulting from different pore sizes over the different field strengths.

In the next chapter, we explored a different type of two dimensional inverse Laplace experiment, an exchange experiment. We performed a transverse relaxation measurement, stored the magnetisation for a mixing period, and then measured transverse relaxation again. By comparing how the ${\cal T}_2$ times change during the mixing times, we can see how fluid molecules are moving in the pore space. While this particular technique has been presented previously, we develop the idea by adding quantification to the results. We integrated the resulting peak intensities in the T_2 exchange spectra and plotted them as a function of mixing time. The on-diagonal peaks, representing signal coming from molecules in their original environment, decrease as a function of mixing time while the off-diagonal peaks, representing signal from molecules that have changed environments, grows logarithmically as a function of mixing time. When we apply the theory from molecular exchange equations, we are able to extract the mixing times from these plots. While our results are promising, due to the unstable nature of the two dimensional Laplace inversion, we urge caution when interpreting quantitative data in these experiments.

The following two chapters discuss modifications to the transverse relaxation exchange experiment to obtain more information regarding the system. We first add pulsed field gradients to the transverse relaxation exchange experiment to separate the signals from oil and water. The gradients are used to attenuate the signal from the faster diffusing component, in this case water. We then correct the remaining signal from the oil back to zero gradient intensity and subtract it from an experiment run with no applied field gradients to recover the water signal. We use this technique to look at the exchange behaviour of oil and water in systems of both oil-wet and waterwet glass spheres. Even without using the diffusion attenuation, the resulting exchange plots are remarkably different depending on the wettability of the sample. When we apply the gradients, we are able to separate the signals from the oil and water. We were unable to perform thorough quantitative analysis upon the systems, though we were able to see the effect of wettability on the movement of the individual fluid components.

In the subsequent chapter, we expand the diffusion attenuation concept to become a full three dimensional experiment. Instead of using the applied field gradients to attenuate a fluid component, we use them to look at the molecular diffusion of a single fluid phase in a porous material. We apply a range of gradient strengths to encode for the molecular movement. We then Fourier transform the three dimensional data along the diffusion axis to produce the propagator of the molecular displacements. We extract planes of two dimensional T_2 - T_2 exchange data from along the propagator. The resulting spectra are remarkably different depending on mixing time and displacement. For short displacements and mixing times, the T_2 - T_2 spectra produce signal that lies along the diagonal. As we move to longer displacements and mixing times, we begin to see cross peaks forming. This is what one would expect to, as molecules that have not moved will still be in their original environment while those that diffuse have the opportunity to enter a new environment.

Again, we attempt quantification upon the plots by integrating the peaks and then plotting the intensities as a function of displacement and mixing time. We are then able to estimate characteristic times of exchange between pores of different and similar sizes. In addition, we are also able to estimate pore radius, inter-pore spacing, and tortuosity. The results we obtain show general agreement with results calculated from X-Ray CT measurements. We find that due to the resolution of the inverse Laplace transform, the measured intensity for cross peaks can be unreliable, leading to uncertainties in the resulting parameter estimates.

Lastly, we look to the future on multidimensional Laplace techniques by attempting a new three dimensional inverse Laplace experiment. We correlate T_2 -D-g in the sample. The amount of memory required for the inversion means that only one of the potential inversion methods attempted was actually viable. The resulting inversions roughly reflect the values seen in the two dimensional inversions, though some of the finer details were lost and we had some erroneous high resulting values. Improvements to the inversion as well as improvement in signal to noise will hopefully provide better resolution and more accurate results.

1 Future research

Scientific research can be likened to fighting a hydra; once we have tackled one question, we find that several more have sprung up in its place. While the work of this thesis provided valuable information about our porous systems, there are several interesting avenues that have yet to be explored and there is only so much time as a PhD student.

An interesting academic experiment would combine the Magic Angle Spinning experiment performed by de Sweit et al. with our T_1-g experiment to see how effectively the spinning cancels the influence of internal gradients in the sample. It was also suggested several times throughout this manuscript to observe driven fluid flow through a porous medium using the propagator resolved transverse relaxation experiment. By using flow, we could probe longer length scales than with diffusion as well as hopefully better resolve some of the weaker cross peaks. This work would best be completed at low field, as compensating for the internal gradients in a sample under driven fluid flow would be fighting an uphill battle at high field.

On a more industrial level, the T_2 - T_2 experiments will hopefully be carried out on a wide range of real world samples for thorough validation. While the samples in this thesis worked quite well, their suitability for the exchange experiments is part of the reason they were chosen for extensive experimentation. We often do not have the luxury to choose the samples we work with, so it is important to see how the technique performs in less than ideal samples.

Beyond this, undoubtedly there are more two dimensional inverse Laplace techniques that have yet to be thought up. With continued experimentation, hopefully the range of multidimensional inverse Laplace spectroscopy techniques will see the wide spread use that the one dimensional inverse Laplace spectroscopy techniques have.

Appendix A

Samples

The main samples used in this thesis are discussed here. The sample is briefly discussed and figures describing the pore size distribution, calculated interpore spacings, and estimated tortuosity measurements are included as well as an X-Ray CT image. Descriptions of how the different sample properties have been obtained are found in section 4.5.4.

I Fontainebleau

Fontainebleau sandstone comes from the Paris Basin in France. The porosity of the sample is approximately 15%. Fontainebleau is a very clean sandstone with very little impurities, with its grains consisting of pure quartz. The very pure nature of the sample means that it produces weaker internal gradients than most other sandstones. This makes it a favoured sample by researchers for NMR work in rock cores. Fontainebleau has well sorted grain sizes, all of similar size, such that it has a very uniform pore space.



Figure A.1: Fontainebleau X-ray CT



Figure A.2: Fontainebleau pore size distribution. The pore diameter distribution labeled $d_{v/s}$ is estimated using a volume to surface area ratio of the pore while those estimated using pore volume alone is labeled d_v .



Figure A.3: Fontainebleau volume-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.4: Fontainebleau pore-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.5: Fontainebleau estimated tortuosity in the x, y, and z directions calculated from images of 300, 600 and 1200 voxels cubed resolution.

II Castlegate

Castlegate is a sandstone that comes from the desert in Utah in the United States. The porosity of the sample is approximately 26%. This sandstone is a "dirtier" sandstone than the Fontainebleau, with paramagnetic inclusions and clay; the sample contains approximately 9% clay by weight. It is the only sample we use containing any significant amount of clay. The paramagnetic impurities will give stronger internal gradients within the sample. While the sample contains more impurities than the Fontainebleau, it is still considered a relatively clean sandstone. The grain sizes of the Castlegate are also fairly well sorted, leading to a homogenous pore space.



Figure A.6: Castlegate X-ray CT



Figure A.7: Castlegate pore size distribution. The pore diameter distribution labeled $d_{v/s}$ is estimated using a volume to surface area ratio of the pore while those estimated using pore volume alone is labeled d_v .



Figure A.8: Castlegate volume-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.9: Castlegate pore-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.10: Castlegate estimated tortuosity in the x, y, and z directions calculated from images of 200 voxels cubed resolution.

III Mt. Gambier

Mt. Gambier is a carbonate outcrop stone taken from the Mount Gambier region in southern Australia. The sample has a porosity of approximately 50%. The limestone is composed of calcium carbonate and is relatively clean from impurities such as paramagnetics or clay, giving the sample relatively mild internal gradients. The "grains" in the sample come from the remains of marine organisms that have been fused together through geological pressures. Shell patterns can be seen in the X-Ray CT image. Because of the disparate grain sizes, the Mt. Gambier sample has a wide range of pore sizes.



Figure A.11: Mt. Gambier X-ray CT



Figure A.12: Mt. Gambier pore size distribution. The pore diameter distribution labeled $d_{v/s}$ is estimated using a volume to surface area ratio of the pore while those estimated using pore volume alone is labeled d_v .



Figure A.13: Mt. Gambier volume-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.14: Mt. Gambier pore-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.15: Mt. Gambier estimated tortuosity in the x, y, and z directions calculated from images of 480 and 960 voxels cubed resolution.

IV Tight-packed quartz sand

The last sample is New Zealand quartz beach sand. The sand itself has no porosity, but it was tight packed and saturated with fluid for experimentation. The tight packed sand produced a porosity of approximately 35%. The sample is relatively clean, though not as clean as the Fontainebleau, as the sand is light tan in colour, indicating some impurities. This will result in the sand having relatively mild internal gradients as well. The grains in the sand are only partially sorted, leading to a broader range of pore sizes in the sample.



Figure A.16: Tight packed Quartz Sand X-ray CT



Figure A.17: Quartz sand pore size distribution. The pore diameter distribution labeled $d_{v/s}$ is estimated using a volume to surface area ratio of the pore while those estimated using pore volume alone is labeled d_v .



Figure A.18: Quartz sand volume-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.19: Quartz sand pore-weighted estimated inter-pore spacing. CMAS spacings are calculated via centre of mass and edt spacings from the Euclidean distance transformation. The dotted lines are projections along either the x, y or z axis.



Figure A.20: Quartz sand estimated tortuosity from images of 125, 250, 500 and 1000 voxels cubed resolution.

Appendix B

Publications from this thesis

- K.E. Washburn, P.T. Callaghan "Tracking pore to pore exchange using relaxation exchange spectroscopy" *Phys. Rev. Let.* 97 175502 (2006)
- C.H. Arns, K.E. Washburn "Multidimensional NMR inverse Laplace spectroscopy in petrophysics" SPWLA, 47th Annual Logging Symposium, Veracruz, June 4-7th, Paper X:1-9 (2006), Bergen, Norway
- K.E. Washburn, P.T. Callaghan "The influence of wettability on fluid exchange between pores" *International Wettability Symposium Confer*ence Proceedings, Sep. 2006
- C.H. Arns, K.E. Washburn "Multidimensional NMR inverse Laplace spectroscopy in petrophysics" *Petrophysics* 48 380 (2007)
- K.E. Washburn, P.T. Callaghan "Propagator resolved transverse relaxation exchange spectroscopy" J. Magn. Reson. 186 337 (2007)
- P. Callaghan, C. Arns, P. Galvosas, M. Hunter, Y. Qiao, K. Washburn "Recent Fourier and Laplace perspectives for multidimensional NMR in porous media" *Magn. Reson. Imag.* 25 441 (2007)

- K.E. Washburn, C.H. Arns, P.T. Callaghan "Pore characterisation through propagator-resolved transverse relaxation exchange" *Phys. Rev. E.* 77 051203 (2008)
- K.E. Washburn, C.D. Eccles, P.T. Callaghan "The dependence on magnetic field strength of correlated internal gradient relaxation time distributions in heterogeneous materials" *J Magn. Reson.* In Press (2008)
- K.E. Washburn, C.H. Arns, P.T. Callaghan "Propagator resolved transverse relaxation exchange spectroscopy" *AIP Conference Proceedings* Submitted (2008)

Bibliography

- F. Bloch, W.W. Hansen, and M. Packard. The nuclear induction experiment. *Phys. Rev.*, 70:474, 1946.
- [2] E.M Purcell, H.C. Torrey, and R.V. Pound. Resonance absorption by nuclear magnetic resonance in solids. *Phys. Rev.*, 69:37, 1946.
- [3] J.T. Arnold, S.S. Dharmatti, and M.E. Packard. Chemical effects on nuclear induction signals from organic compounds. J. Chem. Phys., 19: 507, 1951.
- [4] E.L. Hahn. Spin echoes. Phys. Rev., 80:580–594, 1950.
- [5] P.C. Lauterbur. Image formation by induced local interactions. *Nature*, 242:190, 1973.
- [6] P. Mansfield and P.K. Grannell. Nmr diffraction in solids. J. Phys. C, 6:422, 1973.
- [7] M.H. Levitt. Spin Dynamics. John Wiley and Sons Ltd, West Sussex, England, 1st edition, 2001.
- [8] N. Bloembergen, E.M. Purcell, and R.V. Pound. Relaxation effects in nuclear magnetic resonance absorption. *Phys. Rev.*, 73:679, 1948.

- [9] A. Abragam. Principles of nuclear magnetism. Clarendon Press, Oxford, 3rd edition, 1961.
- [10] D. Traficante. Relaxation. can t2 be longer than t1? Conc. Magn. Reson. Part A, 3:171, 1991.
- [11] P. Mansfield and P.G. Morris. NMR imaging in biomedicine. Academic Press, New York, NY, 1st edition, 1982.
- [12] H. Nyquist. Thermal agitation of electric charge in conductors. *Phys. Rev.*, 32:110, 1928.
- [13] J. Stepisnik, V. Erzen, and M. Kos. Nmr imaging in the earth's magnetic field. Mag. Reson. Med., 15:386–391, 1990.
- [14] P.T. Callaghan, C.D. Eccles, T.G. Haskell, and P.J Langhorne. Earth's field nmr in antarctica: A pulsed gradient spin echo nmr study of restricted diffusion in sea ice. J. Magn. Reson., 133:148–154, 1998.
- [15] S. Appelt, H. Kuhn, F.W. Hasing, and B. Blumich. Chemical analysis by ultrahigh-resolution nuclear magnetic resonance in the earth's magnetic field. *Nature Phyds.*, 2:105–109, 2006.
- [16] D.I. Hoult and R.E. Richards. Critical factors in the design of sensitive high resolution nuclear magnetic spectrometers. *Proc. Roy. Soc.*, A344: 311, 1975.
- [17] H.Y. Carr and E.M. Purcell. Effects of diffusion on free precession in nuclear magnetic resonance experiments. *Phys. Rev.*, 94:630–638, 1954.
- [18] S. Meiboom and D. Gill. Aging and non linear rheology in suspensions of peo-protected silica particles. *REv. Sci*, 29:688, 1958.

- [19] J. Karger and W. Heink. The propagator representation of molecular transport in microporous crystallites. J. Mag. Reson., 51:1, 1983.
- [20] E.O. Stejskal and J.E. Tanner. Spin diffusion measurements spin echoes in presence of a time-dependent field gradient. J. Chem Phys., 42:288, 1965.
- [21] J.M. Fauth, A. Schweiger, J. Braunschweiler, J. Forrer, and R.R. Ernst. Elimination of unwanted echoes and reduction of dead time in threepulse electron spin-echo spectroscopy. J. Magn. Reson., 66:74–85, 1986.
- [22] E.J. Fordham, S.J. Gibbs, and L.D. Hall. Partially restricted diffusion in a permeable sandstone: observations by stimulated echo pfg nmr. *Magn. Reson. Imag*, 12:279, 1994.
- [23] L.L. Latour, Li. L., and C.H. Sotak. Improved pfg stimulated-echo method for the measurement of diffusion in inhomogeneous fields. J. Magn. Reson. B, 101:72, 1993.
- [24] D. Wu, A. Chen, and Johnson C.S. An improved diffusion-ordered spectroscopy experiment incorporating bipolar-gradient pulses. J. Magn. Reson. A, 115:260, 1995.
- [25] G.H. Sorland, B. Hafkskold, and O. Herstad. A stimulated-echo method for diffusion measurements in heterogeneous media using pulsed field gradients. J. Magn. Reson., 124:172–176, 1997.
- [26] J.G. Seland, M. Bruvold, H. Brurok, P. Jynge, and J. Krane. Analyzing equilibrium water exchange between myocardial tissue compartments using dynamical two-dimensional correlation experiments combined with manganese-enhanced relaxography. *Mag. Reson. Med.*, 70:051305, 2004.

- [27] L.K. Hoiland, K. Spildo, and A. Skauge. Fluid flow properties for different classes of intermediate wettability as studied by network modelling. *Transport in Porous Media*, 70:127–146, 2007.
- [28] J.L Barrat and L. Bocquet. Large slip effect at a nonwetting fluid-solid interface. *Phys. Rev. Let.*, 82:4671–4674, 1999.
- [29] P.M. Singer, G. Leu, E.J. Fordham, and Sen P.N. Low magnetic fields for flow propagators in permeable rocks. J. Magn. Reson., 183:167, 2006.
- [30] J Arnold, C. Clauser, R. Peching, S. Anferova, V. Anferon, and B. Bluemich. Porosity and permeability from mobile nmr core-scanning. *Petro.*, 47:306, 2006.
- [31] R.C. Wilson and M.D. Hurlimann. Relationship between susceptibility induced field inhomogeneities, restricted diffusion, and relaxation in sedimentary rocks. J. Magn. Reson., 183:1, 2006.
- [32] G.H. Sorland, H.W. Anthonsen, J.G. Seland, F. Antonsen, H.C. Wideroe, and J. Krane. Exploring the separate nmr responses from crude oil and water in rock cores. *App. Magn. Reson.*, 26:471, 2004.
- [33] R.L. Kleinberg and M.A. Horsfield. Transverse relaxion processes in porous sedimentary rock. J. Col. Inter., 88:195, 1993.
- [34] C.H. van der Zwaag, E. Veliyulin, T. Skjetne, A.E. Lothe, R.M. Holt, and O.M. Nes. Deformation and failure of rock samples probed by t1 and t2 relaxation. *Mag. Reson. Imaging*, 21:405, 2003.
- [35] P.J. McDonald, J.P. Korb, J. Mitchell, and L. Monteilhet. Surface relaxation and chemical exchange in hydrating cement pastes: A twodimensional nmr relaxation study. *Phys. Rev. E*, 72:011409, 2005.

- [36] C. Casieri, F. De Luca, and P. Fantazzini. Pore-size evaluation by singlesided nuclear magnetic resonance measurements: Compensation of water self-diffusion on transverse relaxation. J. App. Phys., 97:043901, 2005.
- [37] D.J. Holland, U.M. Scheven, P.J. Middelberg, and L.F. Gladden. Quantifying transport within a porous medium over a hierarchy of length scales. *Phys. Fluids*, 18:033102, 2006.
- [38] M.L. Johns, A.J. Sederman, L.F. Gladden, A. Wilson, and S. Davies. Using mr techniques to probe permeability reduction in rock cores. *AIChE*, 49:1076, 2004.
- [39] F. Stallman, C. Vogt, J. Karger, K. Helbig, and F. Jacobs. Aging and non linear rheology in suspensions of peo-protected silica particles. J. Chem. Phys., 119:9609, 2003.
- [40] Q. Chen, A.E. Marble, B.G. Colpitts, and B.J. Balcom. The internal magnetic field distribution and single exponential magnetic resonance free induction decay in rocks. J. Magn. Reson., 175:300, 2005.
- [41] J.H. Strange. Cryoporometry: a new nmr method for characterising porous media. Nondestructive Testing and Evaluation,, 11:261 – 271, 1994.
- [42] O. Petrov and I. Furo. Characterizing porous materials through the melting and freezing behaviour of pore-filling fluids. *Mag. Reson. Imag.*, 25:579 – 579, 2007.
- [43] S.D. Beyea, S.L. Codd, D.O. Kuethe, and E. Fukushima. Studies of porous media by thermally polarized gas nmr: current status. *Magn. Reson. Imag.*, 21:201–205, 2003.

- [44] R.W. Mair, R. Wang, M.S. Rosen, D. Candela, D.G. Cory, and R.L. Walsworth. Applications of controlled-flow laser-polarized xenon gas to porous and granular media study. *Magn. Reson. Imag.*, 21:287–292, 2003.
- [45] G.E. Pavlovskaya, Z.I. Cleveland, K.F. Stupic, R.J. Basaraba, and T. Meersmann. Hyperpolarized krypton-83 as a contrast agent for magnetic resonance imaging. *Proc. Natl. Acad. Sci.*, 102:1827518279, 2005.
- [46] G. Tastevin and P.J. Nacher. Nmr measurements of hyperpolarized 3he gas diffusion in high porosity silica aerogels. J. Chem. Phys, 123:064506, 2005.
- [47] K.R. Brownstein and C.E. Tarr. Importance of classical diffusion in nmr studies of water in biological cells. *Phys. Rev. A.*, 19:2446 – 2453, 1979.
- [48] J.P. Korb, S. Godefroy, and M. Fleury. Surface nuclear magnetic relaxation and dynamics of water and oil in granular packings and rocks. *Mag. Reson. Imag.*, 21:193–199, 2003.
- [49] R.C. Selley. *Elements of Petroleum Geology*. W.H. Freeman and Company, New York, 1st edition, 1985.
- [50] N. Weidner and J Folkman. Tumoral vascularity as a prognostic factor in cancer. *Important Advances in Oncology*, 2:167–190, 1996.
- [51] J.J. Howard. Quantitative estimates of porous media wettability from proton nmr measurements. *Magn. Reson. Imag.*, 16:529, 1998.
- [52] J.J. Howard. Wettability and fluid saturations determined from nmr t1 distributions. Magn. Reson. Imag., 12:197, 1994.

- [53] M. Fleury and F. Deflandre. Quantitative evaluation of porous media wettability using nmr relaxometry. *Magn. Reson. Imag*, 21:385, 2003.
- [54] J.G. Seland, K.E. Washburn, H.W. Anthonsen, and J. Krane. Correlations between diffusion, internal gradients, and transverse relaxation in porous systems containing oil and water. *Physical Review E*, 70:051305, 2004.
- [55] Y.-Q. Song. Using internal magnetic fields to obtain pore size distributions of porous media. Con. Magn. Reson., 18A:97–110, 2003.
- [56] P.N. Sen and S. Axelrod. Inhomogeneity in local magnetic field due to susceptibility contrast. J. App. Phys., 86:4548, 1999.
- [57] McConnell. Reaction rates by nuclear magnetic resonance. J. Chem. Phys, 28:430–431, 1958.
- [58] R.G.S Spencer and K.W. Fishbein. Measurements of spin-lattice relaxation times and concentrations in systems with chemical exchange using the one-pulse sequence: breakdown of the ernst model for partial saturation in nuclear magnetic resonance spectroscopy. J. Magn. Reson., 142:120–135, 2000.
- [59] J.D.J. Ingle and S.R. Crouch. Spectrochemical Analysis. Prentice Hall, New Jersey, 1st edition, 1988.
- [60] L Venkataramanan, Y-Q Song, M.D. Hurlimann, and M. Flaum. Solving fredholm integrals of the first kind with tensor product structure in 2 and 2.5 dimensions. *IEEE Singal Process*, 50:1017–1026, 2002.
- [61] Y.Q. Song, L. Venkataramanan, M.D. Hurlimann, M. Flaum, P. Frulla,

and C. Straley. T-1 t-2 correlation spectra obtained using a fast twodimensional laplace inversion. J. Magn. Reson., 154:261–268, 2002.

- [62] G. Arfken. Mathematical Methods for Physicists. Academic Press, Orlando, FL, 3rd edition, 1985.
- [63] Groetsch C.W. Inverse Problems in the Mathematical Sciences. Informatica International, Inc, Baltimore, MD, 1st edition, 1993.
- [64] L. Elden and I. Skoglund. Algorithms for the regularisation of illconditioned least squares problems with tensor product structure and applications to space-variant image restoration. *Technical Report*, 34: 561–580, 1982.
- [65] G. Strang. Introduction to Linear Algebra. Wellesley-Cambridge Press, Cambridge, MA, 3rd edition, 1998.
- [66] C.L Lawson and R.J. Hansen. Solving least squares problems. Prentice Hall, Englewood Cliffs, NJ, 1st edition, 1974.
- [67] P.C. Hansen. The truncated svd as a method for regularization. *BIT*, 27:534–553, 1987.
- [68] A.N. Tikhonov. Solution of incorrectly formulated problems and the regularization method. Dokl. Akad. Nauk., 151:501–504, 1963.
- [69] G.H. Golub and C.F. Van Loan. Matrix computations. Johns Hopkins, Baltimore, MD, 3rd edition, 1996.
- [70] P.C. Hansen. Analysis of discrete ill-posed problems by means of the l-curve. SIAM Review, 34:561–580, 1992.

- [71] Y.Q. Song, L. Venkataramanan, and L. Burcaw. Determining the resolution of the laplace inversion spectrum. J. Chem. Phys., 122:104104, 2005.
- [72] J.H. Lee, C. Labadie, C.S. Springer, and G.S. Harbison. Two dimensional inverse laplace transform nmr: Altered relaxation times allow detection of exchange correlation. J. Am. Chem. Soc., 115:7761–7764, 1993.
- [73] B.Q. Sun and G. Dunn. Probing the internal field gradients of porous media. *Phys. Rev. E*, 65:051309, 2002.
- [74] P.T. Callaghan, S. Godefroy, and B.N. Ryland. Use of the second dimension in pgse nmr studies in porous media. *Magn. Reson. Imag.*, 21: 243–248, 2003.
- [75] P.T. Callaghan and I Furo. Diffusion-diffusion correlation and exchange as a signature for local order and dynamics. J. Chem. Phys., 120:4032– 4038, 2004.
- [76] D. de Swiet, M. Tomaselli, M.D. Hurlimann, and A. Pines. In situ nmr analysis of fluids contained in sedimentary rock. J. Mag. Reson., 133: 385, 1998.
- [77] R.M. Cotts, M.J.R. Hoch, and T. Sun. Pulsed field gradient stimulated echo methods for improved nmr diffusion measurements in heterogeneous systems. J. Magn. Reson., 83:252–266, 1989.
- [78] G.H. Sorland, D. Aksnes, and L. Gjerdaker. A pulsed field gradient spin-echo method for diffusion measurements in the presence of internal gradients. J. Magn. Reson., 137:397, 1999.

- [79] G.H. Sorland, J.G. Seland, J. Krane, and H.W. Anthonsen. Improved convection compensating pulsed field gradient spin-echo and stimulatedecho methods. J. Magn. Reson., 142:323, 2000.
- [80] M.D. Hurlimann. Effective gradients in porous media due to susceptibility differences. J. Magn. Reson., 131:232–240, 1998.
- [81] J. Karger, H. Pfeifer, and S. Rudtsch. The influence of internal magnetic field gradients on nmr self-diffusion measurements of molecules absorbed on microporous crystallites. *Mag. Reson. Imaging*, 21:193, 1989.
- [82] M Winkler, M. Zhou, M. Bernardo, B. Endeward, and H. Thomann. Internal magnetic gradient fields in glass bead packs from numerical simulations and constant time diffusion spin echo measurements. *Magn. Reson. Imag.*, 21:311, 2003.
- [83] J.P. Korb, M.W. Hodges, T.H. Gobron, and R.G. Bryant. Anomylous surface diffusion of water compared to aprotic liquids in nanopores. *Mag. Reson. Imag.*, 60:3097, 2003.
- [84] L. Monteilhet, J.P. Korb, J. Mitchell, and P.J. McDonald. Observation of exchange of micropore water in cement pastes by two-dimensional t-2 t-2 nuclear magnetic resonance relaxometry. *Phys. Rev. E*, 74:061414, 2006.
- [85] K.E. Washburn and P.T. Callaghan. Tracking pore to pore exchange using relaxation exchange spectroscopy. *Phys. Rev. Let*, 97:175502, 2006.
- [86] R.R. Ernst, G. Bodenhausen, and A. Wokaun. Principles of Nuclear Magnetic Resonance in One and Two Dimensions. Clarendon Press, Oxford, 1st edition, 1987.

- [87] B. Manz, J.D. Seymour, and P.T. Callaghan. Pgse nmr measurements of convection in a capillary. J. Magn. Reson., 125:153–158, 1997.
- [88] M.D. Hurlimann and D.D. Griffin. Spin dynamics of carr-purcellmeiboom-gill-like sequences in grossly inhomogenous b_0 and b_1 fields and application to nmr well logging. J. Magn. Reson., 143:120–135, 2000.
- [89] J. Mitchell, J.D. Griffith, J.H.P. Collins, A.J. Sederman, L.F. Gladden, and M.L. Johns. Validation of nmr relaxation exchange measurements in porous media. J. Phys. Chem., 127:234701, 2007.
- [90] J.G. Seland, G.H. Sorland, H.W. Anthonsen, and J. Krane. Combining pfg and cpmg nmr measurements for separate characterization of oil and water simultaneously present in a heterogeneous system. *App. Magn. Reson.*, 24:41, 2003.
- [91] K.F. Morris and C.S. Johnson. Diffusion-ordered two-dimensional nuclear magnetic resonance spectroscopy. J. Am. Chem. Soc., 114:3139– 3141, 1992.
- [92] P. Stilbs, K. Paulsen, and P.C. Griffiths. Global least-squares analysis of large, correlated spectral data sets: Application to component-resolved ft-pgse nmr spectroscopy. J. Phys. Chem., 100:8180–8189, 1996.
- [93] M.M. Britton, R.G. Graham, and K.J. Packer. Nmr relaxation and pulsed field gradient study of alginate bead porous media. J. Magn. Reson., 169:203–214, 2004.
- [94] R.J.S. Brown and I. Fatt. Measurements of fractional wettability of oilfield rocks by nuclear magnetic resonance methods. *Petroleum Trans*actions, 207:381–397, 1956.

- [95] H. Guan, D. Brougham, K.S. Sorbie, and K.J. Packer. Wettability effects in a sandstone reservoir and outcrop cores from nmr relaxation time distributions. J. Petro. Sci. Eng., 34:35–54, 2002.
- [96] B.Q. Sun and G. Dunn. A global inversion method for multi-dimensional nmr logging. J. Magn. Reson., 172:152–160, 2005.
- [97] J.P. Butler, J.A. Reeds, and S.V. Dawson. Estimating solutions of first kind integral equations with nonnegative constraints and optimal smoothing. SIAM J. of Num. Anal., 18:381–397, 1981.
- [98] J.E. Tanner. Use of the stimulated echo in nmr diffusion studies. J. Chem Phys., 52:2523–2526, 1970.