NMR Studies of Carbon Dioxide Sequestration in Porous Media



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Preface

The work presented in this dissertation was carried out in the Department of Chemical Engineering and Biotechnology at the University of Cambridge between October 2008 and June 2012. All the work described in this dissertation is believed to be original, except where explicit reference is made to other authors. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. This dissertation has not been previously submitted in part, or in whole, to any university for any degree, diploma or other qualification. This dissertation does not exceed 65,000 words or 150 figures, including bibliography, tables and equations.

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Publications and Conferences

The work presented in this thesis has resulted in the following refereed publications:

Hussain, R., Pintelon, T.R.R., Mitchell, J. & Johns, M.L. (2011) Using NMR displacement measurements to probe CO₂ entrapment in porous media. *AIChE Journal*. 57 (7), 1700–1709.

Hussain, R., Mitchell, J., Hammond, P., Sederman, A.J. & Johns, M.L. (2013) Monitoring water transport in sandstone using flow propagators: A quantitative comparison of nuclear magnetic resonance measurement with lattice Boltzmann and pore network simulations. *Advances in Water Resources*. 60, 64–74.

Hussain, R., Vogt, S.J., Honari, A., Hollingsworth, K.G., Sederman, A.J., Mitchell, J. & Johns, M.L. (2014) Interfacial tension measurements using MRI drop shape analysis. *Langmuir*. 30, 1566–1572.

The following conference presentations have also come out of this work:

Hussain, R., Pintelon, T.R.R., Mitchell, J. & Johns, M.L., Using NMR propagator measurements to probe CO₂ entrapment in porous media, 10th Bologna Conference on Magnetic Resonance in Porous Media, Leipzig, Germany. 12–16 September 2010. Poster presentation.

Hussain, R., Sederman, A.J. & Johns, M.L., NMR/MRI Studies of Carbon Sequestration in Porous Media, Graduate Conference, Department of Chemical Engineering & Biotechnology, University of Cambridge, UK. 26–27 April 2011. Oral presentation.

Summary

Carbon dioxide (CO_2) sequestration in the sub-surface is a potential mitigation technique for global climate change caused by greenhouse gas emissions. In order to evaluate the feasibility of this technique, understanding the behaviour of CO_2 stored in geological rock formations over a range of length- and time-scales is crucial. The work presented in this dissertation contributes to the knowledge in this field by investigating the two-phase flow and entrapment processes of CO_2 , as well as other relevant fluids, in porous media at the pore- and centimetre-scales using a combination of lab-based nuclear magnetic resonance (NMR) experimental techniques and lattice Boltzmann (LB) numerical simulation techniques.

Pulsed field gradient (PFG) NMR techniques were used to acquire displacement distributions (propagators) of brine flow through a model porous medium (100 µm glass bead packing) before and after the capillary (residual) trapping of gas-phase CO₂ in the pore space. The acquired propagators were compared quantitatively with the corresponding LB simulations. In addition, magnetic resonance imaging (MRI) techniques were used to characterise the extent of CO₂ trapping in the bead pack. The acquired NMR propagators were compared to LB simulations applied to various CO₂ entrapment scenarios in order to investigate the pore morphology in which CO₂ becomes entrapped. Subsequently, MRI drop shape analysis techniques were used to identify a pair of analogue fluids which matched certain key physical properties (specifically interfacial tension) of the supercritical CO₂/water system in order to extend the work to conditions more relevant to CO₂ sequestration in the sub-surface, where CO_2 is likely to be present in the supercritical phase. As before, NMR propagator measurements and MRI techniques, along with LB simulations, were used to characterise the capillary trapping of the CO₂ analogue phase in glass bead packs, as well as two different types of rock core plugs - relatively homogeneous Bentheimer sandstone, and heterogeneous Portland carbonate.

In addition to capillary trapping, the effect of vertical permeability heterogeneity, such as is often present in underground rock formations, was investigated for the flow of miscible (water/brine) gravity currents in model porous media (glass bead packs), using MRI techniques such as 2D spin-echo imaging and phase-shift velocity imaging. Finally, a preliminary investigation was made into the effect of particle- and pore-size distributions on the gas/liquid (air/water) interface for porous media consisting of glass bead and sand packs of different average particle size using quantitative MRI techniques.

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Nomenclature

Acronyms and initialisms

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
ADC	Analogue to digital converter
ADSA	Axisymmetric drop shape analysis
APGSTE	Alternating pulsed gradient stimulated echo
BRICS	Brazil, Russia, India, China, and South Africa
CCS	Carbon capture and storage
CDE	Convection dispersion equation
CFD	Computational fluid dynamics
CPMG	Carr-Purcell-Meiboom-Gill
CSI	Chemical-shift imaging
D3Q19	3D nineteen-speed hydrodynamic lattice
DAMTP	Department of Applied Mathematics and Theoretical Physics
DI	De-ionised
DRW	Directed random walk
ECBM	Enhanced coal bed methane
EDTA	Ethylene-diamine-tetraacetic acid
EM	Electro-magnetic
EOR	Enhanced oil recovery
EPI	Echo planar imaging
ET	Echo time
FID	Free induction decay
FLASH	Fast low angle shot
FOV	Field-of-view
FT	Fourier transform
FWHM	Full width at half-maximum
GHG	Greenhouse gas
GLBE	Generalised lattice Boltzmann equation
IDA	Image and data analysis (software)

IFT	Interfacial tension
IPCC	Intergovernmental Panel on Climate Change
LB	Lattice Boltzmann
LBGK	Lattice-Bhatnagar-Gross-Krook
LGA	Lattice gas automata
MATLAB	Matrix laboratory (software/language)
MIP	Mercury intrusion porosimetry
MR	Magnetic resonance
MRI	Magnetic resonance imaging
MRRC	Magnetic Resonance Research Centre
MRT	Multiple-relaxation time
MSME	Multi-slice multi-echo
NMR	Nuclear magnetic resonance
ODE	Ordinary differential equations
PDE	Partial differential equations
PEEK	Polyether ether ketone
PEG	Polyethylene glycol
PFG	Pulsed field gradient
PGSE	Pulsed gradient stimulated echo
PTFE	Polytetrafluoroethylene
RARE	Rapid acquisition with relaxation enhancement
r.f.	Radiofrequency
RHS	Right-hand side
RSS	Residual sum-of-squares
RT	Repetition time between experiments
SE	Spin echo
SIMPLE	Semi-implicit method for pressure linked equations
SNR	Signal-to-noise ratio
SRT	Single-relaxation time
SSE	Stimulated spin echo
TMS	Tetramethylsilane
UNFCCC	United Nations Framework Convention on Climate Change
VEXSY	Velocity exchange spectroscopy

WAG	Water-alternating-gas
XMT	X-ray microtomography

Latin symbols

A	Area of cross-section	m^2
A(v)	Frequency response to NMR signal	Hz
A_i	Lattice Boltzmann constant	-
Bo	Static axial magnetisation vector	Т
B ₁	Radiofrequency (transverse) magnetisation vector	Т
Beff	Effective magnetisation vector	Т
B_i	Lattice Boltzmann constant	-
Bo	Bond number	-
Ca	Capillary number	
C_i	Lattice Boltzmann constant	-
D	Effective diffusivity	m s ⁻¹
D_0	Diffusion coefficient	m ² s ⁻¹
D_i	Lattice Boltzmann constant	-
\overline{D}_{p}	Average particle diameter	m
Ε	Energy	J
<i>E</i> ()	Normalised NMR signal	-
$F_i^{\rm inj}$	Fraction of phase <i>i</i> in inlet stream	-
G	Applied magnetic field gradient	G cm ⁻¹
GPhase	Applied magnetic field gradient in phase direction	G cm ⁻¹
GRead	Applied magnetic field gradient in read direction	G cm ⁻¹
GSlice	Applied magnetic field gradient in slice direction	G cm ⁻¹
G_i	Gravity counter-current flow velocity function of phase <i>i</i>	kg m ⁻² s ⁻²
Н	Depth of fixed-permeability layer	m
Ι	Spin quantum number	-
L	Characteristic length scale	m
Μ	Net magnetisation vector	-
M ₀	Net magnetisation at equilibrium	-
Mz	Net magnetization in z-direction	-
Ν	Number of items/repeats	-

N_{higher}	Population of higher energy spins	-
N_i	Population of spin state <i>i</i>	-
N_{jump}	Number of diffusive steps	-
N_{lower}	Population of lower energy spins	-
N _{max}	Total number of seeded voxels	-
$N_{\rm RARE}$	RARE factor	-
Nseed	Current number of seeded voxel	-
М	Mach number	-
M _{ij}	Collision matrix	-
<i>O</i> ()	Orders (higher than)	-
Р	Pressure	Pa
Р	Spin angular momentum	kg m ² s ⁻³
P()	Probability distribution function	-
$\overline{P}()$	Ensemble average probability distribution	-
Pc	Capillary pressure	Pa
P_i	Pressure of phase i , e.g. gas (g) or water (w)	Pa
Pe	Péclet number	-
Q	Volumetric flow rate of fluid	m ³ s ⁻¹
Q	Non-dimensional inlet flux	-
$Q_{\rm C}$	Critical non-dimensional inlet flux	-
R	Dynamic displacement	m
R	Radius	m
Re	Reynolds number	-
Rep	Reynolds number for flow in a packed bed	-
S	Skewness of probability distribution	-
S()	NMR Signal	-
S_0	Maximum signal amplitude	-
$S_{\rm H}$	Horizontal length scaling parameter	m
S_{T}	Temporal scaling parameter	S
S_i	Saturation of phase <i>i</i>	-
Sir	Residual saturation of phase <i>i</i>	-
Т	Absolute temperature	Κ
Т	Non-dimensional time	-

T_1	Spin-lattice relaxation time constant	S
T_2	Spin-spin relaxation time constant	S
T_{2}^{*}	Total apparent spin-spin relaxation time constant	S
T_2'	Reversible spin-spin relaxation time constant	S
U	Velocity	m s ⁻¹
U_i	Darcy velocity of phase <i>i</i>	m s ⁻¹
V	Volume	m ³
V_i	Volume of phase <i>i</i> per unit cross-sectional area	m ³
W	Width	m
X_N	Non-dimensional front position of gravity current	-
С	Solute concentration	kg m ⁻³
Ci	Displacement in direction <i>i</i> over LB time-step	m s ⁻¹
d_{cpi}	Capillary dispersion rate of phase <i>i</i>	s ⁻¹
$d_{ m p}$	Bead (particle) diameter	m
$d_{\rm pore}$	Effective pore diameter	m
dt	DRW algorithm time-step	S
$f_i^{(G)}$	Viscous dominated fractional flow function of phase <i>i</i>	-
f_i	LB particle distribution function	-
f_i^{eq}	LB equilibrium particle distribution function	-
$f_{ m p}$	Friction factor for flow in packed beds	-
$f_{ m sw}$	Frequency sweep width	Hz
g	Magnetic field gradient pulse	G cm ⁻¹
ginc	Increment in magnetic field gradient pulse	G cm ⁻¹
g	Acceleration due to gravity	m s ⁻²
h	Planck's constant (6.62×10^{-34})	m ² kg s ⁻¹
j	Sampling factor	-
k	Reciprocal space vector	m ⁻¹
k	Permeability	m ²
k_B	Boltzmann constant (1.38×10^{-23})	kg m ⁻² s ⁻² K ⁻¹
<i>k</i> _{ri}	Relative permeability of phase <i>i</i>	-
ld	Diffusion length	m
n	Particle density	-
		xiii

<i>m</i> ₁	Angular momentum quantum number	-
p_{c}	Capillary pressure	Pa
p_i	Pressure of phase <i>i</i>	Pa
q	Dynamic reciprocal space	m ⁻¹
q	Dimensional flux	m ² s ⁻¹
qinc	Increment in q -space	m ⁻¹
r	Displacement / position vector	m
<i>r</i> _i	Radius of curvature of arc <i>i</i>	m
r _m	Mean radius of curvature	m
S	Arc length / skewness	m / -
t	Time	S
t _d	Dwell time	S
tp	Dwell time of phase gradient	S
u	Velocity vector	m s ⁻¹
и	Darcy velocity / velocity in x-direction	m s ⁻¹
$u_{ m LB}$	Lattice speed	-
u_i	Local Darcy velocity of phase i / velocity in direction i	m s ⁻¹
up	Pore velocity	m s ⁻¹
v	Velocity in <i>y</i> -direction	m s ⁻¹
W	Velocity in z-direction	m s ⁻¹
X	Displacement / position vector	m
Xadv	Displacement due to advection	m
Xdif	Displacement due to diffusion	m
x_N	Front position of gravity current	m
Ζ	Height below datum level in the vertical $(z-)$ direction	m
Greek sym	abols	
Δ	PFG NMR timescale	S

Δ	PFG NMR timescale	S
Δ	Incremental change in variable	-
Λ	Permeability ratio	-
Ω_i	LB collision operator	-

γ Gyromagnetic ratio (2.675 × 10 ⁸ for ¹ H)	rad s ⁻¹ T ⁻¹
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γ^3	Adjusted skewness	m ³
δ	Magnetic field gradient pulse duration	S
$\delta_{ m dd}$	Dirac delta function	
$\delta_{ m ppm}$	Chemical shift of a nucleus	-
З	Order	-
ζ	Displacement of fluid in axial direction	m
$\langle \zeta \rangle$	Mean displacement of fluid in axial direction	m
$\left< \zeta \right>_0$	Expected mean displacement of fluid in axial direction	m
θ	Contact angle / ratio of measured to expected displacement	rad / -
κ	Permeability	m ²
λ_i	Mobility of phase <i>i</i>	-
μ	Magnetic moment vector	A m ²
μ	Viscosity	Pa s
$\mu_{ ext{eff}}$	Brinkman effective viscosity	Pa s
v	Kinematic viscosity	m ² s ⁻¹
V LB	Lattice kinematic viscosity	-
v	Frequency	Hz
$\rho(\mathbf{r})$	Spin density at position r	m ⁻³
$ ho_i$	Density of fluid <i>i</i>	kg m ⁻³
σ	Root mean square width/ standard deviation	m
σ^2	Variance	m ²
σ_{ij}	Interfacial tension between phases <i>i</i> and <i>j</i>	kg m ⁻² s ⁻²
τ	Lattice Boltzmann relaxation time constant / half echo-spacing	S
$ au_{ m null}$	Nulling time	S
ϕ	Phase shift	rad
$\phi_{ m inc}$	Increment in phase shift	rad
$\phi_{\rm net}$	Net phase shift	rad
ω	Angular frequency	rad s ⁻¹
ω_0	Larmor frequency	rad s ⁻¹

1 Introduction

1.1 Background to CO₂ Sequestration

Carbon dioxide (CO₂) is widely encountered in industry as a by-product of processes such as combustion and fermentation. In addition, it is used as a raw material in the production of chemicals such as urea and methanol, as a refrigerant in solid form, and as an injected gas in enhanced oil recovery (EOR) methods. CO₂ is also a greenhouse gas (GHG), accounting for the overwhelming majority of total GHG emissions into the environment. It is emitted to the atmosphere mainly due to the combustion of fossil fuels from many different sectors, such as transportation, residential, commercial, industrial, and electricity generation (Pachauri & Reisinger, 2007). It was estimated that in 2010 the total amount of CO₂ emitted into the atmosphere globally, from fossil-fuel burning, cement production, and gas flares, was 31.6 Gt (Boden et al., 2010), with China, USA, India and Russia being the most emitting countries (see Figure 1.1). This number is expected to increase steadily in coming years, with the growth of emerging national economies such as the BRICS (Brazil, Russia, India, China, and South Africa) leading to increased global energy demand (IEA, 2010). Of particular concern is the fact that the concentration of CO_2 in the atmosphere has increased greatly in the last two hundred years or so, from around 280 ppm in pre-industrial times to the present level of 396 ppm (Dlugokencky & Tans, 2013). The United Nations Framework Convention on Climate Change (UNFCCC), which came into effect on 21 March 1994, acknowledged the role of anthropogenic GHG emissions in contributing towards climate change and the adverse effects of climate change on the planet (UN, 1992). Subsequently, the UNFCCC ratified the Kyoto Protocol on 11 December 1997, which called for industrialized countries to reduce emissions of GHGs in order to stabilise their concentrations in the atmosphere and thus limit the effect of global warming (UN, 1998). The protocol came into effect in 2005, and as of 2010, aims to limit the global temperature rise to below 2 °C.

It is against this backdrop that several climate change mitigation techniques have been put forward and researched as a means to lower the concentration of GHGs in the atmosphere. It is widely recognised that no single method will be able to, on its own, reverse the trend of anthropogenic emissions; instead, a 'portfolio approach' is required. One such approach was proposed by Pacala & Socolow (2004), who outlined a range of current technologies that are

sufficiently developed to help stabilise GHG emissions for the next 50 years if some or all of them are used in conjunction. These technologies, in addition to the reduced use of fossil fuels, include energy efficiency, substituting gas-fired power plants for coal-fired ones, CO_2 capture and storage (CCS), the use of nuclear and renewable power sources, and reducing deforestation. A more recent report (IEA, 2010) estimated that in a base case scenario, CO_2 emissions would go up to 57 Gt by 2050 and would need to be reduced to 14 Gt in order to meet climate targets; it was estimated that up to 19 % of this reduction could be achieved through the use of CCS, making it a significant contributor to climate change mitigation efforts. The basic premise of CCS involves the capture of CO₂ emitted from large point sources such as coal-fired power plants and its subsequent separation, transportation and entrapment through a variety of methods, as illustrated in Figure 1.2. One of these methods, the geological sequestration of CO₂, is the focus of the work presented in this thesis and consequently is discussed below. However, for a thorough discussion of other trapping methods such as mineral carbonation, ocean storage and industrial use of CO₂, the interested reader is directed to the comprehensive Intergovernmental Panel on Climate Change (IPCC) report on CCS (Metz et al., 2005).



Figure 1.1 World map showing total CO₂ emissions by country in 2010, on a megatonne (Mt) of carbon basis. Data used in this figure was obtained from Boden et al. (2010). The figure was made using the GunnMap 2 tool by Gunn Interactive (http://lert.co.nz/map/).

Geological sequestration involves the storage of CO_2 underground in natural sub-surface reservoirs such as depleted oil and gas fields, coal seams and saline aquifers, as illustrated in

Figure 1.3. In some cases, the CO_2 storage may be combined with EOR processes. EOR is a mature market technology, which has already been demonstrated to be economically feasible; as such, it may prove to be one of the most affordable CO_2 storage options (Nakicenovic et al., 1993). Currently, over 30 Mt of CO₂ are injected annually for the purpose of EOR (Solomon et al., 2008). In addition, a study on the potential market for economic, incremental oil production with EOR concluded that there is capacity for storing 10 to 13 Gt, oil prices permitting, of CO₂ with EOR in the USA (Ferguson et al., 2009). This is a significant amount as it represents about two years' worth of emissions in that country. However, the storage of CO_2 in depleted oil and natural gas reservoirs purely for sequestration purposes (i.e. without EOR) is not always economically feasible (Metz et al., 2005). Another possibility, still at the developmental stage, is the injection of CO_2 into unmineable coal seams (i.e. those are too deep or too thin to be economically mined). This would have the added benefit of displacing methane gas which is adsorbed on the coal surface and could therefore be used for enhanced coal bed methane (ECBM) recovery, which would offset the cost of the CO₂ storage (DOE/NETL, 2007). In addition, many unmineable coal seams are located near large CO₂ point sources such as power plants (Reeves, 2001), which is a significant advantage for this method of CO₂ storage.



Figure 1.2 Potential routes for the sequestration of CO₂ emitted as a by-product of fossil fuel combustion and industry. The dashed and solid arrows represent net flows of energy and CO₂, respectively.



Figure 1.3 Storage options for the geological sequestration of CO₂ in the sub-surface. The photographs used in making this schematic were obtained from the Wikimedia Commons database (http://commons.wikimedia.org/wiki/Main_Page) and used under the Creative Commons Attribution-ShareAlike 4.0 International License (http://creativecommons.org/licenses/by-sa/4.0/). Accessed on 13 February 2014.

The storage of CO_2 in deep saline aquifers is also of considerable interest, as such aquifers comprise the highest capacity for CO_2 storage out of all geological formations (Metz et al., 2005); in addition, using large regional aquifers located near to power plants for storing CO_2 could potentially avoid the need for long transport pipelines (Smith, 1999). The main processes by which CO_2 can be sequestered in aquifers usually involve the injection of a bulk CO_2 phase, which rises due to buoyancy and is trapped under a layer of suitable lowpermeability cap rock—a process known as hydrodynamic trapping. Other trapping mechanisms (in order of increasing timescale) include solubility trapping, in which gradual subsurface CO_2 dissolution creates a local denser phase hence establishing convection currents and mixing (Ennis-King et al., 2005), and mineral trapping, whereby CO_2 is converted into carbonate minerals such as calcite by reactions with the mineral/rock matrix. Although mineral trapping is potentially the most stable mechanism for long-term retention of CO_2 , the rate of reaction between the injected CO_2 and the rock matrix would need to be speeded up greatly in order for it to be a viable option for geological sequestration (Metz et al., 2005).

Another key trapping mechanism, which can be induced by water flooding following bulk CO_2 injection, is retention of CO_2 in water-wet pore space as discrete gas pockets or bubbles through the action of capillary forces; this is referred to as capillary or residual trapping (Bachu et al., 1994). These bubbles of immobile gas are hereafter referred to as ganglia, in order to be consistent with terminology used to describe the entrapment of non-aqueous phase liquids by the same physical process. It is estimated in the case of CO_2 sequestration that capillary trapping might account for a residual gas saturation of up to 25 % (Holtz, 2002). However, it is important to note that the amount of residually trapped CO₂ depends heavily on the pore structure of the rock in which it is trapped, of which there is considerable variation amongst different geological formations. Early work, done mainly on twodimensional glass micromodels using both oil/water displacements and mercury injection (Wardlaw, 1980, 1982; Wardlaw & McKellar, 1981), showed that the main geometric factors affecting residual non-wetting phase trapping are the pore-throat size ratio (by which it is meant the ratio of the bulk pore size to that of the openings, or 'throats', which link different pores together), the distribution of pore-size heterogeneity within the rock (specifically, the presence of non-random heterogeneities such as clusters of pores of a particular size) and the connectivity of the pore space (e.g. as given by the mean coordination number or average number of pore-throat connections). Previously, characterization of the pore space of real systems such as reservoir rocks was limited to invasive techniques such as pore casting (Wardlaw, 1980) or mercury-intrusion porosimetry (Portsmouth & Gladden, 1991), but more recent advances in pore-scale imaging and modeling (e.g. using X-ray tomography) have enabled direct estimation of complicated parameters such as relative permeability (e.g. Arns et al. (2004)) and in-situ imaging of non-wetting phase trapping (e.g. Iglauer et al. (2010)), enabling the size distribution of the ganglia to be correlated to the pore network topology. More recently, Pentland et al. (2012) applied such imaging techniques to the trapping of CO_2 in various media such as bead and sand packs and sandstone and found that media with narrower throats trapped more CO_2 , although the relationship with other parameters such as pore-throat size ratio and coordination number was not as straightforward.

While it is evident that capillary trapping provides a very stable and rapid sequestration mechanism, and is therefore the main focus of the work presented in this thesis, how best to economically achieve this physical state on a field scale is still open to debate (Metz et al., 2005; Saadatpoor et al., 2010). Burton & Bryant (2009) proposed a process in which captured CO₂ is dissolved in brine which is extracted from, and subsequently re-injected into, the target aquifer. This technique, known as 'surface dissolution', was shown in their preliminary analysis to be technically feasible and in some ways more advantageous than injecting bulk-phase CO₂ into underground rock formations. Its advantages included greater density of the saturated brine eliminating the risk of buoyancy-driven leakage, 40 % smaller volume footprint compared to hydrodynamic trapping, and a greater range of injection depths in the sub-surface. The approach is, however, more expensive than hydrodynamic trapping, mainly due to the increased capital costs of drilling extraction wells in parallel with the wells for injection.

In order to demonstrate the long-term viability of geological CO₂ sequestration on an industrial scale, several large-scale example projects are underway at present, and many others are in the planning or construction phases (GCCSI, 2012). The oldest of these is the Sleipner project in Norway, where CO₂ is injected into the Utsira saline aquifer at a depth of 800-1000 m below sea level. Over 13 Mt of CO₂ have been injected since the start of the project in 1996, and the progress of the injected CO₂ through the formation is tracked using seismic imaging and wellhead pressure measurements for modelling and analysis purposes (StatoilHydro, 2009). Other major projects included the In Salah project in Algeria, where 1 Mt of CO₂ was injected annually between 2004 and 2012 into a 2000 m deep saline aquifer in the Krechba sandstone formation, and the Weyburn-Midale project in Canada, where around 3 Mt of CO₂ are injected annually into the Weyburn and Midale oilfields for EOR. More information about these, and other, projects is available at the Global CCS Institute website (http://www.globalccsinstitute.com/).

Despite its feasibility from a technical point of view, as illustrated by the example projects described above, there are however several challenges facing the widespread implementation of CO_2 sequestration in the sub-surface. Most importantly, if CO_2 levels in the atmosphere are to be significantly reduced, the CO_2 must be stored underground in such a way that it does not escape. As CO_2 stored in depleted oil and gas wells or saline aquifers will be typically

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present at depths of below 800 m it is expected to be in a dense, supercritical form, with its density being close to that of some hydrocarbons (with a specific gravity of between 0.5–0.8, compared to ~ 0.8 for hydrocarbons). Therefore it is essential that the trapping mechanisms of CO₂ within the pore structure are well understood and that there is a well-sealed cap rock over the reservoir to keep the CO_2 from escaping. Carbon dioxide well blowouts (i.e. the large localised release of CO_2 from a storage reservoir to the surface in a relatively short time) are a potential hazard, both to humans and the environment; Holloway et al., 2006 illustrated this by analogy with natural geological CO₂ emissions, e.g. in volcanic and hydrothermal regions. In addition, Benson et al. (2002) studied the technological aspects and outcomes of industrial liquid waste disposal in deep geological formations, natural gas storage in underground reservoirs, and nuclear waste storage in underground repositories as an analogue to the potential storage of CO_2 in the sub-surface. They concluded that depleted oil and gas reservoirs are easier to develop than aquifer storage projects because the geologic structure and cap rock are usually well characterised from existing wells. Ultimately, however, apart from the suitability and robustness of sequestration techniques, there are three main factors that will determine the success or otherwise of carbon sequestration as a mitigating strategy for CO_2 emissions: the availability and capacity of geological storage sites, the cost of geological storage compared to other climate change mitigation methods, and public acceptance of such projects (Hepple & Benson, 2002).

In addition to the geological sequestration of CO₂, some of the work presented in this thesis is motivated by the increasing pressure on global water supplies (UNDP, 2006). A considerable proportion of potable water comes from underground freshwater aquifers close to the Earth's surface. These aquifers can suffer water quality reduction due to saltwater intrusion as a consequence of over-exploitation and rising sea levels. In addition, it is possible that the displacement of brine from saline aquifers due to CO₂ injection may also lead to saltwater intrusion. Therefore, understanding the transport properties of water in underground rock formations is critical when addressing these issues. In general, fluid flow through rock is also important for oil, gas, and mineral extraction (Bai, 1992; Maitland, 2000; Suicmez et al., 2008), contaminated land clean-up (Mulligan et al., 2001), and disposal of hazardous waste such as nuclear fuel (Bates et al., 1992). Measuring flow in these optically opaque systems has traditionally been limited to techniques such as analysis of tracer breakthrough (Rashidi et al., 1996; Klise et al., 2008) or bulk pressure drop measurements (Tsakiroglou & Payatakes, 2000), most of which are conducted in small laboratory-scale (sub-metre) samples of cored reservoir material or ideal porous media.

Given the scope of the challenges outlined above, it is evident that gaining a physical understanding of the transport of CO_2 in multi-phase flow, through porous media systems such as rock formations, is of great importance in order to gain knowledge about where in the pore space the CO_2 is trapped and whether it will remain trapped for the long term. Such knowledge may be acquired through an integrated approach involving studies conducted over several length- and time-scales, from lab-scale investigations to reservoir-scale example projects such as the ones outlined earlier. Data from such studies may then be used to develop numerical simulation models in order to enable prediction over time-scales which cannot be studied practically. Within this broad framework, the scope of this project is encompassed in the following aims:

- 1. To study the single- and two-phase flow of CO₂ in porous media (as CO₂ injected into the ground will inevitably be present alongside either water and/or oil phases) using nuclear magnetic resonance (NMR) experimental techniques. The project aims to advance the scientific pore-scale understanding of these processes using a mainly lab-based approach.
- 2. To develop numerical simulation models based on lattice Boltzmann (LB) techniques, and to use the experimental data generated through the first aim for model validation.

The second aim stated above follows on from the first, as despite the advantages of NMR techniques, such measurements are limited to sample lengths that will fit within the confines of the NMR magnet geometry—typically, less than 100 mm. Therefore, to upscale the measured flow properties to the reservoir-scale, reservoir simulators are necessary. In addition, the NMR measurements are also limited in terms of spatial resolution (typically, tens of microns) and thus simulations may be needed in order to facilitate the interpretation of the experimental data at the scale of individual pores.

The specific aims relating to different parts of the project are found in the subsequent chapters; a brief overview of each chapter is presented in Section 1.3.

1.2 Techniques Used in This Dissertation

The experimental techniques used in this dissertation, as previously mentioned, are based on the phenomenon of NMR. NMR techniques such as imaging and velocimetry are particularly useful for measuring multi-phase (gas-liquid or liquid-liquid) transport processes in porous systems (Sederman *et al.*, 1998). NMR has been used to study fluid flow in both artificial porous media such as bead packs (e.g. Hussain et al. (2011)) and real rock cores such as sandstone (e.g. Hussain et al. (2013)) and carbonate (e.g. Scheven et al. (2005)).The advantages of NMR include:

- It is non-invasive and non-intrusive, and can be used on optically opaque systems.
- It is chemical species-selective.
- It can distinguish between different fluid phases.
- It can be used to image in one, two or three dimensions, at a spatial resolution of up to tens of microns.
- It is able to quantify molecular diffusion and fluid displacements over length-scales on the order of microns and time-scales on the order of milliseconds to seconds through the use of pulsed field gradient (PFG) NMR. This is particularly valuable in systems where the pore scales are below the resolution of imaging (Packer *et al.*, 1998).

The use of NMR as an experimental technique does, however, suffer from certain limitations. One of these is that materials with large ferromagnetic and paramagnetic content cannot be used. This problem was avoided in the work presented in this dissertation by using model porous media consisting of randomly-packed glass ballotini as well as rock cores low in ferromagnetic content, such as Bentheimer sandstone and Portland carbonate. Another limitation which arises when using NMR with porous media samples is the presence of background magnetic field gradients due to susceptibility differences between solid surfaces and liquid in the pores. These background gradients can distort the NMR signal, thereby causing undesirable effects such as broader spectral line-widths and imaging artefacts, and are made worse at higher surface-to-volume ratios (i.e. the ratio of the solid/liquid interfacial surface area to the void volume of the solid matrix). However, this limitation was mitigated to some extent by using borosilicate glass ballotini instead of soda lime glass where available, as borosilicate is known to exhibit the smaller susceptibility differences.

In addition to experimental work, numerical simulations were also conducted and were used to interpret the experimental results presented in this thesis. These simulations were carried out using a lattice Boltzmann (LB) approach to simulate the hydrodynamic flow field in porous media, coupled with a directed random walk (DRW) algorithm to simulate the combined effects of advection and diffusion of fluid particles in the flow field. The advantages of using LB are its relative stability and ease of implementation, thus making it less computationally expensive compared to other computational fluid dynamics (CFD) techniques—which generally require a more refined simulation 'mesh' around sharp geometries. LB techniques have been successfully validated against experimental data for flow in porous media systems such as glass bead packs in previous studies, e.g. Manz et al. (1999).

1.3 Dissertation Overview

Chapter 1 – In this introductory chapter, a brief overview of the background of geological CO₂ sequestration is provided, as well as the motivation behind this project.

Chapter 2 – The basic theory of NMR and MRI, as well as that of LB simulations is described, with a focus on the techniques used in this project. In addition, a brief introduction of concepts relating to flow in porous media is presented.

Chapter 3 – Single-phase alternating pulsed gradient stimulated echo (APGSTE) NMR displacement propagators were acquired of brine flow through a model porous medium (100 μ m glass bead packing) and a Bentheimer sandstone core plug. The propagators were compared quantitatively with corresponding LB simulations. In order to create residual (capillary) CO₂ trapping, carbonated brine was flowed through the model porous medium and various NMR techniques such as 1D and 2D imaging and propagator measurements were used to characterise the extent of capillary trapping of CO₂ coming out of solution. The acquired NMR propagators were compared to LB simulations applied to various CO₂ entrapment scenarios in order to investigate the pore morphology in which CO₂ becomes entrapped.

Chapter 4 – An analogue system was identified, which matched certain key physical properties of the supercritical CO_2 /water system. In order to verify the interfacial tension of the analogue fluids, MRI techniques were used to acquire droplet profiles, which were subsequently analysed using axisymmetric drop shape analysis (ADSA).

Chapter 5 – Capillary trapping of the supercritical CO₂/water analogue system identified in Chapter 4 was studied in different porous media using NMR and MRI techniques. Singlephase APGSTE NMR displacement propagators were acquired for the aqueous phase in glass bead pack, Bentheimer sandstone, and Portland carbonate core samples. The samples were then flooded with the supercritical CO₂ analogue phase followed by the aqueous phase in order to encourage capillary trapping in the pore space. The extent of capillary trapping was measured using displacement propagators of the aqueous phase after trapping as well as quantitative 1D NMR spin-echo profiles with T_1 inversion nulling. Additionally, a coreflood analysis method was used to analyse in-situ saturation data. Finally, a lattice Boltzmann simulation method similar to that employed in Chapter 3 was used to interpret the trapping mechanism on the pore-scale in the Bentheimer sandstone.

Chapter 6 – The effect of vertical permeability heterogeneity on the flow of miscible gravity currents in porous media was investigated, using MRI techniques such as 2D spin-echo imaging and phase-shift velocity imaging. Quantitative MRI spin-echo images were acquired in a dual-layered porous medium consisting of different glass bead sizes, showing the time-evolution of injected gravity currents with fixed inlet flux. In addition, velocity maps were acquired of the system in steady state which provided insight into the position where override occurred, as well as on the relative flux in the two layers. The experimental data obtained here on a 3D porous medium were used to validate a theoretical model. Finally, some preliminary results from a 3D CFD model of the two-layer system are presented.

Chapter 7 – The effect of particle- and pore-size distributions on the gas/liquid interface was investigated for porous media consisting of glass bead and sand packs of different average particle size. Quantitative MRI techniques, such as T_2 -preconditioned 2D RARE and 2D spinecho images were used to visualise two-phase gas/water displacement flow in different porous media initially saturated with a wetting aqueous phase, after injection with a non-wetting gas phase (air).

Chapter 8 – Conclusions are drawn from the work presented in this dissertation and further research work is proposed to enable the continuation of this project.

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2 Theory

2.1 Introduction

In this chapter, a brief outline of the relevant nuclear magnetic resonance (NMR) and lattice-Boltzmann (LB) theory is presented, along with theory relating to fluid flow in porous media.

2.2 Nuclear Magnetic Resonance

This section aims to briefly describe some of the fundamental theory relating to NMR, from its quantum mechanical basis to the spectroscopic techniques used in the work presented in this dissertation. For a more comprehensive discussion of NMR fundamentals, the interested reader is directed to Callaghan (1993).

2.2.1 Origins

The discovery of the nuclear magnetic resonance (NMR) phenomenon is a relatively recent one by modern scientific standards. The first NMR experiments were performed independently by Bloch et al. (1946) and Purcell et al. (1946) at Stanford and Harvard universities, respectively. However, it was not until the discovery of the chemical shift effect (Arnold et al., 1951) and the construction of permanent magnets with more homogeneous magnetic fields, leading to higher resolution spectra (Anderson, 1956; Arnold, 1956), that the technique's true utility was realised. Since the development of NMR imaging (NMRI, commonly referred to as MRI) originally proposed by Lauterbur (1973), the main application of NMR has been in the field of medical *in vivo* imaging to visualise the internal structure and function of the human body. However, its use has spread in recent years to include wideranging applications in research fields relevant to chemical engineering and on-line monitoring of chemical processes. Comprehensive reviews of relevant techniques and applications have been conducted by Gladden (1994) and Mantle & Sederman (2003), with the former focused on conventional NMR spectroscopy and the latter on dynamic processes requiring fast, spatially resolved imaging techniques.

2.2.2 Principles of NMR

NMR spectroscopy exploits a quantum mechanical property of atomic nuclei called 'spin' (here denoted by **P**), which is a type of angular momentum. Like all quantum mechanical properties, its magnitude, P, can be specified in terms of a quantum number, I, according to the equation

$$P = \frac{h}{2\pi} \left[I(I+1) \right]^{1/2},$$
(2.1)

where *h* is Planck's constant and *I* can take the values 0, $\frac{1}{2}$, 1 ... and so on. As angular momentum is a vector quantity **P** has an associated directional quantum number m_I which can take 2I+1 different values in the range [-I, -I+1, -I+2, ..., I]. The projection of *P* along an axis *z* is given by

$$P_z = \frac{h}{2\pi} m_I. \tag{2.2}$$

In the case of spin, the influence of an external, static, magnetic field will cause the magnetic moments of the spins to align with the direction of the field, say z. For example, consider a nucleus with $I = \frac{1}{2}$. When projected along the z axis there are thus two possible values of the spin directional quantum number, $+\frac{1}{2}$ and $-\frac{1}{2}$. This means that the nucleus has two spin energy levels. For a particular nucleus to show NMR effects it must have a non-zero nuclear spin (i.e. I > 0). Certain nuclei, such as the naturally abundant isotopes ¹²C and ¹⁶O, have I = 0 which means that they are not detectable in an NMR experiment. In general, NMR is most useful for nuclei with $I = \frac{1}{2}$ (also known as 'spin- $\frac{1}{2}$ ' nuclei), such as ¹H and ¹³C. Nuclei with $I > \frac{1}{2}$, such as ²H and ¹⁴N, do have magnetic properties but also possess electric quadrupole moments (i.e. their nuclear charge distribution is not spherically symmetric), which results in broader absorption lines in their NMR spectra. The NMR experiments described in this thesis were done exclusively on ¹H, and therefore the following discussion about nuclear magnetic moments relates to spin- $\frac{1}{2}$ nuclei.

The spin **P** of a nucleus is directly proportional to its magnetic moment μ by the gyromagnetic ratio, γ , which is specific to each nucleus. Thus for example, the gyromagnetic ratio of ¹H is 2.675 x 10⁸ rad s⁻¹ T⁻¹. When no external magnetic field is present, the energy of each individual nucleus is independent of its orientation, and hence of m_I . If an external static magnetic field **B**₀ is applied along the *z*-direction, the magnetic moments of the nuclei will

align themselves in high $(+\frac{1}{2})$ and low $(-\frac{1}{2})$ energy states. This phenomenon is known as the Zeeman effect (Figure 2.1). The energy of a magnetic moment, μ , is thus given by

$$E = \mathbf{\mu} \cdot \mathbf{B}_{\mathbf{0}} = -\mu_z B_0 = -\gamma P_z B_0 = -\gamma \hbar m_I B_0, \qquad (2.3)$$

where $\hbar = h / 2\pi$. However, as the selection rule governing transitions between the energy states is $\Delta m_I = \pm 1$, the energy gap between the two states is given by

$$\Delta E = \left| \gamma \hbar B_0 \right|. \tag{2.4}$$

This energy gap may also be represented by the Bohr frequency condition,

$$\Delta E = hv, \tag{2.5}$$

which relates the difference in energy states to the frequency of electromagnetic radiation which, when absorbed or emitted, causes a transition between the two states.



Figure 2.1 The Zeeman effect as applied to a spin-½ nucleus under the influence of an external static magnetic field B₀.

The population distribution between the higher and lower energy states at thermal equilibrium is given by a Boltzmann distribution:

$$\frac{N_{higher}}{N_{lower}} = \exp\left(\frac{-\hbar\gamma B_0}{k_B T}\right);$$
(2.6)

the difference in population between the two energy states gives rise to a 'net magnetisation vector', M_0 , which can be thought of as a bulk material property (due to the large number of nuclei present in a typical sample) and thereby treated the same way as a magnetic moment in classical mechanics. It is this 'vector model' which will be used subsequently in this chapter to describe NMR experiments.

Equating the RHS of Equations (2.4) and (2.5) gives the result:
$$\omega_0 = \gamma B_0. \tag{2.7}$$

Here ω_0 (= $2\pi v_0$), expressed in rad s⁻¹, is known as the Larmor frequency. This equation is one of the most important relationships in NMR and it implies that **M**₀ precesses about **B**₀ at a frequency ω_0 due to the torque exerted by the field upon the magnetic moment. Typically, NMR spectrometers use a **B**₀ field in the range 1.5–12 T (Harris, 1986). This results in required frequencies of the order 10–10² MHz, which is in the radiofrequency (r.f.) range of the EM spectrum.

2.2.3 Spin excitation and detection

In order to detect an NMR signal, a transverse sinusoidal magnetic field **B**₁, which is small compared to **B**₀, is applied to the nuclei in the presence of **B**₀ typically by means of an r.f. pulse. Thus **M**₀ will precess about **B**₁ in addition to **B**₀ for the duration of the r.f. pulse, Figure 2.2(a). In order to simplify the complex motion of **M**₀, it is useful to choose a 'rotating frame' of reference which rotates about **B**₀ at the Larmor Frequency, ω_0 , Figure 2.2(b).

Following such a perturbation, the transverse component of M_0 will undergo precession in the transverse (*x*-*y*) plane and induce an oscillatory voltage in an r.f. coil, which can be detected as an NMR signal. The amplitude of this voltage, which is small (typically measured in μ V) is proportional to the transverse magnetisation. This signal is known as the 'free induction decay' (FID) as the signal intensity decays exponentially; the reason for this decay is discussed in Section 2.2.5. An r.f. pulse of sufficient duration to rotate M_0 completely into the transverse plane (and thus get maximum signal intensity) is known as a 90° or $\pi/2$ pulse; a pulse of twice the duration, assuming the same pulse power level, is known as a 180° or π pulse and will therefore rotate M_0 into the negative longitudinal axis. The pulses usually applied in NMR are short in duration and thus excite a large frequency bandwidth that covers the entire chemical shift range of any particular nucleus. These intense, 'non-selective' pulses are known as 'hard' pulses; as we shall see later (Section 2.2.7), there are also less intense, 'selective' pulses known as 'soft' pulses. The simplest NMR experiment involves the application of a single hard pulse and is therefore also termed as 'pulse-acquire'.



Figure 2.2 The effect of an r.f. pulse on the magnetisation vector M (blue) seen from the (a) Cartesian coordinate frame; (b) Rotating coordinate frame with frequency ω_0 . The green arrow represents the initial position, M₀, of the magnetisation vector.

The frequency response A(v) to the time domain signal intensity of the FID, S(t), is expressed in the following relationship:

$$A(\nu) = \int_{-\infty}^{+\infty} S(t) \exp(i2\pi\nu t) dt \,. \tag{2.8}$$

Therefore, by performing a Fourier transform (FT) on the FID signal, a resonance spectrum can be obtained in the frequency domain. A typical FID signal i.e. for a single-resonant chemical component follows an exponential decay; this results in a Lorentzian line shape in the frequency domain, as shown in Figure 2.3. Practically, the NMR signal is sampled digitally at discrete time points.

The time between successive sampling points is known as the dwell time t_d and is inversely proportional to the frequency range f_{sw} , also known as the sweep width. The maximum frequency range that can be sampled is $1 / 2t_d$, which is known as the Nyquist frequency. The signal is obtained by an r.f. receiver and is mixed with the outputs of reference r.f. oscillators, which are 90° out of phase with each other and operated at the Larmor frequency, a process known as 'heterodyne mixing'. This mixing means that the separate in-phase ('real') and quadrature ('imaginary') signals, M_x and M_y , may be detected. The separate signals can be used in the procedure of phase cycling, which is a powerful technique allowing the selection of certain types of NMR signals of interest, while removing those signals which are unwanted (e.g. due to incoherence or imperfections in the spectrometer hardware). The details of phase cycling are not discussed in this chapter, but the interested reader is directed to Levitt (2001) for more details.



Figure 2.3 FID signal shown in the (a) time domain (b) frequency domain after Fourier transform (real signal shown), for a single chemical component. The frequency bandwidth or line-width of the resonance spectrum is usually expressed as the full width at half maximum (FWHM) of the peak, as indicated on the diagram.

2.2.4 The chemical shift effect

When an external magnetic field is applied to a nucleus, the electrons orbiting it will arrange in such a way as to oppose the applied field, thus 'shielding' the nucleus. This shielding causes the resonant frequency of the nucleus to deviate from the Larmor frequency, a phenomenon known as chemical shift. The extent of the chemical shift varies depending on the local electronic environment of the nucleus, which can vary depending on which chemical groups the nucleus in question is attached to or adjacent to. For example, in a molecule of ethanal (CH₃-CHO), the chemical shift of a hydrogen atom on the first carbon is different from that of the one on the second carbon. The shielding reduces the applied magnetic field by a factor σ , and hence the effective magnetic field experienced by a nucleus is termed **B**_{eff}. However, as different NMR spectrometers have different field strengths, the chemical shift of a nucleus, δ_{ppm} , is usually expressed as the resonant frequency *v* of that nucleus compared to a reference nucleus, tetramethylsilane (TMS), and calculated in units of parts per million (ppm):

$$\delta_{\rm ppm} = \frac{(\nu - \nu_{\rm ref})}{\nu_{\rm ref}} 10^6$$
 (2.9)

2.2.5 Relaxation

The process by which the magnetisation returns to thermal equilibrium is known as relaxation, of which there are two types, spin-lattice (T_1) relaxation, and spin-spin (T_2) relaxation. The former occurs in the direction of the **B**₀ field (i.e. along the *z*-axis) and the latter occurs in the transverse (*x*-*y*) plane.

Spin-lattice (T_1) relaxation involves the net magnetisation returning to its equilibrium state parallel to **B**₀, and hence thermal equilibrium, by the transfer of energy between the spins and their surroundings (i.e. the 'lattice'). The relaxation process can be described mathematically by the first order differential equation

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}.$$
(2.10)

One way of measuring T_1 is by the 'inversion recovery' method (Vold et al., 1968) whereby a 180° pulse is applied to rotate **M**₀ into the negative z-axis, thereby causing pure T_1 relaxation to occur (assuming a perfect inversion). A 90° pulse is then applied after a time τ to enable signal to be detected at that temporal point. The boundary condition in this case is $M_z(0) = -M_0$ and therefore the solution to Equation (2.10) becomes

$$M_{z}(t) = M_{0}(1 - 2e^{-t/T_{1}}).$$
(2.11)

The T_1 value is thus obtained by fitting a curve to the data using the expression shown in Equation (2.11). It is important to allow a time delay of $5 \times T_1$ or greater between successive acquisitions in this experiment, as this allows at least 99 % of the magnetisation to reach thermal equilibrium before the next 90° pulse, thus ensuring residual longitudinal magnetisation does not interfere with subsequent acquisitions. In general, a commonly followed rule-of-thumb is to keep the time between successive acquisitions in an NMR experiment, known as the repetition time or RT, to at least $3 \times T_1$, thereby ensuring that 95 % of the magnetisation is fully relaxed before the subsequent excitation. However, this is not always possible, in which case the NMR signal reaches an 'equilibrium saturation' where the overall signal intensity is less than that which would be seen if the spins were fully relaxed. This effect is known as T_1 weighting, and may be useful depending on the system being studied.

 T_1 is typically of the order of seconds for protons in pure liquids at room temperature. The introduction of paramagnetic ions such as Gd^{3+} or Mn^{2+} into the system can drastically reduce the T_1 due to the interaction of the unpaired electrons in the ions with the magnetic field, which induces alternating magnetic field gradients, thereby reducing the time required for the nuclear spins to reach thermal equilibrium. Shortening the T_1 can be very advantageous as it reduces the time between signal acquisitions, thereby shortening experiment times.

Spin-spin (T_2) relaxation occurs due to interactions between molecular spins, resulting in the loss of phase coherence of the spins and hence the decay of the transverse magnetisation. It is an irreversible process which follows an exponential decay with relaxation time constant T_2 . Another cause of signal decay is due to local inhomogeneities in the B_0 magnetic field. This causes spins in different parts of the sample to precess at different Larmor frequencies and hence de-phasing occurs. The combined effects of spin-spin relaxation, T_2 , and the reversible spin de-phasing T_2' can be expressed in terms of an overall relaxation time constant T_2^* , also sometimes called the 'apparent transverse relaxation constant', according to

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'},\tag{2.12}$$

where T_2' is the contribution to T_2^* due to field inhomogeneities and is inversely proportional to the variation in the magnetic field, ΔB_0 . The effect of T_2' is to shorten T_2^* and thus broaden the line shape in the frequency domain. The value of T_2^* can thus be measured directly from the FID signal in a pulse-acquire experiment, or from the full width at half maximum (FWHM) of the Fourier transformed data in the frequency domain, for a single component. The frequency bandwidth Δv of the Lorentzian line shape is often taken as the FWHM, therefore

$$T_2^* = \frac{1}{\pi(\Delta \nu)}.$$
 (2.13)

The NMR signal may only be observed for as long as it retains coherence, which in the case of the pulse-acquire is limited by T_2^* ; therefore, the local magnetic field is often 'shimmed' in order to make it as homogeneous as possible. Shimming involves the use of special gradient coils to produce magnetic field gradients which counter the effect of field homogeneities; these corrective gradients may be non-linear (e.g. 'higher order' gradients may have spatial profiles that vary as z^2 , z^3 , zy etc.). A more homogeneous B_0 field also results in narrower spectral peaks in the frequency domain, which enables better separation of peaks arising due to different chemical shifts. However, in some systems with many phase boundaries, such as porous media, the magnetic susceptibility difference at the interface between different phases gives rise to small 'background' magnetic field gradients, which have the same effect as local inhomogenieties in the magnetic field; these are discussed in more detail in Section 2.2.8. Chapter 2: Theory

2.2.6 The spin echo and stimulated echo

Apart from the FID, there are two other commonly encountered types of signal in spin- $\frac{1}{2}$ NMR experiments: the spin echo or Hahn echo (Hahn, 1950), and the stimulated echo. The spin echo consists of a 90° r.f. pulse followed by a 180° pulse, Figure 2.4(a), which reverses the effects of de-phasing due to T_2' effects and causes the spins to effectively refocus (as illustrated in Figure 2.5). One way of measuring the T_2 of a system is by using a CPMG pulse sequence (Carr & Purcell, 1954; Meiboom & Gill, 1958) which consists of a series of 180° r.f. pulses after the initial 90° pulse each separated by a time delay 2τ . Each 180° pulse produces an echo, the amplitude of which decays by pure T_2 relaxation. Unlike the Hahn echo, the CPMG pulse sequence suffers less due to displacement artefacts, such as those due to molecular diffusion. This is because the application of successive 180° pulses causes a time-averaging of the signal attenuation due to diffusion, which varies as $1 / n^2$, where *n* is the number of 180° pulses in the CPMG train, as shown by Carr & Purcell (1954). Thus, the CPMG pulse sequence is often preferred for T_2 measurements.



Figure 2.4 Basic NMR pulse sequences: (a) Hahn echo (b) Stimulated echo.

The stimulated echo is created by applying a series of three 90° r.f. pulses, Figure 2.4(b). The first 90° pulse tips the magnetisation vector \mathbf{M}_0 into the *x*-*y* plane and is followed by a second one applied after a time τ_1 , putting \mathbf{M}_0 parallel to the *z*-axis, where it undergoes T_1 relaxation for a time τ_2 until the application of the third pulse, which enables the formation of an echo after a further τ_1 (Figure 2.6). A homospoil gradient is usually applied between the second and third pulses to get rid of any leftover magnetisation in the transverse plane due to an imperfect pulse tip angle; this removes any remaining FID signal and also prevents the

formation of unwanted spin echoes. It is worth noting that the maximum amplitude of the stimulated echo signal is $M_0/2$, which is half that of the spin echo, due to projection of only half the transverse magnetization along the *z*-axis during the storage period. However, as the signal relaxation can be mainly due to T_1 effects (depending on the duration of τ_2), the stimulated echo does not necessarily lead to a lower signal-to-noise ratio compared to a similar experiment run with a spin-echo sequence. This point is discussed further in Section 2.2.8 in relation to diffusion experiments.



Figure 2.5 The spin echo: (a) Application of a 90° r.f. pulse at t = 0 tips the magnetisation vector from its equilibrium state (green) into the *x-y* plane (dark blue); (b) In the *x-y* plane, spins at different locations lose phase coherence due to field inhomogeneities and begin to precess at different frequencies, with faster spins shown in darker blue and slower spins in lighter blue. Application of a 180° r.f. pulse at $t = \tau$ rotates the magnetisation about the y-axis; (c) The order of the spins is now reversed, with the slower spins 'ahead' of the faster spins; (d) this leads to the spins regaining coherence or 'refocusing' at a point in time $t = 2\tau$.

2.2.7 Magnetic resonance imaging

The use of magnetic field gradients and k-space

Thus far, we have considered cases where the magnetic field experienced by the sample is static, barring inhomogeneities which are undesirable. However, we will now consider the effect of imposing a magnetic field gradient, **G**, across the sample in addition to the **B**₀ field. The application of such a gradient causes the Larmor frequency to vary spatially with position \mathbf{r} , according to

$$\omega(\mathbf{r}) = \gamma (B_0 + \mathbf{G} \cdot \mathbf{r}) . \qquad (2.14)$$

The NMR signal, dS, from a volume element, dV, is proportional to the local spin density $\rho(\mathbf{r})$ and can be written (neglecting the constant of proportionality) as:

$$dS (\mathbf{G}, t) = \rho(\mathbf{r}) \exp[i\gamma (B_0 + \mathbf{G} \cdot \mathbf{r})t] dV \quad .$$
(2.15)

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It should also be noted that Equation (2.15) assumes that the gradient strength G is sufficiently large that T_2 relaxation effects are slow compared to the de-phasing caused by the applied gradient and can therefore be neglected. Before detection, the signal is heterodyned with a reference frequency of γB_0 (i.e. the 'on-resonance' condition), which results in the removal of this frequency from the observed signal. Thus, for a constant magnetic field gradient **G**, and by representing the volume integral as a triple integral over $d\mathbf{r}$, the signal amplitude over the entire sample becomes:

$$S(t) = \int \int \int \rho(\mathbf{r}) \exp[i\gamma \mathbf{G} \cdot \mathbf{r}t] d\mathbf{r} .$$
(2.16)



Figure 2.6 The stimulated echo: (a) 90° r.f. pulse at t = 0 tips the magnetisation vector from its equilibrium state (green) into the x-y plane (dark blue); (b) In the x-y plane, spins at different locations begin to de-phase due to field inhomogeneities, with faster spins shown in darker blue and slower spins in lighter blue; (c) The second 90° r.f. pulse at $t = \tau_1$ rotates the spins into the negative z-axis where they undergo T_1 relaxation; (d) After a further time τ_2 another 90° pulse rotates the spins back to the x-y plane; (e) The spins refocus after a further time τ_1 . In the time between (c) and (d) a homospoil gradient is applied to get rid of stray magnetisation in the x-y plane owing to pulse imperfections.

At this point it is useful to define the reciprocal space vector \mathbf{k} , such that

$$\mathbf{k} = \frac{\gamma \mathbf{G}t}{2\pi} \,. \tag{2.17}$$

The '**k**-space' formalism was introduced by Mansfield & Grannell (1973) in order to help simplify the description of MRI experiments. Substituting for **k**, Equation (2.16) becomes:

$$S(\mathbf{k}) = \iiint \rho(\mathbf{r}) \exp[-i2\pi \mathbf{k} \cdot \mathbf{r}] d\mathbf{k}, \qquad (2.18)$$

which has the form of a Fourier transform. Therefore, it follows that the Fourier conjugate of Equation (2.18) gives the spin density distribution:

$$\rho(\mathbf{r}) = \iiint S(\mathbf{k}) \exp[-i2\pi \mathbf{k} \cdot \mathbf{r}] d\mathbf{k} .$$
(2.19)

Hence, by scanning and acquiring **k**-space data, an image of spin density may be reconstructed via a 1, 2, or 3D FT. It is possible to traverse **k**-space either by moving in time or by incrementing the applied gradient strength, as is evident from Equation (2.17). It is also important to note that a point in **k**-space does not correspond to a location in real space but contains information about a gradient strength and its corresponding Larmor frequency.

A common method used for sampling **k**-space is the 'spin-warp' method, whereby a single line of **k**-space is acquired in a linear raster. This is done by acquiring the signal (e.g. using a spin echo pulse sequence) during the application of a 'read gradient', **G**_{Read}. After the first 90° pulse, and before the application of a gradient, the spins are at the centre of **k**-space (i.e. $\mathbf{k} = 0$). The first application of the read gradient, is before the 180° pulse and shifts the spins to the leading (i.e. positive) edge of **k**-space (say, $k_{\text{Read}} = +\text{K}$). The 180° pulse then inverts the spins, via the centre of **k**-space, to k = -K. The second application of the read gradient, then allows data to be acquired for the entire line of **k**-space, as shown in Figure 2.7. Thus a 1D profile of spin density is obtained in the read direction. The use of a read gradient to sample **k**-space in this way is known as 'frequency encoding'. The field-of-view (FOV) in the frequency encoding direction is given by

$$FOV = \frac{2\pi}{\gamma G_{\text{Read}} t_{\text{d}}}.$$
(2.20)



Figure 2.7 (a) Pulse sequence for the acquisition of a 1D profile by the application of a read gradient. (b) Diagram showing the sampling trajectory in k-space. Data are acquired during step 3, as indicated by the blue arrow. (c) Cross section of a sample tube of water in the x-y plane; (d) Resulting 1D profile after application of G_{Read} in the *x*-direction.

To sample a second dimension of k-space a phase gradient GPhase can be applied in order to shift the data acquisition in k-space in the new direction, a process known as 'phase encoding'. The magnitude of GPhase is varied by ramping the gradient strength in increments of ΔG_{Phase} , thus enabling the acquisition of successive lines of k-space in a 'raster', or scanning pattern of parallel lines, Figure 2.8. The field-of-view in the phase direction is given by the inverse of the spacing between k-space points, which is determined by ΔG_{Phase} . However, a disadvantage of 2D spin-warp imaging is that data acquisition times may be long depending on the image resolution and the T_1 of the sample e.g. a typical 256 × 256 pixel image presented in this dissertation took approximately 1 h 40 min to acquire, with a recycle time of 3 s and 8 signal averages.



Figure 2.8 (a) Pulse sequence for 2D spin-warp imaging. (b) Diagram showing the sampling trajectory in k-space for the first phase encoding gradient (step 1). Data are acquired during step 3, as indicated by the blue arrow. Subsequent applications of the phase encoding gradient shift the acquisition up the k-space grid, as indicated by the small coloured arrows.

Selective excitation ('soft') r.f. pulses

So far, the pulse sequences discussed have used short, (typically of the order of tens of microseconds) non-selective, r.f. pulses which typically excite all the frequencies in a given sample. These are also known as 'hard' pulses. However, at times it is desirable to acquire spectral information from a given section of the sample, e.g. in the case of a 2D image; this is done through the use of longer duration, 'soft' r.f. pulses. In order to select a particular slice of the sample, a slice gradient, **G**_{Slice} is used to spatially encode the spins before selective excitation via a soft pulse. The position and thickness of the slice selected can be adjusted by altering the offset (resonant) frequency and duration of the soft pulse; a longer duration corresponds to a narrower frequency bandwidth. The soft pulses used for slice selection are typically refocusing (i.e. 180°) pulses applied after the initial 90° pulse. The durations of these soft pulses are typically a few hundred microseconds. Figure 2.9(a) shows an example of a spin echo with a 180° refocusing pulse. Figure 2.9(b) shows a 2D projection of a sample with two different slices selected at locations z_1 and z_2 along the axis sample, with slice thickness Δz ; these slices correspond to soft pulses of bandwidth $\Delta \omega$ at offset frequencies ω_1 and ω_2 , as shown in Figure 2.9(c).



Figure 2.9 (a) Spin echo with a soft 180° pulse used for slice selection. (b) 2D projection of a sample with slices of thickness Δz selected at different locations, shown in blue and red. (c) Plot of frequency vs. axial position - the dashed line corresponds to G_{Slice} and therefore the gives the offset frequencies ω_1 and ω_2 which correspond to the slice locations z_1 and z_2 .

Theoretically, the desired slice-selective pulse would correspond to a top hat (boxcar) function in the frequency domain, in order to excite a clearly defined region of the sample; the time domain soft pulse would then correspond to the sinc function, i.e. sin t/t. However, as the sinc function is infinite in the time domain, in practice it would have to be truncated. This truncation takes the form of a convolution of a sinc and a top hat function in the time domain, and hence produces undesirable side lobes in the frequency domain. Provided that these lobes are sufficiently small, these pulses may still be utilized without providing too great a source of error, and are thus still relatively extensively used. Another common choice for the soft pulse shape in the time domain is the Gaussian function, as its Fourier transform also results in a Gaussian, thereby giving a smooth excitation profile. In this case, the frequency bandwidth $\Delta \omega$ of the selected slice corresponds to the FWHM of the Gaussian pulse shape in the frequency domain. Other pulse shapes, e.g. hermite pulses, are used as well; for an overview of the subject of shaped pulses in NMR, the interested reader is directed to McDonald & Warren (1991).

Fast imaging techniques

As previously mentioned, the 2D spin-warp pulse sequence suffers from poor temporal resolution for most systems, and thus is generally suitable for steady-state systems or those that can be described by time-averaged properties such as turbulent flow. For observing dynamic phenomena, several 'fast' imaging techniques exist, such as FLASH, EPI and RARE. These techniques allow 2D image acquisitions typically in the range of milliseconds to a few

seconds, depending on the spatial resolution and amount of signal averaging used. In this thesis, the RARE (Rapid Acquisition with Relaxation Enhancement) imaging technique is used, and is discussed in more detail here.

The RARE imaging pulse sequence (Hennig et al., 1986) allows acquisition of multiple lines of **k**-space from a single excitation by using 180° refocusing r.f. pulses, in an analogous manner to a CPMG sequence, with phase encoding used for each echo. The number of times per excitation that the magnetisation is refocused is known as the RARE factor, N_{RARE} (typically between 1 and 64). As the 180° pulses refocuses chemical shift or magnetic susceptibility artefacts, the maximum value of N_{RARE} that can be used for a given sample (before unacceptable degradation in SNR) is limited by the pure T_2 of the species being imaged. The RARE pulse sequence is shown in Figure 2.10(a), along with the **k**-space sampling trajectory in Figure 2.10(b).



Figure 2.10 (a) Pulse sequence for 2D RARE imaging technique. (b) Diagram showing the sampling trajectory in k-space for the first phase encoding gradient (step 3). Data are acquired during step 4, as indicated by the purple arrow, followed by the phase unwinding gradient (step 5) that returns the magnetisation to the centre line of k-space prior to the next 180° refocusing pulse.

The read and phase directions are as in the spin-warp sequence; however there is an extra phase unwinding gradient after each acquisition which is of equal amplitude but opposite direction to the phase encoding gradient. This returns the magnetisation to the centre line of \mathbf{k} -space before each refocusing pulse such that the spin and stimulated echoes add coherently,

thereby increasing the SNR and preventing artefacts. In addition, unwanted signals are also suppressed by the use of soft r.f. pulses and homospoil gradients before and after the r.f. pulses, as the application of multiple r.f. pulses can cause undesired FIDs and echoes to develop. Due to the presence of both spin and stimulated echoes, the signal decay depends on T_1 and T_2 relaxation. This relaxation weighting can be desirable, as it may be exploited to enhance relaxation contrast in some cases. However, it can also mean that the RARE images are not quantitative, in terms of signal intensity being a simple function of spin density; in later chapters, we discuss how this limitation can be overcome. Practically, in 2D RARE, the r.f. pulse frequency can be incremented with each excitation to acquire data from other slices while the magnetisation in previously sampled slices is recovering; this allows the acquisition of several slices simultaneously and is known as 'multi-slice, multi-echo' (MSME) RARE. Lines in **k**-space are acquired in an alternating order and rearranged during processing, a process known as interleaving.

2.2.8 NMR velocimetry

One of the many advantages of NMR microscopy is its applicability to the measurement of translational motion, which includes both coherent motion (i.e. bulk flow) and incoherent motion (i.e. diffusion and dispersion). The systems considered in the work presented in this dissertation were measured under coherent flow conditions. The measurement of flow is mainly done using pulsed field gradient (PFG) NMR techniques (Stejskal & Tanner, 1965). In this experiment, two short gradient pulses of amplitude *g* and duration δ are applied to the sample, separated by a time interval Δ . Methods of NMR velocimetry which use PFG techniques are also known as phase contrast methods. Another technique for studying flowing systems using NMR is through time-of-flight (TOF) methods (e.g. Axel et al., 1986); however, as these methods are not used in this thesis they are not discussed here. A detailed review on both phase contrast and TOF methods can be found in Fukushima (1999).

The application of a gradient pulse **g** of duration δ imparts a spatially dependent phase shift, ϕ , to the spin of a nucleus at a position **r** within the sample thus:

$$\boldsymbol{\phi} = \gamma \delta \mathbf{g} \cdot \mathbf{r} \ . \tag{2.21}$$

After a time interval of Δ another gradient pulse of equal magnitude but opposite sign is applied. If the nucleus remains at position **r**, the magnetisation is entirely re-phased and there

is no net phase shift. However, if the system is undergoing translational motion and the same nucleus has moved to a new position \mathbf{r}' , the application of the second gradient pulse will cause a corresponding phase shift, $-\gamma \delta \mathbf{g} \cdot \mathbf{r}'$. An example of a basic PFG experiment is the pulsed-gradient spin echo (PGSE), Figure 2.11. In this pulse sequence, the negative sign is due to the effective inversion of the gradient by the 180° r.f. pulse. Hence the net phase shift will be

$$\phi_{\rm net} = \gamma \delta \mathbf{g} \cdot (\mathbf{r}' - \mathbf{r}) , \qquad (2.22)$$

where higher-order motion terms, such as those due to acceleration, have been ignored. The value of ϕ_{net} is thus proportional to the average velocity, *u*, in the direction of the applied gradient pulses, over the time interval Δ :

$$\phi_{\text{net}} = \gamma \delta \, g u \, \Delta \, . \tag{2.23}$$

It should be noted that so far we have assumed the applied gradient pulses are rectangular; in case of a non-rectangular pulse, the term δg should be substituted by the first moment of the gradient pulse. The two opposite gradient pulses used for motion encoding in this way are known as a bipolar pair.

Data acquisition in q-space and the displacement propagator

The NMR signal acquired at the centre of the echo after a bipolar gradient pair, $S(\mathbf{g})$, is normalised relative to the signal without gradients, S(0). This normalised signal, $E(\mathbf{g})$, represents an ensemble average of a phase term, $\exp[i\gamma\delta\mathbf{g}\cdot(\mathbf{r'}-\mathbf{r})]$, and is weighted by the spin density $\rho(\mathbf{r})$, as well as the conditional probability for a spin to move from \mathbf{r} to $\mathbf{r'}$ over the time interval Δ , $P(\mathbf{r} | \mathbf{r'}, \Delta)$, thus:

$$E(\mathbf{g}) = \int \rho(\mathbf{r}) \int P(\mathbf{r} | \mathbf{r}', \Delta) \exp[i\gamma \delta \mathbf{g} \cdot (\mathbf{r} - \mathbf{r}')] d\mathbf{r}' d\mathbf{r} . \qquad (2.24)$$

Defining a reciprocal space vector, **q**, and a dynamic displacement vector **R** such that $\mathbf{q} = \frac{\gamma \delta \mathbf{g}}{2\pi}$ and $\mathbf{R} = \mathbf{r}' - \mathbf{r}$, Equation (2.24) may be re-written as

$$E(\mathbf{q}) = \int \overline{P}(\mathbf{R}, \Delta) \exp(i2\pi \mathbf{q} \cdot \mathbf{R}) d\mathbf{R} , \qquad (2.25)$$

where

$$\overline{P}(\mathbf{R},\Delta) = \int \rho(\mathbf{r}) P(\mathbf{r} \mid \mathbf{r}',\Delta) d\mathbf{r} .$$
(2.26)

The term $\overline{P}(R,\Delta)$ is known as the displacement propagator, and is equivalent to the probability distribution of displacements averaged across the sample. It is clear from

Equation (2.25) that there is a Fourier relationship between $E(\mathbf{q})$ and $P(\mathbf{R},\Delta)$; the displacement propagator thus can be obtained by sampling in **q**-space and applying a Fourier transform to the acquired data. This concept is analogous to that of **k**-space in MRI, and similarly, **q**-space can be sampled by incrementing the value of g, as shown in Figure 2.11. The FOV of displacements is hence given by:

$$FOV = \frac{2\pi}{\gamma \delta g_{inc}},$$
(2.27)

where g_{inc} is the increment by which g is increased between acquisitions. Figure 2.12 shows examples of displacement propagators in a circular pipe for the case of pure self-diffusion and pure coherent laminar flow. The propagator for pure self-diffusion takes the form of a Gaussian distribution, thereby enabling the diffusion coefficient to be calculated from fitting to the echo signal attenuation data.



Figure 2.11 The PGSE pulse sequence. $\delta \ll \Delta$ by the narrow pulse approximation, which assumes that the gradient pulse is sufficiently short in duration that the spins do not undergo significant translational motion effects during its application.

Tanner (1970) proposed that for certain systems where T_1 is appreciably larger than T_2 , e.g., viscous liquids, plastic crystals, quadrupolar coupling systems, and systems with a large interfacial surface area, it would be more advantageous to use a stimulated echo instead of a spin echo, as the decay of the stimulated echo has T_1 rather than T_2 dependence (Section 2.2.6). The resulting pulse sequence is known as the pulsed field gradient stimulated spin echo (PFG SSE) or pulsed gradient stimulated echo (PGSTE), Figure 2.13. The stimulated echo would thus allow for measurements at longer observation times, Δ , which would be useful for studying the time-dependence of the effective diffusivity of spins, e.g. in

restricted geometries. Measuring at longer Δ would also allow for greater signal attenuation due to diffusion, e.g. in systems with low diffusivities and short T_2 or where gradient strength is limited (Burstein, 1996).



Figure 2.12. Displacement propagators in a circular pipe for: (a) pure self-diffusion (b) laminar flow occurring in the axial (z-)direction in the absence of self-diffusion. z_{max} is the point in (b) at which the maximum velocity occurs. Note the Gaussian and rectangular probability distributions in (a) and (b) respectively.



Figure 2.13 The PGSTE pulse sequence (Tanner, 1970).

In some types of heterogeneous systems (e.g. porous media or biological systems), background gradients due to susceptibility differences may be present, which cause attenuation in the echo signal and hence a decrease in the observed value of T_2 (Cotts et al., 1989). The use of pairs of bipolar gradient pulses either side of Δ cancels some of the effects of these field heterogeneities by removing the cross term between the background gradients and the applied gradient, as shown by Karlicek & Lowe (1980). This technique, commonly known as alternating pulse gradient stimulated echo or APGSTE, was implemented and further developed in the pulse sequences of Cotts et al. (1989), and is discussed in more detail in Chapter 3. The acquisition of **q**-space may also be combined with imaging in **k**-space in order to obtain spatially resolved propagators for each image pixel; however, this technique tends to be time-consuming. In the work presented in this dissertation, 1D PFG methods are used for **q**-space sampling and propagator reconstruction. 2D velocity images were obtained using the net phase-shift method, as outlined next.

Net phase-shift method

As Equation (2.23) shows, the net phase shift on the spins in a sample is proportional to the average velocity of the spins. However, the absolute value of the phase shift itself is arbitrary. Therefore in order to calculate the average velocity, two different flow gradient strengths are used, so that the incremental phase shift is

$$\phi_{\rm inc} = \gamma \delta g_{\rm inc} u \Delta , \qquad (2.28)$$

where the value of g_{inc} is known. By combining this method with a 2D imaging sequence such as the spin-warp method, Figure 2.8, the average coherent velocity in each image voxel may be determined by subtracting two flow-encoded images to produce a 2D phase-shift map. However, as the values of the phase shifts range between 0 and 2π , with $\phi + (2\pi)n$ being equivalent to ϕ (where *n* is a real integer), the gradient strengths and timings must be chosen so as to match the expected range of velocities in the system being measured. Obtaining phase shifts outside the desired range, i.e. $0 < \phi < 2\pi$, is known as 'fold-over' or aliasing.

In additional to the motion encoding bipolar pair, other gradients may be present, such as background gradients (e.g. in a porous medium sample) or imaging gradients, which can introduce errors into the value of the net phase-shift obtained. This can be corrected for retrospectively by acquiring an identical phase-shift map with no flow (a 'zero offset') and subtracting it from the original data.

2.2.9 The NMR spectrometer

A modern large NMR spectrometer, with imaging, consists of four main components: a permanent high-field magnet, a transmitter, a receiver and a computer. A schematic of the main sub-components is shown in Figure 2.14. A detailed discussion on NMR hardware is beyond the scope of this thesis; however, the interested reader is referred to Keeler (2005) and Callaghan (1993). Increasingly, smaller benchtop NMR systems, which are low-field and

often utilise permanent magnets are becoming more common due to their portability, lower cost and convenience.



Figure 2.14 Schematic of a modern NMR spectrometer. Here, the term ADC stands for 'Analogue to Digital Converter'.

Some of the common practical considerations to be faced when using NMR include:

- The sample holder or container must be made of a dielectric material (e.g. glass, ceramic, plastics or resin) that is invisible to the r.f. field.
- Ferromagnetic materials must not be used in or near the magnet as they may be attracted by the B_0 field. Similarly, samples containing ferromagnetic species often suffer from severe r.f. field distortions.
- Hardware limitations such as the power of the r.f. coil, the maximum strength and switching times of the gradients, and the duties imposed on the gradient and r.f. coils must be taken into account when designing experiments.

In the work presented in this dissertation, most of the NMR experiments were carried out using a Bruker BioSpin AV85 spectrometer equipped with a 2 T horizontal-bore superconducting magnet operating at a ¹H resonant frequency of 85.18 MHz, Figure 2.15. However, some experiments were also carried out using a Bruker AV400 spectrometer

equipped with a 9.4 T vertical-bore superconducting magnet operating at a ¹H resonant frequency of 400 MHz. The r.f. coils used for signal excitation/detection were of the birdcage type and both spectrometers were equipped with shielded gradient coils providing magnetic field gradients in the *x*-, *y*- and *z*- directions.



Figure 2.15 The Bruker BioSpin AV-85 horizontal bore NMR spectrometer.

2.3 Lattice-Boltzmann Simulations

This section provides a brief overview of the background theory relating to lattice Boltzmann (LB) hydrodynamic simulations. In particular, the LB simulation results presented in this dissertation used the single-relaxation time (SRT) lattice Bhatnagar-Gross-Krook (LBGK) method to simulate flow in porous media. For this purpose, the in-house code developed by Dr Farid Sani and Dr Simon Sullivan (Sullivan et al., 2005) was used.

2.3.1 Origins

The origins of the LB method can be traced back to the lattice gas automata (LGA) model, which was proposed by Frisch et al. (1986) as a simplified model for molecular dynamics. and was later extended (Frisch et al., 1987) to include a Boltzmann equation to describe the bulk behaviour of the fluid particles (Frisch et al., 1987; Prosperetti & Tryggvason, 2007). However, the LGA model suffered from several drawbacks such as large statistical noise, limited range of physical parameters, and difficulties in 3D implementation (Rothman & Zaleski, 2004); to overcome some of these difficulties, the LB method was proposed (McNamara & Zanetti, 1988; Higuera & Jimenez, 1989), which replaced the discrete particle model of LGA with a statistical description of the Boltzmann equation using particle distribution functions. This model was subsequently built upon, resulting in the well-known LGBK model (Qian et al., 1992; Chen et al., 1992), which is the most popular LB model due to its simplicity, despite being limited to relatively low Reynolds numbers. The original LBGK model was built on a single-relaxation time (SRT) approximation (Bhatnagar et al., 1954). The multiple-relaxation time (MRT) LB equation, also known as the generalised LB equation (GLBE), was developed later on by d' Humières (2002) and offered several improvements on its predecessor as well as improved numerical stability, although is more computationally expensive as a result.

The LB method has been successfully applied to simulate fluid flows in many different complex geometries; Raabe (2004) gives an overview for engineering applications. The application of LB to flow in porous media is discussed in Chapter 3.

2.3.2 SRT LB model

The single-relaxation time (SRT) LB model is mesoscopic, as it combines fluid dynamic properties at both the microscopic and macroscopic scales by tracking distribution functions, $f_i(\mathbf{x},t)$, which represent 'pseudo-particles' moving from node to node on an ordered lattice, where \mathbf{x} is the lattice location vector. The particle distribution functions move in direction *i* (*i* = 0, 1, ..., *n*), where *n* + 1 is the number of discrete particle velocities at each node (Chen & Doolen, 1998). Starting from an initial state, the LB distribution functions evolve by either

streaming (i.e. moving in direction *i*) or by collision. The effect of collision causes $f_i(\mathbf{x},t)$ to relax toward an equilibrium particle distribution $f_i^{eq}(\mathbf{x},t)$ (Qian et al., 1992) and this relaxation can be described by the lattice Boltzmann equation:

$$f_i(\mathbf{x} + \mathbf{c}_i, t+1) - f_i(\mathbf{x}, t) = \Omega_i(f_i(\mathbf{x}, t)), \qquad (2.29)$$

where each particle distribution function covers a distance $|\mathbf{c}_i|$ over each unit time-step, thus moving with velocity \mathbf{c}_i . The term $\Omega_i(f_i(\mathbf{x},t))$ is known as the collision operator and represents the rate of change of $f_i(\mathbf{x},t)$ caused by collisions. The rules governing the collisions are designed such that mass and momentum are conserved according to the continuity and Navier-Stokes equations (for an incompressible fluid):

$$\nabla \cdot \mathbf{u} = 0 \tag{2.30}$$

and

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho} \nabla P + \nu \nabla^2 \mathbf{u}, \qquad (2.31)$$

respectively. Underlying physical phenomena such as the viscous transfer of momentum and viscous dissipation are automatically determined by the action of the particle collision. Thus the LB method simplifies the computational steps required for the kinetic model such that the macroscopic time-averaged properties of microscopic phenomena obey Equations (2.30) and (2.31). This is in contrast to conventional computational fluid dynamics (CFD) techniques where the governing partial differential equations (PDEs) are solved numerically by transforming them into a system of approximating ordinary differential equations (ODEs) and integrating them numerically using finite difference methods. The rest of this section describes briefly the derivation of the LBGK equation from Equation (2.29), which is the fundamental equation in the simulation code used.

As stated previously, mass and momentum are conserved as the particles move from node to node, which is done using the following rules:

$$\sum_{i=1}^{m} \Omega_i = 0, \text{ and } \qquad \sum_{i=1}^{m} \mathbf{c}_i \Omega_i = 0.$$
(2.32)

Similarly, the fluid density and momentum density functions are defined as

$$\rho = \sum_{i=1}^{m} f_i(\mathbf{x}, t), \text{ and } \qquad \rho \mathbf{u} = \sum_{i=1}^{m} \mathbf{c}_i f_i(\mathbf{x}, t), \qquad (2.33)$$

respectively.

The lattice node spacing $\Delta \mathbf{x}$ and time-step Δt are small—of the order ε , where $\varepsilon \to 0$. Performing a Taylor expansion in space and time, the continuum form of Equation (2.29) can be obtained (Chen & Doolen, 1998), where $O(\varepsilon^2)$ terms have been ignored:

$$\frac{\partial f_i}{\partial t} + \mathbf{c}_i \cdot \nabla f_i + \varepsilon \left(\frac{1}{2} \mathbf{c}_i \mathbf{c}_i : \nabla \nabla f_i + \mathbf{c}_i \cdot \nabla \frac{\partial f_i}{\partial t} + \frac{1}{2} \frac{\partial^2 f_i}{\partial t^2} \right) = \frac{\Omega_i}{\varepsilon} .$$
(2.34)

Similarly, $f_i(\mathbf{x},t)$ can be expanded locally around $f_i^{eq}(\mathbf{x},t)$ to give

$$f_i(\mathbf{x},t) = f_i^{eq}(\mathbf{x},t) + \mathcal{E}f_i^{(neq)}(\mathbf{x},t), \qquad (2.35)$$

where depends on the macroscopic variables density and density momentum (Eq. (2.30)) and must satisfy the following constraints:

$$\sum_{i} f_{i}^{eq}(\mathbf{x},t) = \rho \text{, and} \qquad \sum_{i} \mathbf{c}_{i} f_{i}^{eq}(\mathbf{x},t) = \rho \mathbf{u} .$$
(2.36)

Similarly, the non-equilibrium function is defined as (again, neglecting $O(\varepsilon^2)$ terms):

$$f_i^{(neq)}(\mathbf{x},t) = f_i^{(1)}(\mathbf{x},t) + \varepsilon f_i^{(2)}(\mathbf{x},t) , \qquad (2.37)$$

and has the constraints

$$\sum_{i} f_{i}^{(k)}(\mathbf{x},t) = 0, \text{ and } \sum_{i} \mathbf{c}_{i} f_{i}^{(k)}(\mathbf{x},t) = 0, \qquad (2.38)$$

for both k = 1 and k = 2.

Inserting the expression for f_i from Equation (2.35) into Equation (2.29) and noting that as $\varepsilon \to 0$, $\Omega_i(f_i^{eq}) = 0$, allows the linearization of the collision operator thus:

$$\frac{\Omega_i(f_i(\mathbf{x},t))}{\varepsilon} = \frac{M_{ij}}{\varepsilon} (f_j(\mathbf{x},t) - f_j^{eq}(\mathbf{x},t)), \qquad (2.39)$$

where $M_{ij} \equiv \frac{\partial \Omega_i(f_i^{eq})}{\partial f_i}$ is the collision matrix (Higuera & Jimenez, 1989), which

determines the scattering rate between directions i and j. M_{ij} depends only on the angle between i and j and only takes a certain set of values. It must also obey the constraints

$$\sum_{i=1}^{m} M_{ij} = 0, \text{ and } \qquad \sum_{i=1}^{m} \mathbf{c}_i M_{ij} = 0, \qquad (2.40)$$

for momentum and mass conservation, respectively. In the SRT model, the local particle distribution is assumed to relax to equilibrium at the rate

$$M_{ij} = -\frac{1}{\tau} \delta_{ij} , \qquad (2.41)$$

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where τ is the LBGK relaxation parameter and δ_{ij} is the Kronecker delta function, defined as 1 (if i = j) or 0 (otherwise). Combining Equations (2.35), (2.39), (2.41), the LBGK collision term is obtained (Bhatnagar et al., 1954):

$$\frac{\Omega_i}{\varepsilon} = -\frac{1}{\tau} f_i^{(neq)} = -\frac{1}{\varepsilon \tau} (f_i^{(1)} + \varepsilon f_i^{(2)}), \qquad (2.42)$$

and hence the LBGK equation, which is the governing equation for motion in the lattice, is given by:

$$f_i(\mathbf{x} + \mathbf{c}_i, t+1) - f_i(\mathbf{x}, t) = -\frac{1}{\tau} (f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t)) .$$

$$(2.43)$$

Thus by collision, $f_i(\mathbf{x},t)$ relaxes towards $f_i^{eq}(\mathbf{x},t)$, with the LBGK relaxation parameter τ determining the viscosity of the simulated fluid. It can be shown (Chen & Doolen, 1998) that by performing a Chapman-Enskog expansion of $f_i^{eq}(\mathbf{x},t)$, the continuity and Navier-Stokes equations can be recovered. The Chapman-Enskog expansion is basically a multi-scale expansion (Frisch et al., 1987), by which macroscopic expressions can be obtained for mesoscopic systems such as LB by grouping the expanded terms in order of the different length- and time-scales. It is also through this expansion that the relationship between the lattice kinematic viscosity and the LBGK relaxation parameter can be derived:

$$v_{LB} = \frac{1}{3} \left(\tau - \frac{1}{2} \right), \tag{2.44}$$

which relates the viscosity (i.e. a bulk parameter of a fluid) to the inter-particle interactions experienced by it.

2.3.3 Model implementation

The SRT LB code used in this work to simulate the flow of an incompressible fluid is based on the method of He & Luo (1997), who proposed the following definition for $f_i^{eq}(\mathbf{x},t)$:

$$f_i^{eq}(n,\mathbf{u};\mathbf{x},t) = nA_i + n(B_i\mathbf{c}_i \cdot \mathbf{u} + C_i\mathbf{c}_i^2\mathbf{u}^2 + D_i\mathbf{u}^2), \qquad (2.45)$$

where **u** is the local fluid velocity, *n* is the local particle density, *n* is an arbitrary constant that can be considered as a measure of the mean particle number density, and A_i , B_i , C_i and D_i are constant coefficients which are only dependent on the lattice used. The local fluid velocity **u** and particle density *n* are given by

$$\mathbf{u}(\mathbf{x},t) = \frac{1}{n} \sum_{i} \mathbf{c}_{i} f_{i}(\mathbf{x},t)$$
(2.46)

and

$$n(\mathbf{x},t) = \sum_{i} f_i(\mathbf{x},t), \qquad (2.47)$$

respectively. The 'non-slip' boundary condition (i.e. u = 0) was used at the fluid-solid interface, as this condition is second-order accurate and relatively computationally inexpensive. In addition, all lattice nodes include a relaxation function with zero velocity, which does not stream but can be altered by collision; this is known as a 'rest channel' and improves the accuracy and stability of the numerical simulation, particularly at low viscosities (Sani, 2002).

In LB, the lattice used may be a 2D or 3D Cartesian grid; in the work presented in this dissertation, the 3D nineteen-speed (D3Q19) hydrodynamic lattice was used. The lattice speed refers to the number of possible directions in which a fluid particle may move. These are shown in Table 2.1 for the D3Q19 lattice. Figure 2.16 shows an illustration of the number of possible directions in which a particle at a particular node may move in a single time-step. It should also be noted that LB simulations are performed using dimensionless 'lattice units', which may be converted to real units by scaling with the appropriate length- and time-scales used, Δx and Δt , corresponding to the spatial resolution of the porous medium 'mask' used (as explained further in Chapter 3) and the real time duration of a single simulation time-step, respectively. For example, the lattice speed u_{LB} may be converted to a real speed u by multiplying by Δx and dividing by Δt . The values of u_{LB} for the D3Q19 lattice are given in Table 2.1, along with the values of the constants A, B, C and D from Equation (2.45).

In order to numerically simulate incompressible flow using the SRT LB model, the Mach number, M (which is defined as u / c_s , where c_s is the speed of sound), must be much lower than one in order to avoid errors due to spurious velocity terms, which are basically second derivatives of velocity squared terms in the Chapman-Enskog expansion (Sullivan, 2006). Therefore, in simulating real systems, where Δx depends on the resolution of the simulation geometry, Δt is adjusted to obtain suitably low Mach numbers. Furthermore, the real viscosity v is related to the lattice viscosity v_{LB} through the scaling factor $(\Delta x)^2 / \Delta t$ as well as through the LB relaxation parameter τ . Accordingly, the choice of Δx and Δt affects the stability, accuracy and rate of convergence of simulations. In the work presented in this thesis, the Mach numbers used were well within the required range, and τ was chosen as Chapter 2: Theory

equal to unity to reduce simulation error, as described by Sullivan (2006); hence, for a given simulation geometry the choice of Δt was determined solely by the kinematic viscosity of the fluids simulated (e.g. 1×10^{-6} m² s⁻¹ for water at 20 °C), according to the relationship:

$$\nu = \nu_{LB} \frac{(\Delta x)^2}{\Delta t} = \frac{1}{3} \left(\tau - \frac{1}{2} \right) \frac{(\Delta x)^2}{\Delta t} = \frac{1}{6} \frac{(\Delta x)^2}{\Delta t}.$$
(2.48)

Table 2.1 Possible directions for particle streaming from a node in the hydrodynamic D3Q19 lattice over a single time-step, along with the lattice speed and the values of the constants A, B, C and D associated with each direction.

Destination of jump	\mathcal{U}_{IB}	Number of	A, B, C, D
(from centre of cube)	(lattice units)	possible	
	(1400100 41110)	directions	
Edge of square	1	6	1/3, 0, 0, -1/2
Corner of square in plane	$\sqrt{2}$	12	1/18, 1/6, 1/4, -1/12
Rest node	0	1	1/36, 1/12, 1/8, -1/24



Figure 2.16 Schematic of the hydrodynamic D3Q19 lattice. Directions with lattice speeds of 1 and $\sqrt{2}$ are shown by the red and green arrows respectively. The rest node, with $u_{LB} = 0$ is shown by the red circle in the centre of the cube.

2.4 Flow in Porous Media

As mentioned in Chapter 1, gaining an understanding of CO_2 pore interactions in porous media, particularly in the presence of two or more immiscible fluid phases, is important in order to be able to predict the long-term behaviour of CO_2 in the sub-surface. In this section therefore, a brief introduction to flow in porous media is given.

The fraction of the bulk volume of a porous medium that is occupied by pore or void space is known as the porosity, ϕ . This concept may be extended further to describe the 'effective' porosity ϕ_{eff} as the void space that forms a continuous phase so that there are no 'dead-end' zones. For the randomly packed glass ballotini samples used in the work described in this report, it is safely assumed that $\phi = \phi_{\text{eff}}$. Another macroscopic pore structure parameter is the permeability, *k*, which is a measure of the 'conductivity' of a porous medium to fluid flow. Permeability is defined by Darcy's law which applies for slow, unidirectional flow and is given by (Dullien, 1992):

$$Q = \frac{kA\Delta P}{\mu L},\tag{2.49}$$

for single-phase flow, where Q is the volumetric flow rate, A is the total cross-sectional area, μ is the dynamic viscosity and ΔP is the pressure drop across a system of length L. All the fluids used in this study are Newtonian, and in settings for which μ is a constant. The superficial fluid velocity, u, is defined as u = Q / A, and the average pore velocity, u_p , is defined as $u_p = u / \phi$.

2.4.1 Capillarity and immiscible liquids

In the case of two-phase immiscible fluid flow, an interfacial tension between the two phases, σ_{ij} gives rise to capillary pressure, which, along with hydrostatic pressure and gravitational forces can alter the local mechanical equilibrium of a system and thus act as a retarding force for penetration of the non-wetting phase into the a pore (Dullien, 1992). The capillary pressure P_c can be expressed as the difference in pressure between the two fluid phases i.e.

$$P_c = P_i - P_j, \tag{2.50}$$

where the subscripts i and j denote each phase. Consider a smooth, non-spherical, curved surface between two immiscible liquids. Two lines AB and CD may be drawn on the surface

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passing through a particular point, say S, with radii of curvature r_1 and r_2 respectively (Figure 2.17). Both r_1 and r_2 lie in planes which are orthogonal to each other and to the plane which is tangential to S. The mean radius of curvature, r_m is therefore:

$$\frac{1}{r_{\rm m}} = \frac{1}{2} \left[\frac{1}{r_1} + \frac{1}{r_2} \right].$$
(2.51)



Figure 2.17 Capillary equilibrium for an arbitrary point S on a smooth fluid surface. The radii of curvature for the orthogonal lines AB and CD are r_1 and r_2 , respectively. The line OS represents the intersection between the planes passing through AB and BC.

By performing a force balance across the interface between the two liquids, the details of which can be found in Dullien (1992), it is possible to derive Laplace's equation for the capillary pressure P_c as a function of σ_{ij} and r_m thus:

$$P_{\rm c} = \frac{2\sigma_{ij}}{r_{\rm m}} \,. \tag{2.52}$$

In immiscible fluid flow another parameter that must be taken into account is the wettability of a fluid. This is defined as the fluid's affinity for solid surfaces. In the case of two-phase flow, the fluid with greater affinity is considered the wetting fluid; the other is then the nonwetting fluid. One common way of describing the wettability of a fluid is through the contact angle, θ , between the liquid/liquid interface and the solid surface. This is illustrated in Figure 2.18. For a drop of fluid resting on a surface, the smaller the value of θ the more wetting the fluid is considered to be In general, a fluid is said to be non-wetting if $\theta > 90^\circ$. For $\theta = 0$ the fluid would be considered 'perfectly wetting'. However, Brown & Fatt (1956) argued that in the case of reservoir rock the concept of a contact angle is not representative due to the complex surface chemistry of the rock, which is composed of many different minerals. For the special case of flow in a cylindrical conduit, it can be shown using simple trigonometry that the new mean radius of curvature, $r_{\rm m}'$, is given by $r_{\rm m}' = r_{\rm m} / \cos\theta$.



Figure 2.18 Profile of a (a) non-wetting and (b) wetting drop of one fluid immersed in another and resting on a flat surface. The interface between the two fluids is shown in blue and the contact angle θ is indicated for both cases.

In two-phase flow in porous media it is useful also to define the concept of relative permeability k_{ri} . This may then be used to modify Darcy's law to take into account two-phase flow, as given by:

$$u_i = \frac{kk_{\rm ri}}{\mu} \frac{\Delta P}{L}, \qquad (2.53)$$

where u_i is the superficial velocity of phase *i*. The value of k_{ri} is a function of the relative phase saturation S_i , which is the fraction of the total pore space occupied by phase *i*, and the capillary pressure P_c . This relationship ($S_i - k_{ri} - P_c$) is the basis of the coreflood analysis shown in Section 5.3.1. In unsteady-state two-phase flow, one fluid usually displaces the other, with capillary forces resulting in a wetting fluid spontaneously displacing a nonwetting fluid from the pore space of the porous medium – a process known as imbibition. The reverse process to imbibition is drainage, whereby a non-wetting fluid displaces a wetting fluid; in this case, capillary forces resist such a displacement and so an external force must be applied which is greater than the capillary force. In steady-state two-phase flow, all macroscopic parameters, including the relative phase saturations, are invariant with time. The two major conceptions of this steady state flow are known as 'channel flow' and 'funicular flow'. In the former, individual pores are channels that are exclusively occupied by either one of the two liquids, with the non-wetting phase preferentially occupying the larger pores. In the latter, the entire surface area of the pores is covered by a film of the wetting phase, with the non-wetting phase present in the centres of the pores it occupies. In most porous systems, a combination of the two effects is present (Dullien, 1992).

One of the main entrapment methods of CO_2 in porous media considered in this dissertation is capillary trapping. This involves the formation of blobs (known as 'ganglia') of the nonwetting phase by capillary forces. At the interface between the two immiscible fluids, the ganglia experience capillary forces that resist their transport through narrow pore necks. Where this net capillary force from all fluid-fluid interfaces exceeds or equals the viscous forces imposed by superficial flow of the surrounding wetting fluid, the ganglia are trapped in the pore space of the porous medium, as illustrated in Figure 2.19. If there is a density difference between the two fluids, this may also affect the stability of the ganglia; in the case of a less dense non-wetting fluid therefore, buoyancy forces will act vertically and thus will add on to the viscous forces if the superficial flow direction is also vertical.



Figure 2.19 Schematic of a mono-disperse bead packing (grey) with a CO₂ ganglion (shown in white) trapped in the continuous water phase (blue). The red and green arrows show the different viscous and capillary forces acting on the ganglion, respectively. Flow direction is indicated by the black arrow.

2.4.2 Dimensionless description of flow processes

The Reynolds number, Re, is a dimensionless group for fluid motion relative to a surface which represents the ratio of inertial to viscous forces and is given by:

$$\operatorname{Re} = \frac{\rho u L}{\mu}, \qquad (2.54)$$

where L is a characteristic length scale of the system under consideration. Alternatively, for flow in packed bed of particles or fibres, the 'particle' Reynolds number, Re_p, may be defined as (Dullien, 1992):

$$\operatorname{Re}_{p} = \frac{\rho u d_{p}}{\mu}, \qquad (2.55)$$

where d_p is the average particle or fibre diameter. At low Re (<< 1) therefore, viscous forces dominate, in what is known as the 'creeping flow' regime.

For immiscible fluids, the ratio of viscous to capillary forces for a particular fluid is given by the Capillary number, Ca:

$$Ca = \frac{u_i \mu_i}{\sigma_{ij}},$$
(2.56)

In addition, if the density of the two fluids is different, then buoyancy effects can also be significant. This is taken into account by the Bond number, Bo, which represents the ratio of buoyancy to capillary forces thus:

$$Bo = \frac{\Delta \rho g L^2}{\sigma_{ij}}, \qquad (2.57)$$

where $\Delta \rho$ is the density difference between the two fluids, g is the acceleration due to gravity, L is a characteristic length scale and σ is the interfacial tension.

2.4.3 Dispersion

The preceding section discusses the presence of two immiscible fluids flowing through the pore space; in such systems the two fluids tend to flow in distinct channels and maintain their own identities. However, this is not the case in miscible flow, either for a single fluid phase or two completely miscible fluids, where it is possible for a fluid to be displaced completely from the pores (Dullien, 1992). This mixing process in miscible flow is known as dispersion.

A very brief introduction is given to dispersion here; for more details the interested reader is directed to Bear (1988).

Fluid molecules flowing within a porous medium will experience an irreversible spreading as they flow, resulting in a distribution of transit times on a macroscopic scale. This spreading, or dispersion, can occur due to both molecular self-diffusion and bulk advection. Consider for example streamlines, which are curves showing the direction that fluid molecules under advection will take. In laminar flow in the absence of self-diffusion, the different streamlines are parallel to one another and do not intersect. However, when diffusion is introduced, radial (i.e. transverse to the bulk flow direction) mixing occurs, which results in the fluid moving from one streamline to another; this is also known as 'Taylor dispersion' (Taylor, 1953). For miscible fluids, this process can be described by a Fickian dispersion model, which implies that mass transport is proportional to the concentration gradient, and is thereby analogous to diffusion (with the dispersion coefficient or dispersivity, D, being dependent on the self-diffusion coefficient of the fluid, D_0 , as well as on the advective flow velocity and the geometry of the porous medium). A useful dimensionless group for characterising dispersion, therefore, is the Péclet number, Pe, which represents the ratio of advective and diffusive effects, and is given for a packed bed by:

$$\operatorname{Pe} = \frac{u_p d_p}{D_0},\tag{2.58}$$

where u_p is the mean pore velocity, d_p is the average particle diameter and D_0 is the selfdiffusion coefficient. At high values of Pe (~10²) therefore, mechanical dispersion dominates, although there is always some contribution of self-diffusion through Taylor dispersion even at high Pe and long Δ (Saffman, 1959).

Another way in which diffusion may cause dispersion is by moving molecules in regions of effectively zero velocity (so-called 'holdup zones') back into the bulk flow. However, in the case of a packing of solid beads (i.e. where the beads themselves are impermeable to the solute), the contribution of holdup to the flow dispersion is negligible (Koch & Brady, 1985). The third type of dispersion occurs due to bulk advection and is known as mechanical dispersion. This arises due to the splitting and recombining of streamlines due to interactions with the solid surface and thus is influenced by the pore structure of the medium under consideration. The streamlines thus split produce a stochastic velocity field due to their

different tortuosities; the resulting dispersion occurs in both the superficial flow (axial) and transverse (radial) directions, although the magnitude of the dispersion will be greater in the superficial flow direction. At long observation times, $\Delta \rightarrow \infty$, the axial dispersion coefficient tends to an asymptotic value, which results in the probability distribution of displacements (i.e. the average propagator) taking on a Gaussian shape, as at long observation times all the fluid molecules will sample the entire pore space (Seymour & Callaghan, 1997).

2.4.4 Pore thinning algorithm

In some of the simulation work presented in this thesis, a 'pore thinning algorithm' was used to divide the pore space of 3D images of different porous media into discrete pores. This algorithm is a variant of morphological thinning, a technique commonly used in image analysis for reducing an image down to a skeleton. Morphological thinning works by subjecting the porous medium image to 'erosion' i.e. adding solid volume elements (voxels) to the surface of solid walls, thereby retaining the connectivity, and hence topology, of the pore space. This method enables various statistics such as pore size distribution, surface-tovolume ratio and coordination number to be obtained from the partitioned data. Moreover, the generalised definition of a pore used in the algorithm makes the method valid for any fully reconstructed image of a 3D porous medium. Such an approach was used by Thovert et al. (1993) to characterise the pore space of a simulated porous medium. The morphological thinning method was subsequently modified by Baldwin et al. (1996) and successfully applied to 3D images of real porous media; it is this modified algorithm which was used in the work presented here. The following paragraphs present a brief overview of the algorithm. For a more detailed description, the interested reader is referred to Baldwin et al. (1996) and Gladden & Alexander (1996).

In the pore thinning algorithm, an individual pore is defined as a section of the pore space which is bound by solid surfaces and planes erected through local minima in hydraulic radius (Dullien, 1992); these minima are commonly referred to as pore 'throats' or 'necks'. The requirement that the pore space remain connected, as used in other morphological thinning techniques, is done away with; hence, the erosion process is carried out in layers, with those regions of the pore space where a minimum hydraulic radius is present being completely eroded faster than the surrounding regions. In this way, the individual pores may be identified and thus partitioned based on the local maxima in pore thinning level.

Figure 2.20 shows an example of the pore thinning algorithm applied to a 3D image of a random spherical bead packing, obtained using MRI. Before the algorithm can be applied the 3D image must be binary-gated, a process whereby 'solid' voxels are assigned a value of 0 and 'void' (or pore space) voxels are assigned a value of 1. A transverse slice extracted from the binary-gated 3D image is shown in Figure 2.20(a); a small section of this slice, shown in Figure 2.20(b), is chosen here for demonstrating the algorithm. The first part of the algorithm involves iteratively performing erosion, or thinning, of the pore space whereby surface voxels (i.e. those void voxels which have one or more faces—out of a maximum of 6—in contact with a solid voxel) are assigned a value corresponding to the iteration number of the process and are treated as solid voxels in all subsequent iterations. This process continues until all such surface voxels are eroded. Figure 2.20(c) shows the section of the 3D image as chosen in Figure 2.20(b), with the different thinning layers indicated by different colours and labelled with the corresponding iteration number.

In the second part of the algorithm, pores in the fully thinned image are identified based on local maxima in the thinning value. This process, like the first part of the algorithm, is also iterative, and proceeds as follows: void voxels at the maximum thinning level are allocated as pores and given a specific identifier number, one for each discrete grouping of voxels, for which connectivity is determined by the presence of a common corner. This condition was used in order to avoid false allocation of multiple pores in the limiting case of a straight line of void voxels at 45° to each of the image axes. The procedure is then repeated for the next highest thinning level, with voxels at this value given the same pore identifier number as the already allocated voxels to which they are connected, and so on until all the voxels are allocated to pores. In the example shown in Figure 2.20(c), four examples of local maxima can be seen; Figure 2.20(d) shows the resultant partitioning of the void space into pores. It is evident from this process that pore necks correspond to local minima in hydraulic radius, which meets the definition of a pore stated earlier.



Figure 2.20 Example of the application of the pore thinning algorithm: (a) shows a transverse slice through a binary-gated 3D image of a random spherical bead packing; (b) shows a close of up of the region highlighted by the red box in (a); (c) shows the erosion process applied to the image in (b), with the different coloured regions corresponding to thinned layers of the void space, shown labelled along with the corresponding iteration number; (d) shows the same image after the pore allocation stage of the algorithm, with the different pores indicated by different colours.

2.5 References

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3 Single Phase and Carbonated Brine Flow in Porous Media

3.1 Introduction

In this chapter, we aim to study mainly single phase flow in porous media, with a view to understanding the transport of water in underground rock formations such as aquifers. We then consider the flow of CO_2 supersaturated brine, leading to capillary or residual trapping of CO_2 in the pore space as ganglia. Some of the experimental techniques and data analysis methods introduced in this chapter are used subsequently in later chapters.

The work presented here is as follows: we acquired experimental single-phase pulsed field gradient nuclear magnetic resonance (PFG NMR) displacement propagators for flow through both a model porous medium (packed bed of 100 µm glass ballotini) and a Bentheimer sandstone core plug. These propagators were then compared quantitatively with corresponding lattice Boltzmann (LB) simulations. The simulated propagators were obtained through the application of a directed random walk (DRW) algorithm to 3D velocity profiles obtained by conducting LB simulations on scaled 3D reconstructions of the porous media, otherwise known as masks. This method is the same, essentially, as that employed by Manz et al. (1999), where further details of the methodology can be sourced. Subsequently, this simulation methodology has been used extensively in the literature in this capacity (Mantle et al., 2001; Harris et al., 2005; Creber et al., 2009), and features frequent favourable quantitative comparisons of simulated displacement propagators against corresponding experimental results. We showed that the simulated propagators give good agreement in general with the experimental results, and the discrepancies which occurred are also discussed.

Finally, we created residual CO_2 in the form of isolated ganglia by flowing carbonated brine through the model porous medium; we then applied various NMR techniques to in order to characterise the CO_2 capillary trapping. The NMR techniques used include both imaging of the water phase in the pore space and propagator measurements to monitor the influence of entrapped CO_2 on water flow characteristics. The acquired NMR propagators were then compared to LB simulations applied to various CO_2 entrapment scenarios. In this manner we sought to investigate the pore morphology in which CO_2 becomes entrapped, and more specifically determine whether the CO_2 ganglia are entrapped preferentially in small pores (which provide more potential bubble nucleation sites, larger local pressure drops per unit length in general encouraging CO_2 ganglia formation and typically smaller pore necks providing larger capillary forces for trapping) or larger pores (which the non-wetting CO_2 will occupy preferentially occupy due to wettability effects). The use of such NMR techniques is essential as the porous medium used was opaque and did not permit direct imaging of the CO_2 ganglia using optical techniques.

3.2 Background

NMR allows water transport to be probed non-invasively in optically opaque systems. NMR offers several advantages over the traditional bulk measurements referred to in Chapter 1, including acquiring signal directly from the moving water nuclei without the need to inject tracer material, and the ability to observe the relative contribution of diffusion and advection to transport over different length and time scales. In particular, NMR pulsed field gradient (PFG) techniques (Stejskal & Tanner, 1965) now comprise a standard set of methods for observing molecular self-diffusion in both bulk liquids and saturated porous media (Stallmach & Kärger, 1999).

One of the applications of PFG NMR is to obtain a displacement, or flow, propagator (Karger & Heink, 1983; Mitra et al., 1992): a probability distribution of molecular displacements averaged across the sample over a given time interval, for systems undergoing advective flow. Flow propagators have been used to quantify single-phase flow in porous media, with most studies focusing on the Stokes' regime of water flowing through glass bead packs (Lebon et al., 1997; Codd & Altobelli, 2003; Britton et al., 2004; Scheven et al., 2004; Akpa et al., 2007) as a proxy for reservoir rock or chemical reactors. Most of the aforementioned studies were done using ¹H NMR, however Akpa et al. (2007) took advantage of the longer T_1 relaxation time of the ¹³C nucleus (which allows for longer transport observation timescales, Δ , to be probed) and used both ¹H and ¹³C NMR to visualise the flow of methanol through a packed bed of glass beads.

Several studies have also focused on water transport in rock core-plugs (e.g. Packer et al., 1998; Johns et al., 2003; Scheven et al., 2005a; Singer et al., 2006; Mitchell et al., 2008b). Packer et al. (1998) performed propagator measurements of single- and two-phase (immiscible liquid) flow in Fontainebleau sandstone. Johns et al. (2003) obtained propagators of a brine solution flowing through a Bentheimer sandstone rock core treated with a polyacrylamide polymer solution in order to investigate how the polymer treatment affects the permeability of the rock. Verganelakis et al. (2005) and Scheven et al. (2005a) measured aqueous phase propagators at different flowrates through both Bentheimer sandstone and Portland carbonate rock cores, with pore spacing described as "heterogeneous" and "very heterogeneous" respectively. In addition, Scheven (2005) showed that propagator measurements may be made outside of an NMR apparatus in the presence of a stray magnetic field using a fixed-field gradient (FFG) technique which would have applications in such areas as well-logging or industrial flow monitoring. More recently, other techniques have been developed to improve upon the standard PFG NMR pulse sequences in porous media, as reviewed by Mitchell & Johns (2009). For example, Buckley et al. (2003) used a pulse sequence, DiffTrain, which dramatically reduced the time taken to acquire propagator measurements but gave results which were identical to those obtained using the conventional APGSTE pulse sequence. Mitchell et al. (2008a) also used 2D NMR correlations of Displacement- T_2 and T_1 - T_2 in order to remove the relaxation time weighting from displacement propagators of flow in porous rocks. Such techniques had previously been applied by Britton et al. (2004) to correct propagators measured for flow in bead packs.

However, despite the advantages of the flow propagator, the measurement is limited to studying advection over the sample length that will fit within the confines of the NMR magnet geometry (typically, less than 100 mm). Therefore, to upscale the measured flow properties to the reservoir-scale, we must turn to reservoir simulators. To predict macroscopic flow across reservoirs reliably, it is first necessary to understand transport observed on the micro-scale. Here, we are concerned with computational methods of modelling flow phenomena that can be compared against the experimental NMR flow propagator measurements. Two approaches for modelling fluid flow in porous media at the pore scale used widely at present are lattice-Boltzmann (LB) and pore network (PN) simulations. In this work, we consider the former; however, a detailed comparison between the two approaches can be found in Hussain et al. (2013).

LB methods utilise a realistic representation of the porous material and are often preferred because of their relatively straight-forward implementation for simulating flow in heterogeneous media (Ferreol & Rothman, 1995). LB is, however, computationally expensive and limited in terms of the domain (sample) size over which flow can be simulated. NMR flow propagators have been used previously to validate LB results for flow through porous media, with favourable quantitative comparisons obtained between experimental and simulated propagators (Maier et al., 1998; Manz et al., 1999; Mantle et al., 2001; Johns et al., 2003; Harris et al., 2005; Creber et al., 2009; Hussain et al., 2011).

3.3 Experimental Methodology

3.3.1 Low-order moment analysis

To provide a quantitative analysis of the displacement probability distribution (the propagator), it is usual to calculate the low-order moments, specifically the first, second, and third order moments, being approximately equivalent to the mean displacement $\langle \zeta \rangle$, the variance σ^2 , and the adjusted skewness γ^3 , respectively.

The quantitative nature of the NMR flow propagator measurement is impaired by longitudinal T_1 and transverse T_2 spin relaxation. Relaxation is enhanced primarily through two mechanisms for liquids flowing in porous media: spins interacting with the solid boundaries will undergo enhanced relaxation due either to modified molecular mobility on adsorption at the surface or proton-electron interactions between the ¹H and paramagnetic species on the pore wall, such as iron bearing clays. Spins moving through a magnetic field gradient induced in pores by the magnetic susceptibility contrast between the solid and liquid will also experience enhanced relaxation. Accordingly, slow-moving (stagnant) and fast-moving (flowing) spins will exhibit relaxation to different extents, and so the relaxation weighting will vary across the displacement probability distribution. Scheven et al. (2004) proposed a post-processing correction to account for the relaxation of stagnant spins. First, the ratio of observed to predicted displacement $\theta = \langle \zeta \rangle / \langle \zeta \rangle_0$ is obtained using the predicted mean displacement $\langle \zeta \rangle_0 = v\Delta$ where v is the mean pore velocity. A Dirac delta function $\delta_{dd}(\zeta)$

of amplitude $(1 - \theta^{-1})$ is then added to $\theta^{-1}P(\zeta, \Delta)$. Overall, the 'corrected' probability distribution, where relaxation-corrected terms are denoted by a prime ('), becomes

$$P(\zeta, \Delta) = (1 - \theta^{-1}) \delta_{dd}(\zeta) + \theta^{-1} P(\zeta, \Delta).$$
^(3.1)

The second and third moments are corrected in a similar way according to

$$(\sigma')^2 = \frac{\sigma^2}{\theta} + \langle \zeta \rangle^2 \frac{\theta - 1}{\theta}$$
(3.2)

and

$$(\gamma')^{3} = \frac{\gamma^{3}}{\theta} + 3\langle \zeta \rangle \sigma^{2} \frac{\theta - 1}{\theta} + \langle \zeta \rangle^{3} \frac{(\theta - 1)(\theta - 2)}{\theta^{3}}.$$
(3.3)

As this correction takes into account signal loss from stagnant spins, the corrected moments are therefore an over-estimate of the true values, which are obtainable through careful and time-consuming determination of T_1 and T_2 as a function of ζ (Mitchell et al., 2008a). However, the post-processing correction is rapid and easy to implement, and provides an upper bound to the moments, in contrast to the lower bound obtained directly from the measured probability distribution. It should be noted however, that at low mean displacements, experimental observation of propagators in rock cores can lead to values of θ which are less than 1, as shown by Waggoner & Fukushima (1996). This indicates that at longer observation times there is preferential relaxation of stagnant spins, assuming a constant velocity. This effect is modulated by exchange between the two populations (i.e. stagnant and flowing spins, which will increase with observation time and also depends heavily on the pore morphology; thus, this correction is not valid for those observation times where the expected mean displacement exceeds that measured using NMR.

3.3.2 Experimental setup

The model porous medium used in these experiments comprised a water-saturated bed of borosilicate glass beads (ballotini) of $100 \pm 20 \,\mu\text{m}$ diameter packed randomly in a cylindrical Perspex column of length 69 mm and internal diameter 37 mm (a schematic of which is shown in Figure 3.1). The bead size was chosen as it gives a pore size similar to that of high-permeability sandstone rock (average pore throat diameter of 43 μ m) (Mitchell et al., 2010). Borosilicate glass ballotini were used as they exhibit smaller background magnetic field gradients due to magnetic susceptibility differences between solid surfaces and liquid, as

compared to soda lime glass. The porosity, ϕ , of the packing was determined gravimetrically to be 0.385 ± 0.005. To prevent air bubbles forming in the column, the ballotini were poured into the column whilst it was fully submerged in deionised water. The NMR experiments detect the water in the pore space directly and no signal is obtained from the glass ballotini or container.

The bead pack was connected to a flow rig consisting of two Teledyne ISCO model 260D syringe pumps to provide continuous flow when required, see Figure 3.2. Two different solutions were pumped through at room temperature: 'ordinary brine' (pH 8.0) consisting of a 2 wt % KCl aqueous solution and 'carbonated brine' (pH 3.6). The pH was measured using a Corning pH meter. Brine was used (as opposed to deionised water) as it more accurately reflects the conditions in geological saline aquifers; in addition, KCl brine also prevents osmotic swelling of the clay content in Bentheimer sandstone [mitchell2008determining]. From CO₂ solubility data (Lewis, 2004), the saturation concentration of CO₂ in water under room conditions is 0.33 wt%. Using Henry's law and the pH data above, the concentration of CO₂ in the carbonated brine was estimated to be 0.65 wt% giving a degree of super-saturation of approximately 2. It is acknowledged that under typical geological reservoir conditions however, the solubility of CO₂ ranges between 2–12 wt% depending on the temperature, pressure and salinity of the formation waters (Bachu & Adams, 2003).

The rock core experiments were conducted on a cylindrical plug of Bentheimer sandstone (length 69 mm; diameter 38 mm). Bentheimer sandstone was chosen for this study because of its favourable NMR response arising from its low clay content (Singer et al., 2006; Mitchell et al., 2008a, 2008b). Bentheimer is a 'massive' sandstone with large grains, a high gas permeability of $\kappa \approx 3 \times 10^{-12} \text{ m}^2$, and a porosity of $\phi = 21.4$ %, as measured by Ether Sham at the MRRC from a calibrated NMR signal intensity. The plug was held in an ErgoTech PEEK core holder with a radial confining pressure of 25 bar, applied via a ¹H NMR-transparent perfluorinated oil (3M Fluorinert FC-43), Figure 3.3. The confining pressure was sufficient to prevent brine bypassing the rock. This sandstone has a mean pore throat diameter of $d = 43 \,\mu\text{m}$, obtained from mercury intrusion porosimetry (MIP) (Mitchell et al., 2010). The plug was saturated with 2 wt% KCl brine to prevent osmotic swelling of the clays. Ordinary brine was passed through the sandstone using the setup shown in Figure 3.2.



Figure 3.1 (a) Schematic of the Perspex flow cell used in NMR experiments (b) Photograph of the cell, packed with 100 µm ballotini.



Figure 3.2 Experimental setup for pumping fluids through the porous media samples. The use of two pumps enables continuous flow via a refill-pump switch mechanism.

3.3.3 NMR measurements

All NMR measurements were performed using a Bruker BioSpin AV85 spectrometer equipped with a 2 T horizontal-bore superconducting magnet, operating at a ¹H resonant frequency of 85.18 MHz. A birdcage radio frequency (r.f.) coil of 55 mm inner diameter and 204 mm length was used for signal excitation/detection. PFG NMR was used to acquire displacement propagators using both a standard APGSTE (alternating pulsed gradient stimulated echo) pulse sequence based on the '13 interval' Cotts pulse sequence (Cotts et al., 1989) and a modified version of the APGSTE sequence incorporating a 180° soft r.f. pulse for slice selection along the axis of the sample, see Figure 3.4(a) and (b), respectively.

The APGSTE sequence was chosen as it minimises the effect of background gradients arising from susceptibility differences between the fluids and the solid matrix. Slice selection was added to the sequence in order to eliminate any signal contribution from the entry and exit regions of the column and in order to select a region of the sample with near uniform CO₂ entrapment to allow for an effective comparison with the simulations.

Model porous medium

1D spin-echo profiles were acquired along the sample in the *z*- (axial) direction, at a spatial resolution of 0.469 mm and a total acquisition time of 12 s. 2D spin-echo images in the *x-y* (transverse) plane of the sample were acquired with a data matrix size of 256×256 points (voxels) for a field of view of 40 mm × 40 mm, thereby giving a pixel resolution of 156 µm. The slice thickness used was 2 mm and the Recycle Time (RT) used for imaging was 5 s resulting in a total image acquisition time of 1 h 25 min. 2D Images were acquired at several locations along the axis of the sample.



Figure 3.3 (a) Schematic of the PEEK rock core holder used for NMR experiments. (b) Photograph of the core holder.



Figure 3.4 (a) APGSTE pulse sequence for displacement propagator acquisition; (b) Modified APGSTE pulse sequence with a 180° Gaussian soft r.f. pulse used for slice-selective signal acquisition, instead of the usual hard 180° r.f. pulse. The NMR signal is acquired at the centre of each echo.

Bentheimer sandstone

Flow propagators were acquired from a selective-slice of thickness 14 mm, centred on the axial midpoint of the sample. The magnetic field gradient strength ranged from $g_z = -10$ to 10 G cm⁻¹ in 32 equally spaced steps. Observation times of $\Delta = 100$, 250, 500 and 750 ms were used and the gradient duration was varied from $\delta = 2.8$ to 0.7 ms. The echo spacing was maintained at $2\tau = 10$ ms to provide consistent T_2 relaxation. The recycle time used was 3.5 s, resulting in a total acquisition time of 15 min per propagator. In order to increase the number of low **q**-space points acquired and hence improve the propagator reconstruction, particularly at the longer observation times, the above measurements were repeated with a reduced gradient range of $g_z = -4$ to 4 G cm⁻¹ and combined with the full **q**-space data. This additional measurement resulted in a total acquisition time of 31 min per propagator.

3.3.4 Experiments performed

The experimental procedure employed for the model porous medium was as follows: the sample saturated with brine solution was placed in the NMR spectrometer and a 1D spin-echo profile was acquired, as well as 2D spin-echo images of slice thickness 2 mm centred at z = 4.5 mm, z = 34.5 mm and z = 54.5 mm. Brine solution was then pumped through the sample at a volumetric flowrate (*Q*) of 20 ml min⁻¹. Displacement propagators were acquired at the various observation times with and without slice selection. The brine was then replaced with carbonated brine solution; *Q* was retained at 20 ml min⁻¹. Flow was maintained until no further CO₂ entrapment was evident based on the acquired 1D MRI profiles. The suite of NMR imaging (under 'no flow' conditions) and displacement propagator experiments was then repeated. The position of the selected slice used for the displacement propagator acquisition was adjusted to a region of relatively homogeneous CO₂ entrapment informed by the acquired 1D MRI profiles. All propagator experiments were performed multiple times to ensure reproducibility.

For the Bentheimer sandstone, brine solution was pumped through the sample at a volumetric flowrate (Q) of 20 ml min⁻¹. Displacement propagators were acquired at the various observation times with and without slice selection.

3.4 LB Simulation Methodology

3.4.1 Description of propagator simulation algorithm

Displacement propagator simulations were performed using a lattice Boltzmann (LB) platform (as outlined in Section 2.3) to describe the flow field and a Lagrangian particletracking algorithm (also denoted as a directed random walk (DRW) algorithm) which was imposed on fluid 'particles' or seeds migrating through the resultant flow field. The DRW algorithm takes into account both diffusive and advective processes experienced by fluid molecules in the porous bed over the observation time, Δ . The observation time is divided into discrete computational time-steps, dt, which specifies the size of the advective and diffusive increments in the position, x. Thus, the advection step Δx_{adv} at any given position is calculated for each coordinate direction i as $u_i dt$, where **u** is the interpolated velocity from the surrounding grid nodes, as determined using LB. The diffusion step size $\Delta \mathbf{x}_{dif}$ is calculated randomly within a Gaussian probability window for which the root mean squared average of the diffusive jump sizes in each coordinate direction is given by $\sqrt{2D_0dt}$, where D_0 is the self-diffusivity of the fluid (e.g., 2×10^{-9} m² s⁻¹ for water at 21 °C). The total displacement of the 'particle' during dt is given by the vector sum of $\Delta \mathbf{x}_{adv}$ and $\Delta \mathbf{x}_{dif}$. The overall displacement of each seed during Δ is defined as the vector sum of all individual $\Delta \mathbf{x}_{adv}$ and Δx_{dif} increments for that 'particle'; collation of all particle displacements results in the final displacement propagator. A flow chart summarising the key operations and decisions of the DRW algorithm is shown in Figure 3.5.

The DRW algorithm was implemented in the C++ programming language. Previous in-house versions were written in C; however, in this work C++ was preferred as it allowed certain additional features such as C++ classes and strings to be utilised. The implementation of the algorithm in C++ also improved the program runtime significantly (by a factor of 2 on the particular computer used for the simulations) compared to previous implementations in C. The following input parameters in the program were user-specified: the array of observation times, Δ (from smallest to largest), the time increment *dt*, and the sampling factor *j* (such that the total number of particles seeded equals the number of particles available in the seeding volume divided by *j*³), which can be increased in order to reduce the simulation running time.



Figure 3.5 DRW algorithm used for displacement propagator simulations from LB flow fields.

From experience, it was found that when selecting the value of dt, a trade-off must be made between reducing computational time and ensuring that diffusive 'jump' is sufficient to prevent the particle being trapped in the solid phase; this is satisfied by the empirical condition $2v_0 dt \le \sqrt{2D_0 dt}$, where v_0 is the mean pore velocity of the interstitial fluid. The value of dt chosen for these simulations was 1×10^{-4} .

The sizes of both of the advective and diffusive displacement steps, as described earlier, are necessarily of the order of less than one voxel width in order to ensure that particles do not follow paths that effectively drive them through the solid matrix. After the initial time-step,

the velocity experienced by the particle for its subsequent step is calculated by taking the linear interpolation of the velocity components in each direction. Similarly, the location of a particle is also determined with reference to the eight surrounding 'nodes' of the voxel the particle is in. If a fluid particle is transported to a position in the simulation mask that corresponds to 'solid', it will undergo a number of diffusive steps, denoted as N_{jump} in Figure 3.5, up to an arbitrarily set maximum of 500; this enables it to diffuse back into the fluid-occupied pore space so that it can undergo another advective step. However, if the particle still remains inside a 'solid', it will be discarded from the simulation and the next fluid particle will be seeded. This mechanism provides a computationally cheap method of simulating collisions between the fluid particles and the solid packing. Once a particle has undergone sufficient time-steps to reach Δ , its overall displacement is recorded in a binary file, for each value of Δ specified. These binary files are then subsequently processed in MATLAB® to give the displacement probability distribution (propagator). Seeded particle numbers of the order of 6×10^5 were used to generate the simulated propagators shown in this chapter.

In previous in-house implementations of the DRW algorithm (Harris, 2005; Harris et al., 2005), seeded particles were considered to have entered into a 'solid' region when all eight of the surrounding nodes had a value of zero, corresponding to solid in the binary gated simulation lattice. However, when this condition was applied to the LB velocity fields being used in this work, the resulting simulated propagators under-estimated the expected mean displacement by a factor of up to 33 %. Upon investigation, it was discovered that a high proportion of seeded particles were getting 'trapped' near the solid/fluid boundary regions, whereby the interpolated velocity was zero or close to zero. Despite this, the particles were not getting diffused back into the fluid-occupied pore space as they did not fulfil the condition of entering into a solid. Thus, dt was incremented, while the particles stayed mainly stagnant once trapped—resulting in an overall weighting of the propagator towards lower displacements. Once the definition of a seeded particle having entered a solid was broadened to include particles where up to half of the surrounding nodes were fluid, this problem was overcome and the mean displacements of the propagators were much closer to the expected value. This is illustrated in Figure 3.6, where simulated propagators in the random monodisperse packing lattice (described in Section 3.4.2) are compared before and after this change in boundary conditions, with all other parameters being equal.



Figure 3.6 Simulated propagators for an observation time of $\Delta = 750$ ms in a mono-disperse packing LB simulation lattice before (dotted and dashed line) and after (solid line) changing the boundary conditions for a seeded fluid particle entering a solid. The dashed vertical line shows the expected mean displacement.

In order to verify that the propagator simulation methodology employed (LB generated flowfields coupled with a DRW algorithm) was working correctly prior to comparison with the NMR experimental data acquired in this work, the code was validated against the 'simple' case of laminar flow in a cylindrical pipe for which experimental and simulated propagator data were available, via a study by Codd et al. (1999). In their study, Codd et al. (1999) acquired experimental propagators at a range of observation times for the flow of octane in a capillary tube of diameter 150 µm using PGSE NMR techniques and simulated these using Monte Carlo methods, with good agreement obtained between the experimental and simulated propagators. The acquired propagators showed the transition from the nearrectangular shape, seen at short observation times, which is expected for Poiseuille flow to the Gaussian distribution, seen at longer observation times, which is typical of Taylor dispersion in the asymptotic limit.

For the comparison with Codd et al. (1999)'s data, a simulation mask of a circular pipe was generated with a diameter of 60 voxels, scaled to 150 μ m. LB hydrodynamic simulations were used to calculate the flow field in the pipe for a mean superficial velocity of 2.6 mm s⁻¹, which was chosen to match Codd et al. (1999)'s experiments. The resulting LB velocity

profile in the axial direction was parabolic as expected according to the Hagen-Pouseuille equation. The DRW algorithm was then used to simulate propagators at observation times of $\Delta = 10$ ms, 100 ms, 500 ms and 1000 ms, with the diffusion coefficient of the fluid set to match the value of 2.35×10^{-9} m² s⁻¹ reported by Codd et al. (1999) for octane. Figure 3.7 shows the simulated propagators generated from the LB simulation overlaid with the experimental and simulated data of Codd et al. (1999). Overall, the two sets of data show very good agreement, and the evolution in propagator shape with increasing observation time is captured accurately. Some small discrepancies exist, which may be attributed to the relatively low number of particles seeded in the propagator simulation, resulting in underrepresentation of certain regions in the flow field. This could be improved by (for example) using a higher-resolution LB simulation mask and/or sampling more particles in the existing simulation mask, both of which would increase the computational time required; however, for the purpose of qualitative comparison with Codd et al. (1999)'s data, the settings used here were considered adequate.



Figure 3.7 Displacement propagators for the flow of octane in a 150 μm capillary tube at a superficial velocity of 2.6 mm s⁻¹ for various observation times. The red lines represent propagators simulated using a combined LB and DRW approach and the black dots and black lines represent experimental and simulated data from Codd et al. (1999). Reproduced with modifications from Codd et al. (1999), Figure 2.

3.4.2 Simulation setup for model porous medium

A 3D MRI image of a mono-disperse bead packing (supplied by Dr Andy Sederman at the MRRC) was used to provide a lattice for the simulation. This image was binary gated to differentiate the fluid-occupied pore space from the solid matrix. The original image consisted of 3 mm diameter beads packed randomly in a 45 mm inner diameter column. The image consisted of 256^3 voxels, and was scaled such that the mean bead diameter matched that employed experimentally (100 µm), resulting in an isotropic spatial resolution of 5.88 µm. This lattice generation procedure was necessary as it is not possible to image the 100 µm bead diameter packing at sufficient resolution to provide the required simulation lattice. A similar simulation lattice generation procedure has been successfully employed before (Creber et al., 2009).

Sample transverse and axial 2D slices extracted from the 3D simulation lattice are shown in Figure 3.8(a) and (b). The solid matrix is shown in black and pore space in white. This was the largest simulation domain practically possible with our computational resources, presenting a column-to-bead diameter ratio of 16; generally a ratio of 10 is considered sufficient to minimise wall packing effects (Delgado, 2006). Nevertheless the simulation domain is necessarily approximately 24 times smaller than the packed column used experimentally for propagator generation. LB simulations were performed on the 3D simulation lattice using the same apparent mean pore velocity of 0.81 mm s⁻¹ as used in the NMR experiments. The resultant velocity images are shown in Figure 3.8(c) and (d) for the corresponding slices in Figure 3.8(a) and (b) - the component in the superficial flow direction has been plotted. These profiles were then used to simulate displacement propagators at a variety of observation times using the DRW algorithm outlined earlier.



Figure 3.8 (a) Transverse and (b) axial slices extracted from the simulation lattice. Pore space is shown in beige. The corresponding velocity images following application of the LB simulation method are shown in (c) and (d) respectively. Velocity is shown in the superficial flow (*z*-) direction. (e) and (f) show the partitioning of the pore space into individual pores in the same slices as above, with the different colour-shaded regions showing the distinct pores.

Different pore environments for CO_2 entrapment were then considered. A pore thinning algorithm (as described in Section 2.4.4) was used to divide the void space in the image into discrete pores. The algorithm was implemented using the in-house Image and Data Analysis (IDA) software. Once the pores were identified, different 'rules' were then applied in terms of allocating pores that became occupied by CO_2 . CO_2 is a non-wetting fluid with respect to water in the bead packs, and thus will preferentially occupy the larger pores. However smaller pores will provide more surface area for ganglia formation from the carbonated brine solution and higher local pressure drops per unit length possibly encouraging local bubble formation. Smaller pores are also more likely to be associated with smaller pore necks which will impose larger capillary forces for ganglia entrapment. Thus utilising the known experimental CO_2 gas saturation from experiments, pores in the simulation lattice were switched from being water saturated to being occupied by CO_2 until the % value for the experimental CO_2 gas saturation was reached for the following scenarios:

Scenario 1 – the smallest pores fill with CO₂ preferentially,

Scenario 2 – the largest pores fill with CO₂ preferentially and,

Scenario 3 – random allocation of pores to be filled with CO₂.

Figure 3.9 shows the resulting pore volume distribution obtained using this method; the volume ranges corresponding to the 'small' and 'large' blocked pores are also indicated. Figure 3.8(e) and (f) show the partitioning of the pore space in the corresponding slices shown in Figure 3.8(a) and (b) respectively, prior to allocation of selected pores as being 'filled' by CO₂. LB flow fields were then recalculated treating CO₂-occupied pores effectively as solids and the propagators re-simulated and compared directly with corresponding experimental measurements.



Figure 3.9 Pore volume distribution for the 3D porous medium simulation mask. The shaded areas correspond to small (light grey) and large (dark grey) pores blocked.

3.4.3 Simulation setup for Bentheimer sandstone

Two different simulation lattices were used to represent the pore space of Bentheimer sandstone: a morphologically thinned image of a bead pack as an artificial substitute for the sandstone, and a binary-gated X-ray microtomography (XMT) image of the rock, obtained from the same larger piece of Bentheimer sandstone as the core plug used in the NMR experiments. The XMT image was supplied by Kreso Kurt Butula and Dmitry Koroteev at Schlumberger Moscow Research.

The first simulation lattice was generated from the random mono-disperse bead pack image described Section 3.4.2. It was shown by Roberts & Schwartz (1985) that electrical conductivity in granular media such as sandstones can be accurately modelled using a representation of the pore space which starts from a close-packing of spheres of uniform

radius and evolves by distorting the grain shape into a set of space-filling polyhedra. This thinning procedure is thought to be analogous to the natural process, known as diagnesis, by which granular materials such as sandstone evolve from unconsolidated, high porosity sediments due to physical and chemical processes such as compaction and sedimentation (Taylor, 1950). In the current work therefore, to mimic this process, the bead pack image was modified using an algorithm (implemented in MATLAB®) which erodes the pores of the original geometry by reassigning surface liquid voxels (defined as liquid voxels in contact with the solid) to solid. Surface voxels with the highest number of faces in contact with the solid matrix (out of a maximum of six possible faces) were reassigned first, and the resulting image was thinned again using by the second highest number of connected faces, and so on, until the porosity of the simulation mask, which we refer to subsequently in the text as the 'artificial lattice', was reduced from the starting value of 47.5 % to 22.8 %, which is close to the measured sandstone porosity. A similar lattice generation strategy was used previously by Johns et al. (2003) and shown to give good qualitative agreement with experimentally obtained propagators in Bentheimer sandstone. The different stages in the generation of the artificial lattice are represented in Figure 3.10. Axial and transverse slices selected from the original 3D image of the mono-disperse packing are shown in Figure 3.10(a) and (b), respectively, and Figure 3.10(c) and (d) show the same slices after application of the pore thinning algorithm.

The second simulation lattice was generated from the 3D XMT image of real Bentheimer sandstone (1500^3 voxels in size). Due to computational limitations on the lattice size useable in the LB simulations, the original image was down-sampled in each direction by a factor of 5 to give a 300^3 voxel simulation mask with an isotropic resolution of $11.15 \,\mu$ m. Isolated solid and liquid voxels (i.e. those surrounded by all six face-sharing neighbours) were removed as these can impact on the numerical stability and running time of the simulation. The porosity of this lattice was 23.5 %, which is consistent with gas porosity measurements for this rock type; the discrepancy with the NMR value may be explained by the smaller sample size of the XMT image not reflecting centimetre-scale heterogeneities of the rock. In order to investigate the effect of spatial variability in the sandstone lattice, the 300^3 voxel mask was further divided into eight separate 150^3 voxel sections. The full size simulation mask is referred to as 'BN300' and the smaller masks as 'BN1' to 'BN8', respectively. Axial and transverse slices extracted from the simulation lattice for the BN300 simulation mask are shown in Figure 3.11(a) and (b), respectively. A visual comparison of the BN300 and

artificial (Figure 3.10(a) and (b)) lattices shows that the two images do not look very similar. In particular, the sandstone image appears to exhibit a variety of different particle sizes and shapes, whereas the thinned bead pack appears much more regular, as expected, but also possesses a reduced curvature compared to the original bead pack, with the surfaces being more angular in general. However, in order to determine whether the artificial lattice is an appropriate mimic of the real rock, a more quantitative comparison between the two simulation masks is required.

A recent study by Vasilyev et al. (2012) showed that the dispersivity (Section 2.4.3) of a porous medium has an inverse relationship to the mean coordination number, i.e., the mean number of connections to each pore body, which is a measure of the connectivity of the pore space. This was explained by the fact that the tortuosity (which varies between 0 and 1, with 1 representing a perfectly straight flow path) and effective porosity of the medium increase as the mean coordination number goes up, leading to smaller variations in the average velocity across pore throats and less flow in diffusion-dominated dead zones. The former reduces the contribution of mechanical dispersion and the latter that of diffusion to the overall dispersivity of the medium. Thus, in order to quantitatively compare the artificial and BN300 lattices, the mean coordination numbers of the two lattices were determined. For this purpose, the pore thinning algorithm described in Section 2.2.4 was used to segregate the pore space into individual pores. The mean coordination numbers thus obtained for the artificial and BN300 lattices were 2.56 and 2.62, respectively, which shows excellent agreement between the two geometries in this respect. Therefore it is expected that the transition to an asymptotic regime for the flowing spins, as measured by the propagator, will be similar in the two lattices. It was also found that the spread of coordination numbers was greater for the sandstone image, as may be expected given its more complex geometry, with a maximum of 6, as opposed to 4 for the artificial lattice. It is also worth noting that the mean coordination number reported here for BN300 is lower than those reported previously in the literature for Berea and Fontainbleau sandstones, which range from 2.8 (Dullien, 1992) to 4.5 (Øren & Bakke, 2003), with a number of values in between, as surveyed by Arns et al. (2004). This lower value may be due to differences between Bentheimer and the other types of sandstone for which data were available, and is also likely dependent on the spatial resolution of the simulation mask and the method used for pore identification.

In addition, the normalised pore volume distributions for the two lattices are shown in Figure 3.12, and are both mono-modal and of similar shape, with a modal pore volume at 1.0×10^{-4} mm³—although the BN300 lattice has fewer pores above the modal volume, resulting in a lower mean pore volume of 8.6×10^{-4} mm³ as compared to 1.4×10^{-3} mm³ for the artificial lattice. A 'mean pore size' was determined for each of the lattices by calculating the inverse of the surface-to-volume (s/v) ratio; this was done by determining the location of voxels at the fluid/solid interface (essentially the first layer of the pore thinning algorithm). The total area of the surface in contact with the fluid was then divided by the total volume of the fluid voxels. It was found that by scaling the artificial lattice using the same isotropic spatial resolution of 11.15 μ m as the BN300 lattice, the mean pore size obtained was 14 μ m, which is close to the value of $12 \,\mu m$ for the BN300 lattice. The permeability of the artificial lattice, as measured using LB simulations with a fixed pressure drop between inlet and outlet, was somewhat higher than that of the BN300 lattice: $6.2 \times 10^{-12} \text{ m}^2$ as compared to 5.6×10^{-12} m². The higher permeability of the artificial lattice may be expected given the presence of a larger average pore size. It should be pointed out that the use of LB simulations to measure permeability was not validated in this study, so the values reported here may not be directly comparable with experimental data, and are thus useful only as a comparison between the two lattices. However, the values for both the lattices are of the same order of magnitude as the typical value for this type of rock of 3×10^{-12} m² reported earlier.

LB simulations were performed on both the artificial and BN lattices using the same apparent mean pore velocity of 1.37 mm s⁻¹, consistent with the NMR experiments. The resultant velocity images were used to simulate displacement propagators at a variety of observation times using the DRW algorithm outlined in Section 3.4.1. The corresponding LB velocity images are shown in Figure 3.10(e) and (f) for the artificial lattice and Figure 3.11(c) and (d) for the BN300 lattice.



Figure 3.10 (a) Axial and (b) transverse slices extracted from the original, unmodified mono-disperse packing lattice. (c) Axial and (d) transverse slices extracted from the thinned bead pack lattice following application of the pore thinning algorithm. In (a-d), the binary scale indicates solid (black) or pore (white). The corresponding velocity images after the application of the LB simulation method are shown in (e) and (f). Velocity is shown in the superficial flow (z-) direction.



Figure 3.11 (a) Axial and (b) transverse slices extracted from the BN 300 lattice; the binary scale indicates solid (black) or pore (white). The corresponding velocity images after the application of the LB simulation method are shown in (c) and (d). Velocity is shown in the superficial flow (*z*-) direction.



Figure 3.12 Normalised pore volume distributions for the BN300 (solid line) and artificial (dashed line) lattices.

3.5 Experimental Results and Discussion

3.5.1 Ordinary brine propagators

Figure 3.13(a) shows displacement propagators acquired for ordinary brine flow in the bead pack using both standard and slice selective APGSTE pulse sequences described in 3.3.3. The soft pulse employed in the slice selective APGSTE pulse sequences excited a slice of thickness 14 mm centred at a position of 34.5 mm along the total sample length of 69 mm, i.e. approximately near the middle of the sample. The small peak centred on zero mean displacement in Figure 3.13(a) for the full sample propagator is associated with entrance and exit effects of the sample and is eliminated by the slice selection. Apart from this minor peak there is excellent agreement between the two methods indicating that transport in the selected region is indicative of bulk behaviour. Figure 3.13(b) shows the evolution in the slice selective propagators as a function of the observation time, Δ ; as Δ increases, the displacement propagator evolves from a skewed exponential shape to a Gaussian shape centred on the mean displacement, as observed frequently in literature (e.g. Scheven & Sen, 2002).

For the Bentheimer core plug, Figure 3.14(b) shows the evolution of the normalised NMR flow propagators as a function of observation time. The peak observed at zero displacement

corresponds to stagnant water undergoing self-diffusion. As expected, the relative size of the stagnant peak decreases with increasing Δ , and the flowing water gives rise to a Gaussian-like peak displaced from the origin, which increases in amplitude as Δ increases (consistent with previous studies, e.g. Mitchell et al. (2008b)). Figure 3.14(a) shows propagators acquired both with and without slice selection. It is evident that the presence of slice selection significantly reduces the stagnant peak. This reduction in stagnant peak signal can be attributed to removing dead zones associated with the inlet and outlet of the rock core holder, and was found to be 30 %, which was calculated by de-convolution of the stagnant and flowing peaks.



Figure 3.13(a) NMR displacement propagators corresponding to an observation time of 500 ms acquired without (broken line) and with (solid line) slice-selection in a 100 μ m bead packing. Slice selection was introduced using the pulse sequence shown in Figure 3.4(b) and excited a region 14 mm thick centred in the middle of the column at a distance of 34.5 mm from the inlet (along a total column length of 69 mm). (b) The evolution in the propagator shape with increasing Δ for brine flowing in the bead pack at Q = 20 ml min⁻¹.



Figure 3.14 (a) NMR displacement propagators corresponding to an observation time of 500 ms acquired without (dashed line) and with (solid line) slice-selection in a Bentheimer sandstone core plug. Slice selection was introduced using the pulse sequence shown in Figure 3.4(b) and excited a region 14 mm thick centred in the middle of the sample at a distance of 34.5 mm from the inlet (along a total sample length of 69 mm). (b) Propagators for brine flowing in sandstone at Q = 20 ml min⁻¹ at the different observation times. The probability distributions have been normalised by plotting the dimensionless function $P(\zeta) \times \langle \zeta \rangle_0$ against $\zeta / \langle \zeta \rangle_0$.

The variation in ratio θ of measured mean displacements $\langle \zeta \rangle$ to the expected mean displacements $\langle \zeta \rangle_0$ is shown in Figure 3.15 as a function of Δ for both the bead pack, in (a), and for the sandstone, in (b). For the bead pack, θ tends to an asymptotic value of 1.08, which is broadly consistent with reported values (Scheven et al., 2005b) for a similar bead pack, where an average θ value of 1.05 was reported. This discrepancy may be explained by the presence of surface signal relaxation effects, which reduces the relative contribution of 'slow' molecules, located near or on relaxing pore walls, to the propagator measurement - thus artificially enhancing the measured mean displacement. It is also worth noting that a systematic error might arise from the porosity in the selected region being slightly different to that measured for the bulk packing. For the sandstone, θ increased monotonically with increasing Δ , and the asymptotic value was estimated at $\theta = 1.1$, which is also consistent with previous studies (Scheven et al., 2005b; Mitchell et al., 2008b).

We determine the uncorrected moments of the propagators directly from the data in Figure 3.13 and Figure 3.14, and the corrected moments using the asymptotic values of θ from Figure 3.15. These results are shown in Table 3.1 and Table 3.2 for the bead pack and Bentheimer sandstone, respectively. Here, the second and third moments are quantified as the rms width, σ , and the skewness, *s*, respectively. The values are consistent with those reported by Scheven et al. (2005b), who conducted experiments over a wider range of mean displacements. As also seen in Table 3.1 and Table 3.2, the discrepancy between the experimentally-obtained and corrected (using the analysis described in Section 3.3.1) moments for the rock are smaller than those for the bead pack, and the skewness for both decreases with increasing mean displacement as the overall propagator shape tends to a Gaussian distribution.



Figure 3.15 Ratio of measured to expected mean displacement, $\theta = \langle \zeta \rangle / \langle \zeta \rangle_0$, for brine flowing in (a) the pack of beads, (b) the Bentheimer sandstone. Asymptotic limits of $\theta = 1.08$ and $\theta = 1.1$ are reached at long observation times for the bead pack and sandstone, respectively.

Table 3.1 Measured mean displacement, rms width, and skewness from the propagators of water flowing in the 100 µm bead pack (Figure 3.13), along with the corrected values calculated according to Eqs. (3.2) and (3.3).

Δ / ms	$\left< \zeta \right>$ / mm	$\left< \zeta \right>_0$ / mm	σ / mm	σ' / mm	s / (-)	s' / (-)
100	0.089	0.081	0.056	-	0.612	-
250	0.222	0.201	0.106	0.118	0.384	0.656
500	0.432	0.403	0.154	0.190	0.167	0.334
750	0.645	0.604	0.192	0.255	0.084	0.213

Table 3.2 Measured mean displacement, rms width, and skewness from the propagators of water flowing in Bentheimer sandstone (Figure 3.14), along with the corrected values calculated according to Eqs. (3.2) and (3.3).

Δ / ms	$\left< \zeta \right>$ / mm	$\left< \zeta \right>_0$ / mm	σ / mm	σ' / mm	s / (-)	s' / (-)
100	0.123	0.137	0.148	0.146	1.429	1.552
250	0.345	0.343	0.325	0.327	0.987	1.087
500	0.720	0.687	0.530	0.550	0.607	0.673
750	1.126	1.030	0.721	0.767	0.252	0.332

3.5.2 CO₂ entrapment in model porous medium

1D NMR profiles of the model porous medium sample were taken along the axial direction both before and after carbonated brine was flowed through the model porous medium sample. The profile acquisition parameters were selected so as to minimise any significant signal relaxation, and were normalised using a homogeneous sample of identical bulk dimensions to the porous media flow cell, consisting of water doped with 0.5 g/L Mn²⁺ ($T_1 = 50$ ms). This corrected for any r.f. inhomogeneities or gradient non-linearities and enabled the determination of calibrated axial brine-saturation profiles for the column; the normalised profiles are shown in Figure 3.16(a), in Figure 3.16(b) the profiles acquired after flowing carbonated brine are re-plotted as % reduction in water content, which corresponds to the relative CO₂ saturation of by inference. Figure 3.16(a) shows that there is a reduction in water saturation as expected after flowing the carbonated brine through the sample, which is due to CO₂ coming out of solution and being trapped in the pore space. The 1D profiles shown in Figure 3.16(b) were acquired at the start and end of propagator acquisition, and confirm that minimal change occurred in CO₂ spatial distribution during propagator acquisition.



Figure 3.16 (a) Normalised 1D NMR profiles across the bead pack sample in the axial-direction for the initially brine-saturated sample (black line) and at the start (red line) and end (green line) of propagator acquisition while flowing carbonated brine through. (b) The same profiles as in (a) converted into % reduction in water content (initial water saturation is assumed to be 100 %). The dotted vertical lines indicate the boundaries of the sample slice used for propagator measurements, and the dashed vertical lines indicate the positions of the 2D cross-sectional images shown in Figure 3.17.

As Figure 3.16(b) shows, the CO₂ saturation is higher near the inlet and decreases gradually along the sample length, with very little trapping observed after z = 57 mm. The decrease in saturation is unlikely due to the pressure gradient across the sample, as the overall pressure drop, estimated to be ~2.6 kPa (using Darcy's law, with the the Cozeny-Karman correlation (Bear, 1988) used to estimate the permeability of the bead pack), is small compared to the ambient outlet pressure. Additionally, the decreasing solubility of CO₂ in water with at lower pressures would tend to favour more CO₂ coming out of solution near the outlet. Another

possible explanation for the decrease in CO₂ saturation may be found by considering the profile of the initially brine-saturated sample in Figure 3.16(b); as the figure shows, the porosity of the sample increases gradually along its length, with an approximate difference of 12 % between the inlet and outlet. This indicates that the column is more closely packed nearer the inlet, which may encourage greater CO₂ ganglion formation due to the presence of smaller pore necks. Figure 3.16 also reveals obvious oscillations in the signal intensity after flowing carbonated brine, with a period of ~3.8 mm (equivalent to 38 bead diameters) on average. The reason for this is unclear, although the oscillations were reproducible and occurred over a broad range of flowrates. The oscillations are unlikely to be related to the large scale saturation variation across the core; however, it is possible that the troughs in Figure 3.16(b) correspond to regions where some segregation of smaller particles occurs due to imperfect mixing when packing the column.

To check that the observed CO₂ trapping occurred in the bulk pore space (and not as large bubbles, e.g. on the order of the length scale of the oscillations seen in Figure 3.16), 2D images with a slice thickness of 2 mm were taken at z = 4.5 mm, 34.5 mm and 54.5 mm along the axis of the column. Like the 1D profiles, the 2D images were also normalised using the homogenous phantom sample described earlier, in order to enable quantitative comparison of the images. Difference maps of the two image sets acquired before and after CO₂ entrapment are shown in Figure 3.17; these have been converted into a % reduction in water content. The error in the difference maps was estimated to be ~3.9 %, based on the relative standard deviation of the signal intensity in the images used for normalisation. The 2D images confirm that the CO₂ is trapped preferentially near the sample inlet, and also show that the trapped CO₂ occurs throughout the entire column cross-section with a slight preference for the upper regions of the cell, due presumably to buoyancy effects. Large regions of CO₂-occupied pore space are not observed; thus, these images are consistent with the CO₂ ganglia locally occupying a small integer number of connected pores, which is reflected subsequently in the simulation lattices and CO₂ entrapment scenarios simulated.



Figure 3.17 Difference maps of 2D image intensity of sample cross-section before and after CO₂ bubble or ganglia formation in the pore space at various positions along the sample axis. As such the images represent the % local reduction in water saturation.

In order to provide a sensible comparison with simulations based by necessity on a smaller lattice, propagators were acquired using slice selection to detect signal only from the region between the dotted black lines in Figure 3.16. CO_2 entrapment in this region was seen to be relatively homogeneous in the axial direction and the average reduction in water saturation was 13 % after entrapment. Figure 3.18 shows the slice-selective displacement propagators obtained for ordinary and carbonated brine solution flowing through the column at 20 ml min⁻¹. Overall, the propagators for both cases are similar, although the differences that do exist are reproduced consistently across all values of Δ . In particular, the larger mean displacements observed in the carbonated brine propagators are consistent with CO₂ being trapped in the pore space and therefore reducing the available cross sectional area for flow, which results in a greater interstitial velocity. These mean displacements, $\langle \zeta
angle$, obtained from Figure 3.18 are shown in Figure 3.19. The relationship between $\langle \zeta \rangle$ and Δ for the two sets of propagators is seen to be linear in both cases, as expected. From the gradients of the lines of best fit in Figure 3.19, the reduction in pore space available for the flow of brine solution was calculated as 12.7 %, which is in good agreement with the 13 % determined from the 1D profile data in Figure 3.16. Hence the pore space available for flow of brine solution was reduced by 13 % in all post-CO₂ entrapment simulations.



Figure 3.18 ¹H APGSTE displacement propagators for ordinary (solid line) and carbonated (dashed line) brine at a flowrate of 20 ml min⁻¹ through the column filled with 100 μ m ballotini. A 180° soft r.f. pulse was added to the APGSTE pulse sequence, which selected a slice of thickness 14 mm centred on z = 34.5 mm and z = 46 mm (along a sample of length 69 mm) for ordinary and carbonated brine respectively. The propagators were acquired at observation times of (a) 100 ms, (b) 250 ms, (c) 500 ms, and (d) 750 ms.



Figure 3.19 Measured mean displacements plotted against observation time with best-fit lines for ordinary (circles) and carbonated (squares) brine propagators respectively.

3.6 Simulation Results and Discussion

3.6.1 Ordinary brine propagators

The simulated flow propagators for the random mono-disperse bead packing geometry are shown in Figure 3.20. The propagator shape evolves from a skew exponential at the shorter observation times to a more Gaussian shape, consistent with experimentally obtained propagators. The first, second and third moment values are given in Table 3.3. For the Bentheimer sandstone simulations, both the artificial and BN 300 lattices are shown in Figure 3.21(a) and (b), respectively. Although the artificial lattice appears to provide a slightly higher stagnant peak compared to the BN300 geometry, the two sets of propagators look remarkably similar. The moments for the two sets of propagators are given in Table 3.4, where the mean displacements are seen to be almost identical, as expected given the similar porosities. Similarly, the mean width and skewness are also very closely matched.



Figure 3.20 Simulated propagators generated from LB flow fields in a 256³ mono-disperse packing lattice.

Table 3.3 Mean displacement, rms width and skewness values for the simulated LB propagators in the mono-disperse packing lattice.

Δ / ms	$\left< \zeta \right>$ / mm	σ / mm	s / (-)
100	0.087	0.050	0.540
250	0.213	0.092	0.370
500	0.418	0.143	0.205
750	0.621	0.184	0.114


Figure 3.21 Simulated propagators generated from LB flow fields in: (a) a thinned mono-disperse packing geometry used to mimic the pore structure of sandstone ("artificial lattice"); (b) a processed XMT image of Bentheimer sandstone ("BN 300" lattice).

In order to investigate the effect of spatial variability in the SCR 300 lattice, moments were determined from flow propagators calculated in eight 150³ voxel subsamples (referred to as BN 1 to 8) extracted from the full XMT image. The moment values were normalized relative to the BN 300 propagator moments given in Table 3.4. The results in Figure 3.22 show that a consistent mean displacement is obtained in all the lattices. Variations between the subsamples are more pronounced in the higher order moments, with two of the subsamples (BN 7 and BN 8) showing significant deviation compared to the BN 300 moments. These results indicate that the LB simulation should be performed on the largest lattice possible, as larger lattices are more representative of the heterogeneous rock structure and provide better averaging of the displacements in the propagator calculation. However, it is worth noting that the smaller geometries were much less computationally expensive than the BN 300 lattice. On the desktop computers available to run the LB simulations, convergence occurred in a few days for the 150³ voxel lattices, whereas two weeks were required for convergence in the 300³ voxel lattice.

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Artificial lattice				
Δ / ms	$\left< \zeta \right>$ / mm	σ / mm	s / (-)	
100	0.142	0.138	1.152	
250	0.344	0.270	0.763	
500	0.660	0.439	0.480	
750	0.963	0.581	0.301	
BN 300 lattice				
Δ / ms	$\left< \zeta \right>$ / mm	σ / mm	s / (-)	
100	0.136	0.133	1.240	
250	0.334	0.263	0.805	
500	0.642	0.426	0.489	
750	0.933	0.563	0.297	

 Table 3.4 Mean displacement, rms width and skewness values for the simulated propagators in the artificial and BN 300 lattices.



Figure 3.22 Comparison of (a) mean displacement, (b) rms width, and (c) skewness, obtained from propagator simulations in the 150³ voxel subsamples BN 1 to BN 8, normalized relative to the moments obtained from the full lattice BN 300 propagator simulations. Simulation values are shown for the observation times $\Delta = 100$ ms (circles), 250 ms (triangles), 500 ms (squares) and 750 ms (diamonds).

3.6.2 Comparison with experiments

Here, we compare the LB simulated propagators with the results obtained from NMR experiments. First, a qualitative comparison is included, whereby the normalized propagators are overlaid to provide a visual comparison of the distributions. A quantitative comparison is then achieved by comparing the low order moments of the probability distributions.

The propagators generated by LB simulation are overlaid on those obtained experimentally in Figure 3.23 for the bead pack and Figure 3.24 for the sandstone. For the bead packing, there is reasonable agreement between experimental and simulation results consistent with published studies (Mantle et al., 2001; Harris et al., 2005; Creber et al., 2009). In this case, the discrepancy between the experimental and simulated propagators may be speculated to be a consequence of the significantly smaller column-diameter to particle diameter ratio used for the simulations compared to that in the actual column. As such, the displacements determined from the necessarily smaller simulation lattice are influenced more heavily by flow heterogeneities due to the column wall.

For the sandstone simulations, we observed that at the shortest observation times shown in Figure 3.24(a) and (b), the simulated and experimental probability distributions show excellent agreement. As the observation time increases, Figure 3.24(c) and (d), the simulated probability distributions significantly under predict the higher displacements compared to the NMR experimental probability distributions. The first, second and third moments from the simulated propagators are shown in Figure 3.25 for the bead pack and Figure 3.26 for the sandstone, along with the expected values obtained from the NMR experimental results. The mean displacement, Figure 3.25(a) and Figure 3.26(a), increases linearly with observation time in all cases as expected, although the increase is more rapid for the simulations compared to the NMR experiment for the mono-disperse packing, and vice versa for the sandstone. However, the discrepancy between the expected and simulated values is not large (\sim 3 % for the bead pack versus \sim 8 % for the sandstone) at the highest observation time.



Figure 3.23 Comparison between experimental (solid line) and simulated propagators (dashed line) for water flowing through a packing of 100 μm borosilicate ballotini at 20 ml min⁻¹, at different observation times Δ.

Similar behaviour is observed for the rms width in Figure 3.26(b) and (e), although the simulated propagators consistently under-estimate the higher-order moments compared to the expected values. For the skewness, Figure 3.26(c) and (f), the simulation follows the same trend as the expected values due to the evolution of the propagator to a more Gaussian shape at long observation times; in this case the experiment and simulation values converge at the longer observation times.

For the Bentheimer sandstone, the convergence seen in Figure 3.26(a) and (b) between the experimental and simulated values for the first and second propagator moments respectively occurs at short observation times when the propagator shape is dominated by the stagnant peak. This discrepancy suggests that the seeded particles in the propagator simulation algorithm are biased towards the slower regions of the LB simulation velocity field. Notwithstanding, the propagator simulation provides accurate probability distributions at high volumetric flow rates and short observation times. Conversely then, we can assume the simulation will function correctly at slow volumetric flow rates and long observation times, where the NMR experiment is unsuitable. The LB simulation will therefore allow realistic slow reservoir flow rates to be monitored over long observation times. We have demonstrated also that an artificial LB lattice generated by morphological thinning of a bead pack is an

appropriate substitute for a direct lattice derived from the rock. The artificial lattice will be used when XMT data are unavailable.



Figure 3.24 Comparison of experimental displacement propagators (black line) with LB simulated propagators in the artificial lattice (black dashed line) and the BN 300 lattice (grey line) for water flowing in sandstone. Propagators were obtained at observation times of (a) $\Delta = 100$ ms, (b) 250 ms, (c) 500 ms, and (d) 750 ms.



Figure 3.25 Comparison of low order moments from LB simulation and NMR experimental propagators in the model porous medium: (a) mean displacement, (b) rms width, and (c) skewness. Expected values are shown in (a) as dots and in (b) and (c) as error bars denoting the lower and upper bounds which correspond to the experimental and corrected results, respectively. Simulation values are shown as squares, for the 3D mono-disperse bead packing lattice.



Figure 3.26 Comparison of low order moments from LB simulation and NMR experimental propagators in Bentheimer sandstone: (a) mean displacement, (b) rms width, and (c) skewness. Expected values are shown in (a) as dots and in (b) and (c) as error bars denoting the lower and upper bounds which correspond to the experimental and corrected results, respectively. Simulation values are shown for the artificial (squares) and BN 300 (diamonds) lattice.

3.6.3 CO₂ entrapment in model porous medium

The propagators simulated for the three scenarios for CO_2 entrapment are shown in Figure 3.27, along with the experimentally obtained propagators for the flow of carbonated brine through the model porous medium. In all cases the volumetric flowrate through the lattices was kept constant and consistent with the pore velocity of the corresponding experimental scenario. Following CO_2 entrapment there is an increase in mean displacement

as expected, and a broadening of the displacement peaks occurs for all scenarios considered. There are subtle differences between scenarios 1 (small pores filled) and 2 (large pores filled). The blocking of the smallest pores in scenario 1 produces a more prominent stagnant peak at all observation times. This suggests that occupation of the smallest pores has the greatest effect on pore space connectivity and the creation of dead volume. Out of the three scenarios, scenario 2 appears to show the best agreement with the experimental data. The results for scenario 3 (random pores filled) appear to be in between those for scenarios 1 and 2, which is to be expected given that scenario 3 effectively represents a random combination of small and large pores occupied by CO₂.

In order to provide a more quantitative comparison of the simulations and the experiments, the ratio of the standard deviation of the carbonated brine propagators, σ_1 , to the standard deviations of the ordinary brine propagators, σ_0 , was calculated. The equivalent σ_1/σ_0 ratio was determined for the experimental data. The resultant ratio data for both the simulations and the experiments is plotted in Figure 3.28. The data for scenario 3 falls in between scenarios 1 and 2, as expected. The best agreement with the experimental data in Figure 3.28 is produced by scenario 2, where CO₂ entrapment occurs in the largest pores. Discrepancies between scenario 2 and the experimental σ_1/σ_0 ratio nevertheless are evident. These probably arise from several potential contributions, including the use of the smaller simulation lattice as discussed previously, the fact that the CO₂ might only preferentially occupy larger pores and not simply all the largest pores as assumed in the simulations, and the fact that in the experiments, CO₂ will only partially occupy many pores whereas in the simulations full individual pore occupancy is assumed. Notwithstanding we conclude from the results in Figure 3.28 that the CO₂ ganglia preferentially form in larger pores.



Figure 3.27 Displacement propagators obtained using APGSTE NMR for the flow of carbonated brine in the model porous medium post-CO₂ entrapment (solid line) and simulated on the modified 256³ simulation lattice with 13 % of the pore space assigned to be CO₂ according to the three scenarios (scenario 1 – red dashed line; scenario 2 – blue dotted line; scenario 3 – green dash-dot line) outlined in the text. Propagators were obtained at observation times of (a) Δ = 100 ms, (b) 250 ms, (c) 500 ms, and (d) 750 ms.



Figure 3.28 Ratio of standard deviations of displacement propagators before and after pore space modification by CO_2 entrapment for different observation times, Δ ; comparison between experiments (squares) and simulation scenarios (scenario 1 – triangles, scenario 2 - crosses; scenario 3 - circles) outlined in the text is shown.

3.7 Conclusions

NMR displacement propagators were acquired for brine flowing through a model porous medium (packed bed of 100 μ m glass ballotini) and a Bentheimer sandstone core plug. The propagators were acquired using a slice selective APGSTE NMR pulse sequence, which enabled selective signal detection from an axial region of the medium, thus eliminating artefacts associated with entry and exit effects. The experimentally obtained propagators, which were acquired over a range of observation times, Δ , were compared quantitatively with LB simulations using a model lattice (for the bead packing) and both a model lattice and a realistic lattice (for the sandstone); the simulations were shown to give good agreement with experiments. The results for sandstone also validate the use of the artificial lattice (morphologically thinned bead pack) for propagator simulation when XMT images of the sandstone rock are unavailable.

In addition, propagators were also acquired after CO_2 entrapment in the pore space of the model porous medium. These propagators were acquired from an axial region of the medium

with relatively homogeneous CO₂ entrapment (average of 13 % of the available pore space), as revealed by 1D NMR profiles of the column used. 2D NMR images revealed relatively homogeneous CO₂ entrapment across the cell cross-section with no large gas-filled regions. Analysis of the displacement propagators showed that the effective porosity of the column occupied by water was reduced by 12.7 % as a consequence of CO₂ entrapment. This was in good agreement with the reduction in water saturation observed in the 1D NMR profiles. Interpretation of the differences in the propagators without and with CO₂ entrapment was facilitated by LB flow and propagator simulations applied to a model lattice. Different scenarios for CO₂ entrapment were considered in the simulations with occupation of the largest pores producing best agreement with the experimental data. Hence we have been able to explore the pore characteristics of where CO₂ ganglia are most likely to form during entrapment.

In this chapter, we have demonstrated the applicability of combining NMR experimental techniques such as displacement propagators and 1D spin-echo profiles with LB flow and propagator simulations to gain insight into porous media where single phase flow is occurring followed later by modifications to the pore space due to the capillary trapping of CO_2 . This approach can now be extended to systems that more accurately reflect conditions in sub-surface aquifers such as higher temperatures and pressures and the use of different types of rock cores. Different mechanisms for CO_2 entrapment will also be explored in the remaining chapters of this thesis.

3.8 References

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4 Selection of a Supercritical CO₂ Analogue

4.1 Introduction

In this short chapter we propose the use of a suitable supercritical CO_2 /water analogue system that is compatible with the available low-pressure experimental apparatus. Magnetic resonance imaging (MRI) techniques were used in order to verify the interfacial tension (IFT) of the CO₂ analogue system (Hussain et al., 2014). The use of MRI to obtain droplet profiles for IFT measurement was validated using immiscible fluids for which literature IFT values were available. The method was subsequently applied to the refractive-index-matched fluid phases of the CO₂ analogue system and to a system with an opaque continuous fluid, both of which preclude the use of conventional optical imaging techniques.

4.2 Background

CO₂ stored in depleted oil and gas wells or saline aquifers for geological sequestration purposes will typically be present at depths of 800 m or below and is thus expected to be in supercritical form (Metz et al., 2005). The transport properties of supercritical CO_2 with water are altered compared to liquid- or gas-phase CO₂ due to its relatively high density and low viscosity. However, the relatively high critical pressure of CO_2 , 73.8 bar, poses a challenge when doing lab-scale MRI on such systems due to the necessity of using nonmetallic materials of construction inside the spectrometer. It is possible to overcome these limitations through the use of materials such as high-performance polymers; however, such setups are not widespread due to the complexity of the instrumentation required (Wallen et al., 2000). In the current experimental setup, a high-pressure nuclear magnetic resonance (NMR) cell was unavailable and thus measurements were conducted at low pressures (i.e. < 4 bar). In order to overcome this limitation, analogue fluids were used in this study to match certain physical properties of the supercritical CO₂/water system. Analogue fluids are commonly used in experimental studies when the real fluids of interest cannot be used under laboratory conditions (e.g. Balmforth & Craster, 2000). In the context of CO_2 sequestration, Neufeld et al. (2010) used analogue fluids to investigate the dissolution of CO_2 in saline aquifers and its subsequent convective behaviour in the bulk, less dense fluid. In the work

presented here, we consider the two-phase immiscible fluid flow of the CO_2 and water phases, for which the Bond number, Bo (as defined in Section 2.4), is important. It is the Bo value which determines, along with the wettability of the porous medium, the extent of capillary trapping of a non-aqueous phase as ganglia in the pore space of a water-saturated porous medium. In this case, therefore, the fluid properties of interest were density, viscosity and interfacial tension, the first two of which were known.

Here, MRI techniques were used to obtain profiles of sessile drops of an aqueous phase in a bulk hydrocarbon phase for interfacial tension measurements. Conventionally, optical imaging techniques using either sessile drop or pendant drop tensiometry are used to obtain these profiles; this was not possible for the hexane/water-glycerol system due to refractive index matching between the two phases which rendered the interface between the two phases invisible to optical techniques (as verified using a pendant drop tensiometer by Dr Michael O'Sullivan at the Bullard Laboratories in Cambridge). MRI is suitable for such systems as it has the advantage of being able to probe optically opaque samples in a non-invasive and nonintrusive way, by exploiting differences in either chemical shift or magnetic relaxation between different chemical species. Although chemical shift (being independent of the instrument used) is the more robust contrast mechanism, it requires the acquisition of data in a frequency dimension in addition to one, two or three spatial dimensions, thus increasing the image acquisition time. For this reason, magnetic relaxation contrast between the two phases was considered the more practical choice in this work. However, it is worth noting that acquisition of useful droplet images using MRI is more challenging compared to optical techniques, due to limited spatial resolution (of the order of tens of microns per pixel), small sample access space (up to a few centimetres in diameter using conventional high field laboratory NMR spectrometers), and long image acquisition times compared to optical techniques.

4.3 Experimental Methodology

4.3.1 Selection of analogue fluids

The specific gravity of supercritical CO₂ ranges from 0.5-0.8 at representative aquifer conditions (Metz et al., 2005). Interfacial tension of supercritical CO₂/reservoir brine is reported by Yang et al. (2005) to be 46 mN m⁻¹; thus the value of Bo for this system is between 6.82×10^{-5} and 1.71×10^{-4} . The comparison was done with a number of organic liquids (see Table 4.1) for which interfacial tension data with water were available (Goebel & Lunkenheimer, 1997; Kim & Burgess, 2001); from this comparison, it was evident that the C_5 - C_7 alkanes and isopropyl myristate fall closest to the middle of the required Bo range. Isopropyl myristate, however, was rejected due to its high viscosity relative to water, and as pentane is extremely volatile at room temperature, hexane and heptane were considered the most suitable options. In addition, the water phase was mixed with glycerol in order to tune the viscosity ratio of the analogue system to match that of supercritical CO_2 and water, using data from Cheng (2008) for the viscosity of the glycerol-water mixture. This was achieved with a 41 wt% glycerol solution for the hexane, and a 47 wt% solution for the heptane. It was assumed for this purpose that the interfacial tension of the alkane/water interface would not be changed significantly by the addition of glycerol, although this is checked below. The interfacial tensions of the two analogue systems were then verified using MRI as detailed in Section 4.3.2.

4.3.2 Axisymmetric drop shape analysis

Axisymmetric drop shape analysis (ADSA) is a technique for the measurement of interfacial properties in two-phase immiscible fluid systems. It involves fitting to an experimental profile of the shape of a drop or bubble of one of the phases in the other with a theoretical curve, the shape of which is determined by capillary and buoyancy forces. The method used for ADSA is described in detail in Rotenberg et al. (1983), but the basic theory is outlined here.

Theory

Figure 4.1 shows a theoretical profile of a sessile drop immersed in a bulk immiscible fluid phase. When the principle radii of curvature, R_1 and R_2 , of the interface between the two

fluids are sufficiently large, the pressure difference, ΔP , across the interface can be described by Laplace's equation of capillarity:

$$\sigma_{ij}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta P , \qquad (4.1)$$

where σ_{ij} is the interfacial tension between two fluids *i* and *j*. For a sessile drop at rest on a horizontal surface the only external force acting is gravity, hence ΔP is a linear function of buoyancy above a selected datum value, ΔP_{0} , according to

$$\Delta P = \Delta P_0 + (\Delta \rho) gz, \qquad (4.2)$$

where $\Delta \rho$ is the density difference between the two fluids, g is the acceleration due to gravity and z is the vertical height below the datum level. The datum level is chosen as the top of the droplet; as shown in Figure 4.1, the symmetry of the droplet means that both radii of curvature have the same value R_0 at the datum point (O), and therefore from Equation (4.1) it can be deduced that $\Delta P_0 = 2\sigma_{ij}/R_0$. Furthermore, setting Equations (4.1) and (4.2) equal for the whole drop yields

$$\sigma_{ij}\left(\frac{1}{R_1} + \frac{\sin\theta}{x}\right) = \frac{2\sigma_{ij}}{R_0} + (\Delta\rho)gz , \qquad (4.3)$$

where R_1 turns in the *x*-*z* plane and R_2 rotates about the axis of symmetry in a plane perpendicular to R_1 and can therefore be described by the geometry shown in Figure 4.1 as $x/\sin \theta$, where θ is the turning angle measured between the tangent to the profile at (*x*, *z*) and the *x*-*z* plane.



Figure 4.1 Schematic of a non-wetting sessile drop to illustrate the coordinate system used.

Due to the symmetry of the droplet the 3D interface between the two fluids can be described using the 2D profile shown in Figure 4.1; mathematically, it is convenient to represent the curve in parametric form, in terms of the arc length from the origin, s, and the turning angle θ , such that the following geometric identities hold:

$$\frac{dx}{ds} = \cos\theta \tag{4.4}$$

and

$$\frac{dz}{ds} = \sin\theta. \tag{4.5}$$

By definition, the rate of change of θ with respect to s is

$$\frac{1}{R_1} = \frac{d\theta}{ds}, \tag{4.6}$$

therefore substituting Eq. (4.6) into Eq. (4.3) and rearranging yields

$$\frac{d\theta}{ds} = \frac{2}{R_0} + \frac{(\Delta\rho)g}{\sigma_{ij}} z - \frac{\sin\theta}{x}.$$
(4.7)

This equation, along with Equations (4.4) and (4.5), form a set of differential equations for *x*, *z* and θ as a function of *s*, subject to the boundary conditions $x(0) = z(0) = \theta(0) = 0$. Simultaneous integration of these three equations gives the shape of the drop for a given R_0 and $\Delta \rho / \sigma_{ij}$. For a given pair of liquids $\Delta \rho$ is known or can be measured, so calculation of the curve enables determination of σ_{ij} . The value of *g* was taken as 9.81 m s⁻². Table 4.1 Theoretical Bo and μ-ratio for the 'CO₂ analogue' systems calculated using literature interfacial tension values from ¹Kim & Burgess (2001) and ²Goebel and Lunkenheimer (1997), along with the values for the supercritical CO₂/water system calculated using typical numbers for density and interfacial tension obtained from Metz et al. (2005) and Yang et al. (2005), respectively. The viscosity values used for supercritical CO₂ were 'typical' values for supercritical fluids (Székely, 2007) as exact values for this system were unavailable.

Fluid (in a two-phase system	Bond Number	Viscosity Ratio
with water)	(× 10 ⁻⁴)	(-)
¹ Mineral oil	0.40	30
¹ Benzene	0.59	0.65
¹ Butyl acetate	1.45	0.70
¹ Benzyl alcohol	2.09	5.5
¹ Isopropyl myristate	0.97	6.5
² Pentane	1.15	0.24
² Hexane	1.04	0.29
² Heptane	0.96	0.39
² Octane	0.89	0.54
² Decane	0.80	0.92
² Dodecane	0.73	1.3
Supercritical CO ₂	0.68-1.71	0.05-0.10

Experimental Setup

MRI experiments were performed using a vertical-bore Bruker AV400 spectrometer operating at a ¹H resonant frequency of 400 MHz. All measurements were done using ¹H NMR. The experimental setup consisted of a glass tube of i.d. 22.6 mm inside a birdcage r.f. coil of i.d. 25 mm. The tube had a layer of PTFE (used due to its non-wetting properties) at its base upon which the aqueous droplet rested. Droplets were formed in situ inside the spectrometer using a Harvard Apparatus syringe pump connected to the cell via 1/8" polymer tubing (Figure 4.2). Five different systems were investigated using this technique:

- i) Water in hexane;
- ii) Water in heptane;
- iii) 41 wt% glycerol-water solution in hexane;
- iv) 47 wt% glycerol-water solution in heptane;
- v) Water in crude oil.

Of these systems, i) and ii) are fluid pairs of known interfacial tension and can be imaged using optical techniques; they were used in order to validate the experimental method. iii) and iv) are refractive-index-matched fluids and thus cannot be imaged using optical techniques. v) also cannot be imaged optically due to the continuous phase (crude oil) being opaque. The organic solvents used in these experiments were supplied by Sigma-Aldrich. For the experiments with crude oil, 'Middle East light' crude ($\rho = 836$ kg m⁻³) was provided by Dr Jon Mitchell at the MRRC.

MRI Experiments

In order to visualise the droplet profiles, spin-echo imaging techniques such as RARE (see Chapter 2.2.7) were utilised. The Recycle Time (RT) used for imaging was varied between 1.0 s and 2.0 s in order to get sufficient T_1 contrast between the two phases. Another technique that was utilised involved the acquisition of multiple echo images, whereby a complete 2D image was acquired at each echo in the CPMG train and the resultant images added together in post-processing. This technique increased SNR compared to a conventional RARE experiment but resulted in longer data acquisition times (34 minutes versus < 1 minute).



Figure 4.2 Schematic of the cell used to obtain drop shape data in the AV400 spectrometer. The cell was initially partially filled with the hydrocarbon phase; the aqueous phase was injected from the top as shown using a Harvard Apparatus syringe pump operating at a constant flowrate of 1.0 ml min⁻¹ in order to generate a droplet at the base of the cell.

However, in cases where the droplet position was not stable (e.g. due to background vibration), RARE was used with several image repetitions which were added together to improve SNR. Images were acquired with a data matrix of 256×256 pixels in size and the imaging field-of-view (FOV) was varied between 17 mm and 25 mm in both the read and phase directions, depending on the droplet size – giving an isotropic pixel resolution ranging from 66 µm to 98 µm. A slice thickness of 1 mm was used for imaging, and image slices were taken through the centre of the droplet.

Data Analysis

Once acquired, the **k**-space data were read into MATLAB® for processing and an edgedetection algorithm based on the method of Canny (1986) was used to determine the coordinates of the droplet profile from the Fourier transformed image. The ADSA equations were then solved using 4th order Runge-Kutta interpolation and fitted to the experimentally obtained droplet profile using the method of least-squares. The fitting parameters solved for were the radius of curvature R_0 and the interfacial tension σ_{ij} .

4.4 Results and Discussion

Figure 4.3 shows an example of edge detection used to extract the droplet profile for an image of a droplet of water in hexane. A theoretical curve was then fitted to the droplet profile using Equation (4.7). For an accurate fit, it is particularly important to obtain a good fit to the droplet profile near the surface, as the wettability of the solid surface plays a major part in determining the droplet shape. However, extracting an accurate profile near the surface can prove challenging due to the limited spatial resolution of the MRI compared to optical techniques. In addition, in the image shown in Figure 4.3 there appears to be a dark region between the interface of the hexane and water. This is more pronounced at the top of the droplet, and as a result the droplet appears to be pushed downwards somewhat below the surface on which the bulk fluid sits. This effect is a chemical shift artefact due to magnetic susceptibility differences between the two phases, and may lead to distortions in the image, as the relative position of the interface is shifted depending on its curvature; however as the effect is relatively small in this case, it was assumed that only the relative position of the droplet is affected, and not its shape. A more detailed explanation of this artefact may be found in Callaghan (2007).



Figure 4.3 (a) MRI image of a drop of water ($\rho = 996 \text{ kg m}^{-3}$) in hexane ($\rho = 654 \text{ kg m}^{-3}$) with an isotropic pixel resolution of 66 µm and a slice thickness of 1 mm. FOV shown is 11.289 mm in the *z*-(vertical) and *x*-(horizontal) directions; (b) the same image as in (a) but with the droplet profile obtained using edge detection shown superimposed in red.

In order to assess the accuracy of the ADSA method, the experimentally obtained droplet profiles for the water-hexane and water-heptane systems were plotted together with the corresponding theoretical profiles obtained using the both the best-fit interfacial tension values and those reported in Goebel & Lunkenheimer (1997) (Figure 4.4). In addition, the residual sum-of-squares (RSS) values were calculated for the fitted curves in order to give a quantitative measure of the relative goodness-of-fit of the two different IFT values for each system. These are reported in Table 4.2, along with the IFT values both from our work and literature. From the data shown in Figure 4.4 and the RSS values in Table 4.2, it is evident that the ADSA curves better predict the droplet profile near the crucial liquid-liquid-solid interface and give a better fit to the experimental data overall.



Figure 4.4 Droplet profiles (crosses) extracted from MRI images of a water droplet in (a) hexane and (b) heptane, along with the corresponding curve fits for the ADSA (green line) and literature (blue line) IFT values. Literature values were obtained from Goebel and Lunkenheimer (1997). (c) and (d) show close-ups of the curve fitting near the liquid-liquid-solid interface for the droplet profiles shown in (a) and (b) respectively.

Table 4.2 Results from the ADSA analysis on systems of known interfacial tension compared with reported literature values from Goebel and Lunkenheimer (1997), along with RSS values of the droplet profile curve fits.

	ADSA Interfacial	Interfacial Tension,		
Hydrocarbon	Tension	RSS	from Literature	RSS
with Water	(mN m ⁻¹)	(m ²)	(mN m ⁻¹)	(m ²)
Hexane	43.2	0.51	51.4	0.76
Heptane	46.5	0.66	51.9	0.74

Table 4.2 also shows that the ADSA technique used under-predicts the interfacial tension values reported in the literature. This under-prediction of the interfacial tension is not surprising and may be explained by the presence of impurities in the hydrocarbon phase. In this study, no further purification was done on the chemicals as received from the

manufacturer, unlike in studies such as the one by Goebel & Lunkenheimer (1997). The values obtained are thus representative of the solvents as they will be used in the subsequent coreflooding experiments. Nevertheless, the interfacial tension values are sensible, thus validating the use of MRI for the ADSA technique. This technique was subsequently extended to systems which, as outlined earlier, cannot be imaged by conventional optical techniques. Figure 4.5 shows the fitted droplet profile curves for these systems, with the corresponding interfacial tension values reported in Table 4.3. The values obtained for the 'analogue' system are very similar to those for the ones with pure water, which confirms that the hexane/glycerol-water system is a suitable choice for the CO₂ analogue, as discussed in Section 4.3.1.

For the crude oil/water system, Buckley & Fan (2005) conducted IFT measurements on a wide range of crude oil samples with varying density and viscosity at a range of different pH values using the pendant drop method, with water as the continuous phase. They reported values for the crude oil/water interface ranging from around 15–25 mN m⁻¹ in the near-neutral pH range. In an earlier study Donaldson et al. (1969) reported IFT values for 43 crude oil samples with 0.1 M NaCl that ranged from 9.9–31.5 mN m⁻¹. Therefore the obtained value of 20.6 mN m⁻¹ from our study shows good agreement with previous literature values.

The interfacial tension values given in Table 4.3 allow the experimental Bond number (Bo) to be calculated for both the analogue systems under consideration. These values are compared, in Table 4.4, with the values for the supercritical CO₂/reservoir brine system. The values in the table show that the Bo values for both hexane and heptane are very close, and fall within the higher end of the required range. However, hexane/glycerol-water was preferred as the CO₂ analogue system, due to the lower viscosity of the 41 % glycerol-water solution $(3.85 \times 10^{-3} \text{ Pa s}, \text{ as against } 5.13 \times 10^{-3} \text{ Pa s}$ for the 47 % solution), thus making it easier to work with.



Figure 4.5 MRI images (slice thickness 1 mm) showing a drop of (a) 41 % glycerol-water solution ($\rho = 1107 \text{ kg m}^{-3}$) in hexane ($\rho = 654 \text{ kg m}^{-3}$) with an isotropic pixel resolution of 98 µm; (b) 47 % glycerol-water solution ($\rho = 1123 \text{ kg m}^{-3}$) in heptane ($\rho = 684 \text{ kg m}^{-3}$) with an isotropic pixel resolution of 98 µm; (c) water ($\rho = 996 \text{ kg m}^{-3}$) in crude oil ($\rho = 836 \text{ kg m}^{-3}$) with an isotropic pixel resolution of 70 µm. (d)-(f) show the extracted droplet profile (red crosses) and the fitted theoretical ADSA curve (blue line) for (a)-(c) respectively.

		ADSA Interfacial
Aqueous Phase	Hydrocarbon Phase	Tension (mN m ⁻¹)
41 % glycerol in water	Hexane	43.0
47 % glycerol in water	Heptane	40.1
Water	Crude oil	20.6

Table 4.3 Interfacial tension results from ADSA analysis on systems which cannot be imaged using conventional optical techniques.

Table 4.4 Expected Bo and Ca values for the 'CO₂ analogue' systems calculated using the experimentally obtained ADSA interfacial tension values, along with the values for the supercritical CO₂/reservoir brine system. The supercritical CO₂/brine Bond number was calculated using typical density and interfacial tension values obtained from ¹Metz et al. (2005) and ²Yang et al. (2005), respectively. The viscosity ratio values from Table 4.1 are also repeated.

	Experimental Bo	Viscosity Ratio	
	(× 10 ⁻⁴)	(-)	
Hexane/glycerol-water	1.65	0.075	
Heptane/glycerol-water	1.67	0.075	
Supercritical CO ₂ /reservoir brine ^{1,2}	0.68-1.71	0.05-0.10	

4.5 Conclusions

In this chapter, we have demonstrated the applicability of MRI techniques for obtaining droplet profiles which can subsequently be analysed to produce reliable interfacial tension measurements. This method was demonstrated on various fluid combinations, with the resultant data being consistent with literature values obtained using optical imaging of droplets. The method is particularly useful, however, for systems where conventional optical imaging techniques cannot be used, such as refractive-index-matched fluids or fluids with an opaque continuous phase, such as water in crude oil.

In addition, the interfacial tension measurements presented here were used to select a supercritical CO_2 analogue system consisting of hexane as the ' CO_2 ' phase and a 41 % glycerol in water solution as the aqueous phase. The analogue fluids were chosen based on matching the Bond number and viscosity ratio to the supercritical CO_2 /brine system. In the subsequent chapter, the use of the CO_2 analogue system for core flooding experiments in various porous media, such as glass bead packs and real rock cores, is presented.

4.6 References

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5 Capillary Trapping of a Supercritical CO₂ Analogue

5.1 Introduction

In this chapter we investigated the two-phase flow of the analogue system identified in the previous chapter, using three different porous media: a model porous medium consisting of a packing of 100 μ m glass ballotini, and core plugs of Bentheimer sandstone and Portland carbonate rock. MRI techniques such as T_1 inversion nulled 1D spin-echo profiles were used to quantify the relative saturation of the two phases over the whole sample and 2D spin-echo images were used to provide information on the spatial distribution of the two phases at various positions along the sample axis. Pulsed field gradient nuclear magnetic resonance (PFG NMR) was used to measure slice-selective chemically-resolved displacement propagators before and after capillary (residual) trapping of the CO₂ analogue. The different methods employed showed good agreement in terms of measuring the amount of residual trapping of the CO₂ analogue. The acquired NMR propagators in the Bentheimer sandstone samples were then compared to lattice Boltzmann (LB) simulations applied to various CO₂ analogue entrapment scenarios, in order to investigate the pore morphology and to determine whether the CO₂ analogue was entrapped preferentially in smaller or larger pores.

5.2 Background

The work presented here involved the use of both PFG NMR and MRI techniques to study two-phase immiscible flowing systems in porous media. The following literature review is therefore divided into two distinct sections, the first of which focuses on PFG NMR, and the second of which focuses on MRI techniques mainly involving the use of chemical shift or relaxation contrast between the two fluids.

5.2.1 PFG NMR

A comprehensive study of two-phase immiscible flow in porous media using PFG NMR was done by Tessier & Packer (1998), the aim of which was to evaluate the importance of wettability, spreading and phase saturations on the transport of fluid in porous media. Propagator measurements were acquired for two-phase (immiscible liquid) flow in Fontainebleau sandstone, resolving the oil and water NMR signals through their different chemical shifts to produce separate propagators for each phase (in this case brine and dodecane). In order to do this a '13-interval' APGSTE sequence similar to the one shown in Figure 3.4a was used (Cotts et al., 1989), but with the addition of a spin-echo at the end; this enabled acquisition of the (symmetrical) full echo, allowing the dispersion component of the signal to be eliminated upon Fourier transform. A number of different experimental scenarios were considered, such as obtaining single-phase propagators of each phase at different relative saturations (one phase was stationary), as well as propagators for the co-flow of oil and water through the sandstone. The simultaneous flowing of the two phases in the rock showed that as the water flowrate was increased, the propagators for fixed oil flow became more diffusion-like, with a stagnant peak dominating. This indicates that the sandstone was water wetting, as the observed propagators could be explained by the water forming a film on the grain surfaces of the rock (which increased in extent at higher water flowrates), thus isolating the non-wetting oil in the larger pores. Finally, a third (NMR-invisible) mobile phase, N_2 gas, was added, which preferentially occupied the largest pores (being the most non-wetting of the three fluids, as it is the least polar) and thus enhanced the residual trapping of the oil by reducing the available porosity for the other two phases. In this case, the propagator measurements probed these changes by showing an increase in the stagnant peak around zero displacement and the lengthening of the tails to long displacements as more fluid is trapped.

A further study on the sandstone sample used by Tessier & Packer (1998) was carried out by Holmes & Packer (2004), who investigated the scenario of co-currently flowing water and oil phases (hexane and dodecane) through the rock. The fraction of water in the injected fluid was varied from 0.06 to 1 and fitting to the attenuation of the PFG NMR echo signal allowed the stagnant fraction of the oil in the rock to be estimated. Their results showed an exponential decrease of the stagnant oil fraction with increasing observation time until reaching an asymptotic limit at $\Delta = 800$ ms. This decrease was explained by the fact that stagnant oil is present in both dead-end pores, which may allow an opening into bulk flow channels, and 'isolated' pores which are almost entirely cut off from the bulk flow. At lower observation times, it is expected that the diffusion of oil in dead-end pores allows it to move back into regions experiencing bulk flow; however, at the longer observation times, this effect becomes negligible as most of the remaining stagnant oil is trapped in isolated pores. Holmes & Packer (2004) also observed an increase in the stagnant oil fraction with increasing relative water saturation at equilibrium for a given observation time, which was consistent with the findings of the previous study by Tessier & Packer (1998).

Khrapitchev et al. (2002) acquired one-dimensional PGSTE NMR propagators, along with two-dimensional velocity exchange spectroscopy (VEXSY) data, of a water/silicone oil mixture flowing in a mono-disperse bead packing at different relative saturations. The propagator results for the stationary phase (water) showed a Gaussian distribution (as expected) at all but the shortest observation times, where the propagators were skewed towards positive displacements. This discrepancy is thought to be an artefact resulting from the spectral overlap between the water and silicone oil peaks, as only half echoes were acquired (as in the work presented in this chapter), meaning that the dispersion component of the signal could not be readily removed. Harris (2005), in his study of water invasion into initially hydrocarbon-saturated bead packs, overcame this problem by first acquiring purely diffusive single-phase signals for oil and water separately in the packing; these were subsequently compared with the echoes acquired for the two phases simultaneously. As oil was the stationary phase in the two-phase experiments, its contribution to the echo shape could be identified, thus allowing the real and imaginary components of the water echo to be isolated. This provided the relevant phase information necessary to construct single-phase propagators. More recently, Creber et al. (2009) fitted Voigt profiles to the NMR signal peaks in order to obtain chemically-resolved APGSTE NMR propagators for quantifying the transport of colloids (in a hexane in water emulsion) through mono-disperse bead packings of different sizes.

5.2.2 MRI

The main MRI techniques by which immiscible two-phase systems may be imaged are: (i) chemical-shift selective imaging; (ii) chemical-shift imaging (CSI); (iii) T_1 or T_2 relaxation contrast; (iv) using NMR inactive nuclei to eliminate one of the phases. In the work presented in this dissertation, techniques (iii) and (iv) were used. Nevertheless, for completeness, all four techniques are included in this review.

Chemical-shift selective imaging involves the use of soft r.f. pulses to excite a specific range of frequencies for either selective-excitation or selective-suppression of peaks corresponding

to different fluid phases within a chemically-resolved system. These techniques were used by Hall et al. (1984) in order to produce phase selective images of an ethanol/water phantom sample. Harris (2005) combined a selective-suppression pulse with RARE in order to image the invasion of water into initially hydrocarbon saturated glass bead packs.

The second technique, CSI, involves the acquisition of the full NMR spectrum at each phase encoded point in the image. This is done by removing the read gradient in a spin-echo imaging sequence (Section 2.2.7), for example. Hall et al. (1986) acquired 2D (one phaseencoding and one spectral-encoding dimension) CSI images of a composite Berea sandstone sample, with one half saturated with water and the other half with dodecane. Dereppe et al. (1991) extended this approach to a limestone (carbonate) rock with both fluids simultaneously present in the pore space; 3D CSI (one spectral-encoding and two phase-encoding dimensions) images were acquired of a water-saturated sample injected with oil, and vice-versa. More recently, Zhang & Balcom (2010) obtained high-resolution 2D CSI images with velocity encoding for water and methanol flow through a cylindrical micro-channel. While this technique has the advantage of being able to quantitatively measure the relative distribution of the two phases in the sample (provided there is chemical resolution between the different components), drawbacks include the relatively long acquisition time compared to other imaging methods and the rapid degradation of signal-to-noise ratio (SNR) at short T_2 .

Relaxation contrast techniques involve exploiting the difference in T_1 or T_2 between the two phases, often by adding a contrast agent (i.e. a dilute paramagnetic species) to lower the T_1 and/or T_2 of one of the phases; however, in some cases the natural contrast between the two fluids is sufficient. Differences in T_1 may be exploited using inversion nulling to remove the signal from one of the phases, as described in Section 5.3.2. This was demonstrated by Hall & Rajanayagam (1987), who used nulling to remove the water signal in 3D images of sandstones containing both water and dodecane. Alternatively, if the difference in T_1 is large enough then a short recycle time may be used to apply different T_1 weighting to each phase and thus obtain sufficient contrast in the images; this approach was used by Johns & Gladden (1998, 1999) to image the capillary trapping and subsequent dissolution of octanol ganglia in the pore space of a 5 mm glass bead packing. Alternatively, increasing the concentration of the contrast agent may lower the T_2 to such an extent that no NMR signal is apparent from the doped fluid. This technique was used by Baldwin & Yamanashi (1988) and Chen et al. (1988); the former acquired images of Berea sandstone samples with different concentrations of water (doped with Mn^{2+}) and oil, and the latter used Ni^{2+} doped water to study the imbibition and drainage of water and oil in an unconsolidated packing of crushed Pyrex glass.

The fourth commonly-used technique for imaging two-phase systems involves the use of a fluid which contains NMR inactive nuclei and is thus 'invisible' to NMR (as was done in Chapter 3 earlier). As the most commonly used nucleus is the proton (1 H), signal from water may be eliminated by using D₂O; this was done by Hall & Rajanayagam (1987) in their study on sandstone mentioned earlier, and also by Maddinelli & Brancolini (1996) in their study on the water flooding of highly heterogeneous carbonate rock cores, using D₂O to displace water from the core samples. Alternatively, it may be possible to use a deuterated or halogenated solvent, such as was done by Harris (2005), who used water to displace fluorinert from a bead pack.

From the above literature survey it is evident that the choice of techniques used for imaging two-phase systems depends on factors such as: the chemical-shift resolution and relaxation contrast between the different species, whether one of the phases is NMR-invisible, as well as practical considerations such as the acquisition time of experiments and the temporal resolution required if not imaging at steady-state. For the purpose of this work, as sufficient chemical shift and T_1 relaxation contrast was present between the two phases, the use of T_1 inversion nulling was considered appropriate (and simpler to implement than chemical-shift selective imaging) in order to quantitatively distinguish between the two phases in 1D profiles; for the 2D images, as obtaining quantitative data was not essential, the use of a short recycle time with spin-echo imaging was considered appropriate, as this technique would result in better signal-to-noise compared to faster imaging techniques such as RARE, which suffers from T_2 weighting effects. The use of chemical-shift imaging (i.e. pure phase-encoding) was considered, but was rejected as being impractical due to the long acquisition times (on the order of hours per image) required.

5.3 Experimental Methodology

5.3.1 Experimental setup

The 'supercritical CO₂ analogue' core flooding experiments were carried out on a 100 μ m borosilicate bead packing (of length 69 mm and diameter 37 mm), and on cylindrical core plug samples of two different kinds of rock: Bentheimer sandstone and Portland carbonate (both of length 60 mm, diameter 38 mm). Details about the bead pack and the Bentheimer sandstone are given in Chapter 3. The pore size distributions of Bentheimer sandstone and Portland carbonate, as measured by mercury intrusion porosimetry (MIP), are shown in Figure 5.1, which was provided by Dr Andy Sederman at the MRRC. As Figure 5.1 shows, Portland carbonate has a much broader pore size distribution compared to Bentheimer sandstone, and hence was chosen as the second rock type for this study. According to Verganelakis et al. (2005), Portland carbonate has a higher permeability (typically between 4–10 μ m²) than Bentheimer sandstone, and is characterised by a network of large, low tortuosity pores which form a preferential path for fluid flow. The porosity of this rock is reported in previous literature studies as 18.0 % (Verganelakis et al., 2005) and 18.5 % (Scheven et al., 2005b), although a direct measurement for the sample used in this study was not available.



Figure 5.1 Pore size distributions of Bentheimer sandstone and Portland carbonate rocks as measured by mercury intrusion porosimetry (figure supplied by Dr Andy Sederman).

The bead pack and core holder were connected to a flow rig consisting of two Teledyne ISCO model 260D syringe pumps to provide continuous flow when required, as described in Chapter 3. Two different solutions were pumped through at room temperature: an aqueous phase consisting of 41 wt% glycerol in water solution (referred to simply as 'glycerol-water'), and an immiscible oil phase consisting of hexane (the 'supercritical CO₂ analogue'). The typical pressure drop range of the fluids pumped through was between 1.2 and 2.8 barg.

5.3.2 NMR measurements

All NMR measurements were performed using a Bruker BioSpin AV85 spectrometer equipped with a 2 T horizontal-bore superconducting magnet, operating at a ¹H resonant frequency of 85.18 MHz. A birdcage radio frequency (r.f.) coil of 55 mm inner diameter and 204 mm length was used for signal excitation/detection.

A modified APGSTE pulse sequence with a 180° soft r.f. pulse for slice selection in the axial (flow) direction was used to acquire displacement propagators. Slice-selection was used as it has been shown to eliminate artefacts due to entry effects (e.g. dead zones at the sample inlet), as described in detail in Chapter 3. However, the acquired APGSTE echoes, unlike the ones presented in Chapter 3, have separate spectral peaks for the different fluid phases, and due to broadening of the peaks in the porous media, some spectral overlap occurs. In order to obtain chemically-resolved propagators therefore, the spectral data were read into MATLAB® and the different peaks selected based on chemical-shift. Profiles were then fitted to the peaks using a least-squares minimisation technique (Marquardt, 1963). The fitted line-shape was a Voigt function, as these have been shown to provide an accurate approximation to the Gauss-Lorentz line-shapes observed in NMR experiments (Grivet, 1997). This method has been used previously in the literature for two-phase (decane and water) propagators in a bead pack (Creber et al., 2009).

As described in Chapter 3, the effects of internal magnetic field gradients (caused by susceptibility differences between the pore-occupying fluid and the solid rock matrix) and surface relaxation cause the measured propagator to be distorted, both by removing fast-flowing spins and thereby supressing the measured mean displacement (in the case of internal field gradients) or by removing slow spins located near pore surfaces or trapped in

micropores and thereby enhancing the measured mean displacement (in the case of surface relaxation). In the case of the heterogeneous carbonate rock, these effects might lead to greater preferential loss of signal from smaller pores compared to sandstone. In order to obtain quantitative measurements in such samples it is therefore necessary to sample **q**-space efficiently, particularly in the pre-asymptotic flow regime, where a sharp peak in the NMR signal near q = 0 is observed due to the large range of displacements observed in the fastflowing channels of the rock. This peak is surrounded by broad 'diffusive wings' due to the stagnant regions of the rock where mainly self-diffusion occurs. In this work, therefore, two different ranges of q-space were acquired for the Portland carbonate propagators, corresponding to the inverse advection length-scale $2\pi/\langle\zeta\rangle_0$, where $\langle\zeta\rangle_0$ is the expected mean displacement, and the inverse diffusion length-scale $1/\sqrt{D_0\Delta}$, where D_0 is the diffusion coefficient and Δ is the observation time, to take into account fast-flowing and stagnant regions respectively. The different q-space ranges were combined in MATLAB® using cubic spline interpolation. This method has been shown by Scheven et al. (2005a) to significantly reduce distortions in propagator measurements on Portland carbonate at flowrates similar to the ones used in this work.

In order to provide an appreciable amount of T_1 contrast between the two phases for imaging, the aqueous phase was doped with a contrast agent, Mn²⁺ (in the form of MnSO₄.H₂O crystals). For the experiments in the bead pack and in the Bentheimer sandstone, a concentration of 3.9 mM Mn²⁺ was used, and a complexing agent, EDTA (Ethylene-diaminetetraacetic acid, in the form of Na₂.EDTA.2H₂O crystals) was added in a 2:1 mole ratio, with the EDTA in excess to prevent precipitation of the Mn-EDTA complex. The Mn-EDTA method is commonly used in the petroleum industry for measurements in rock (mainly sandstones) in order to prevent the Mn²⁺ ion reacting with the rock matrix (Robinson et al., 1974). A disadvantage of using EDTA is that it affects the water proton relaxation rate of Mn^{2+} due to complexation, meaning that a greater concentration of Mn^{2+} is needed to achieve the same reduction in T_1 (Oakes & Smith, 1981). However, in carbonates, the use of EDTA is not required (Horkowitz et al., 1997); hence for the experiments with Portland carbonate only, a Mn^{2+} concentration of 3.0 mM was used. For the propagator measurements, the glycerol-water solution that flowed through the sample was not doped, as the allowable observation time Δ is limited by T_1 . Due to the low molar concentrations of Mn-EDTA used it was assumed that the effect on interfacial tension could be ignored.

In order to obtain quantitative 1D NMR spectra and spin-echo profiles of the two-phase system, T_1 inversion nulling was used, which exploits the difference in T_1 between the two phases in order to remove the signal contribution to the echo of one of the phases. This method works well provided the difference in T_1 is sufficiently large. Figure 5.2 shows the pulse sequence used for acquiring 1D spin-echo profiles with inversion recovery; as the figure shows, the technique involves using a 180° r.f. pulse in order to put the spin magnetisation in the transverse axis, following a time delay, τ_{null} , after the initial 90° excitation pulse. The value of τ_{null} (i.e. the 'nulling time') is chosen such that the unwanted signal passes through zero when the 180° pulse is applied, which occurs when τ_{null} is equivalent to 0.693 (i.e. ln 2) × T_1 of the phase to be nulled. As the correct τ_{null} value can only be determined when the sample is saturated with both phases, a process which is irreversible, pre-saturated samples of each of the three different porous media were used for calibrating the inversion recovery sequence. Fresh, glycerol-water saturated samples were then used for the actual coreflood experiments.

In the work presented here, inversion nulling was used to eliminate the signal from the oil phase, thus making the profiles quantitative with respect to the amount of aqueous phase in the system. In order to account for errors in the pulse length of a single pulse, which can affect the performance of the inversion recovery sequence, a composite $90_x^{\circ}-180_y^{\circ}-90_x^{\circ}$ pulse (Levitt & Freeman, 1979) was used at the start of the sequence. 2D spin-echo images were also acquired, using a conventional spin warp imaging sequence as in previous chapters, with a short recycle time used to provide T_1 contrast between the two phases. These images were not quantitative.



Figure 5.2 Pulse sequence for 1D NMR spin-echo profile with T_1 inversion recovery. A composite 90_x° -180_y°-90_x° pulse is used at the start of the sequence.
In the Portland carbonate rock, due to the broad variations in pore size, the T_2 value of fluid in the rock varies spatially. In order to account for this variation, a CPMG echo train (Section 2.2.5) was added to the front of the pulse sequence shown in Figure 5.2. By acquiring a series of 1D profiles with *n*-echoes preceding it, where the value of *n* was increased between successive profiles, each profile can be 'pre-conditioned' with a different T_2 weighting. This allows a T_2 relaxation curve to be fitted to each point along the profile and thus extrapolated backward to obtain the signal intensity, I_0 , with no T_2 weighting. This technique, while allowing quantitative 1D profiles to be obtained, does reduce the temporal resolution that can be achieved without the use of T_2 pre-conditioning. The same principle was also applied to the 2D spin-echo images in order to remove the effects of T_2 weighting.

100 µm bead pack

Flow propagators were acquired from a selective-slice of thickness 14 mm, centred on the axial midpoint of the sample. The magnetic field gradient strength ranged from $g_z = -10$ to 10 G cm⁻¹ in 32 equally spaced steps. A range of observation times, Δ , were chosen: 250 ms, 500 ms, 750 ms and 1 s, each corresponding to a single propagator acquisition. The gradient duration was varied from $\delta = 5.0$ to 2.0 ms to provide a suitable bandwidth in *q*-space. The RT was 2.5 s, resulting in a total acquisition time of 5 min per propagator. The echo spacing was maintained at $2\tau = 10$ ms to provide consistent T_2 relaxation. All propagator measurements were repeated to ensure reproducibility.

1D spin-echo profiles with T_1 inversion nulling ($\tau_{null} = 320$ ms) were acquired along the sample in the *z*- (axial) direction, at a spatial resolution of 0.469 mm; a RT of 125 ms was used, resulting in a total acquisition time of 2 s. 2D spin-echo images in the *x*-*y* (transverse) plane of the sample were acquired with a data matrix size of 256 × 256 voxels for a field of view of 40 mm × 40 mm, thereby giving an isotropic spatial resolution of 156 µm. The slice thickness used was 2 mm and the RT used for imaging was 125 ms resulting in a total image acquisition time of 2 min 8 s. 2D images were acquired at several locations along the axis of the sample.

Bentheimer sandstone

For the Bentheimer sandstone, flow propagators were acquired from a selective-slice of thickness 14 mm, centred on the axial midpoint of the sample. The magnetic field gradient strength ranged from $g_z = -10$ to 10 G cm⁻¹ in 32 equally spaced steps. A range of observation

times, Δ , were chosen: 100 ms, 250 ms, 500 ms and 1 s, each corresponding to a single propagator acquisition. The gradient duration was varied from $\delta = 2.8$ to 0.7 ms to provide a suitable bandwidth in **q**-space. The RT used was 2.5 s, resulting in a total acquisition time of 5 min per propagator. An inversion delay of $\tau_{null} = 420$ ms used for inversion nulling; otherwise, the parameters used in the 1D profiles and 2D spin-echo images were the same as for the bead pack.

Portland carbonate

For the Portland carbonate, flow propagators were acquired from a selective-slice of thickness 14 mm, centred on the axial midpoint of the sample. **q**-space data were acquired at two different ranges, $|\mathbf{q}|_1$ and $|\mathbf{q}|_2$, in 64 equally spaced steps; the two ranges were then combined using a cubic spline interpolation function in MATLAB® to give the resulting propagator. Observation times, Δ , of 500 ms, 750 ms and 1 s were chosen. The RT used was 3.0 s, resulting in a total acquisition time of 26 min per propagator. Table 5.1 shows the different **q**-space ranges acquired along with the calculated values according to the criteria set by (Scheven et al., 2005a); for the inverse diffusion length-scale $1/\sqrt{D_0\Delta}$, the desired ranges could not be set as the maximum **q**-space value was limited by the available gradient strength of 10 G cm⁻¹. The mutual diffusion coefficient value for the glycerol-water mixture, 4.80×10^{-10} m² s⁻¹, was obtained from D'Errico et al. (2004). The available gradient strength also sets a lower bound on the observation times that can be acquired.

$\Delta / \mathrm{ms}^{-1}$	500	750	1000	
$2\pi/{\left<\zeta ight>_{0}}$ / $10^4~{ m m}^{-1}$	1.54	1.03	0.77	
$ q _1 / 10^4 \text{ m}^{-1}$	1.58	1.04	0.78	
$1/\sqrt{D_0\Delta}$ / $10^4~{ m m}^{-1}$	6.45	5.27	4.56	
$ q _2 / 10^4 \text{ m}^{-1}$	2.13	2.13	2.13	

Table 5.1 Calculated optimum q-space ranges for propagator acquisition in Portland carbonate, along with the actual ranges used in experiments.

 T_2 preconditioned 1D NMR spin-echo NMR profiles were acquired in the *z*-(axial) direction with a spatial resolution of 391 µm, with each complete acquisition consisting of 12 profiles, each preceded by a CPMG echo train with *n* echoes, where *n* was varied between 1 and 64.

The echo spacing used was $2\tau = 1$ ms. In addition, inversion nulling was used with $\tau_{null} = 450$ ms and the RT used was 100 ms, resulting in a total acquisition time of 37 s. 2D spin-echo images were acquired with a data matrix size of 128×128 voxels for a field of view of 62.8 mm × 62.8 mm, thereby giving an isotropic spatial resolution of 491 µm. A 12-point T_2 preconditioning was applied as for the 1D profiles, with an echo spacing of $2\tau = 2$ ms. The slice thickness used was 2 mm and the RT used for imaging was 100 ms, resulting in a total acquisition time of 11 min.

5.3.3 Experiments performed

The experimental procedure employed for the core flooding experiments was as follows: after placing the saturated sample in the r.f. coil of the NMR spectrometer, glycerol-water was flowed through it (at a volumetric flowrate, Q, of 6 ml min⁻¹ for the bead pack and 10 ml min⁻¹ for the sandstone and carbonate cores), and displacement propagators with slice selection were acquired at various observation times. Lower volumetric flowrates were used for the bead pack experiments as the Perspex cell used has a lower working pressure range than the rock core holder. The sample was then saturated with the doped Mn-EDTA solution and 2D spin-echo images were acquired at various positions along the sample axis, following which it was flooded with the supercritical CO₂ analogue (Q = 6 ml min⁻¹ for the bead pack and 10 ml min⁻¹ for the rock cores) until equilibrium was reached. 1D NMR profiles with T_1 inversion nulling were acquired before and after. The Mn-EDTA doped glycerol-water was then flowed through the system again ($Q = 9 \text{ ml min}^{-1}$ for the bead pack and 20 ml min⁻¹ for the rock cores) until residual hexane trapping occurred. 1D NMR profiles and 2D spin-echo images were re-acquired. The non-doped glycerol-water was then flowed through and displacement propagators were re-acquired at the same flowrate and observation times as previously. Table 5.2 shows a summary of the NMR protocols employed along with notes on their use.

Protocol	Notes	
1D NMR FID spectra	Acquired both without (for single-phase) and with	
	(for two-phase) inversion nulling	
1D NMR spin-echo profiles	Acquired both without (for single-phase) and with	

Table 5.2 NMR protocols used for single- and two-phase measurements.

	(for two-phase) inversion nulling. <i>T</i> ₂ preconditioning
	was added for the measurements in carbonate rock.
APGSTE NMR propagators (slice-	Acquired while flowing glycerol-water before and
selective)	after the residual trapping of hexane
2D NMR spin-echo images	Acquired for both the single- and two-phase systems
	at various slices along sample axis. T_2 preconditioning
	was added for the measurements in carbonate rock.
T_1 and T_2 measurements	Acquired using standard inversion-recovery and
	CPMG pulse sequences, respectively

5.3.4 Coreflood analysis

A coreflood interpretation method, as described here, was used to aid the interpretation of some of the data presented in this chapter. The method was proposed by (Goodfield et al., 2001) for analysing in-situ saturation data in the absence of external pressure drop measurements; it is applicable for two-phase immiscible displacements with a uniform immobile initial saturation, and assumes that the sample can be treated as a 1D homogeneous system. It aims to relate the local phase velocity to the relative permeability by accounting for the influence of viscous, gravity, and capillary forces. This method has been previously applied in studies on the two-phase flow of supercritical CO₂/water in glass bead packs and Berea sandstone (Suekane et al. (2006) and Suekane et al. (2009), respectively), as well as EOR studies of supercritical CO₂/oil displacement (Liu et al., 2011; Zhao et al., 2011) and oil/water residual trapping (Setiawan et al., 2012) in bead packs. The starting point for this method is Darcy's law for two-phase flow, in which the velocity of phase *i* can be expressed as follows:

$$U_i = -k\lambda_i \left(\frac{\partial p_i}{\partial z} + \rho_i g\right),\tag{5.1}$$

where λ_i is the mobility, of either glycerol-water (w) or hexane (o) in this case, defined by:

$$\lambda_{i} = k_{i} / \mu_{.} \tag{5.2}$$

The pressures in each phase are related through the capillary pressure, p_{cw} , according to the usual definition:

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$$p_{cw}(S_w) = p_o(S_w) - p_w(S_w).$$
(5.3)

As the volume change of the fluids (i.e. glycerol-water and hexane) due to pressure drop in the core is negligible, it can be assumed that the total Darcy velocity U(t) is known and thus the Darcy equation for each phase may be re-arranged in order to separate the pressure and fractional flow terms. Thus for the displacing phase, CO₂, this becomes:

$$U_{o} = U(t) \frac{\lambda_{o}}{\lambda_{w} + \lambda_{o}} \left(1 + \frac{kg(\rho_{w} - \rho_{o})}{U(t)} \lambda_{w} \right) - k \frac{\lambda_{o}\lambda_{w}}{\lambda_{w} + \lambda_{o}} \frac{dp_{cw}}{dS_{w}} \frac{\partial S_{w}}{\partial z},$$
(5.4)

At this point, we define the viscous-dominated fractional flow function, f_o , the gravity counter-current velocity function, G_o , and the capillary dispersion rate, d_{cpw} , thus:

$$f_o(S_w) = \frac{\lambda_o}{\lambda_o + \lambda_w},\tag{5.5}$$

$$G_o(S_w) = g(\rho_o - \rho_w) \frac{\lambda_o \lambda_w}{\lambda_o + \lambda_w}, \text{ and}$$
(5.6)

$$d_{cpw}(S_w) = -\frac{\lambda_o \lambda_w}{\lambda_o + \lambda_w} \frac{dp_{cw}}{dS_w},$$
(5.7)

Substituting the terms from Equations, (5.5), (5.6) and (5.7), Equation (5.4) may be written as

$$U_o = U(t)f_o(S_w) + kG_o(S_w) + kd_{cpw}(S_w)\frac{\partial S_w}{\partial z},$$
(5.8)

where the terms on the RHS are viscosity-, buoyancy- and capillary pressure-dependant, respectively. In particular, f_o represents the mobility ratio of CO₂, G_o takes into account the effect of buoyancy, and d_{cpw} corresponds to the counter-current flow term associated with capillary imbibition.

Alternatively, f_o and G_o may be combined into a single term, the gravity fractional flow, $f_o^{(G)}$, thus:

$$f_o^{(G)}(S_w, U) = f_o(S_w) + \frac{k}{U}G_o(S_w) .$$
(5.9)

This allows Equation (5.8) to be further simplified to

$$U_o = U(t)f_o^{(G)}(S_w, U) + kd_{cpw}(S_w)\frac{\partial S_w}{\partial z}.$$
(5.10)

The purpose of the above formulation of Darcy's equation for two-phase flow is to represent the phase velocity of the displacing fluid in terms of two independent functions, $f_o^{(G)}$ and d_{cpw} , which control the saturation in the core either in the case of constant U(t), as is the case here, or where the effect of gravity is small compared to viscous and capillary forces. It is this form, Equation (5.10), which will be used in the subsequently-described data analysis to determine the values of $f_o^{(G)}$ and d_{cpw} , and thus the relative effect of capillary and viscous forces respectively.

Data analysis

The coreflood data analysis was done using the numerical software MATLAB®. In order to implement the algorithm on a discrete data set, cubic spline interpolation was used to smooth the data for S_w as a function of z and t. The first part of the analysis involved using a 'mass balance' approach to calculate the local phase velocities. The phase volume of hexane per unit cross-sectional area, V_o , between the core inlet (z = 0) and current position z is given by

$$V_{o}(z,t) = \int_{0}^{z} \phi(z) S_{o}(z,t) dz , \qquad (5.11)$$

where S_o is the hexane saturation at position z and time t. Performing a mass balance over the sample allows the local hexane and water phase velocities to be expressed as:

$$U_o(z,t) = U(t)F_o^{\text{inj}}(t) - \frac{\partial V_o(z,t)}{\partial t}, \text{ and}$$
(5.12)

$$U_{w}(z,t) = -\frac{\partial V_{w}(z,t)}{\partial t},$$
(5.13)

where $F_o^{\text{inj}}(t)$ is the fraction of hexane injected into the sample at time *t*. In this case, the inlet stream comprises only hexane, so $F_o^{\text{inj}} = 1$.

For a fixed saturation level S_w^* , Equation (5.10) may be rewritten as:

$$U_{o}(z^{*},t) = U(t)f_{o}(S_{w}^{*}) + kd_{cpw}(S_{w}^{*})\frac{\partial S_{w}}{\partial z}\Big|_{z^{*},t},$$
(5.14)

where z^* represents the values of z in the z-t plane for a particular S_w^* . As U(t) is a constant in this work, Equation (5.14) gives $U_o(z^*,t)$ as a linear function of $\frac{\partial S_w}{\partial z}\Big|_{z^*,t}$; both these terms may

be calculated from the observed saturation data for different values of S_w^* and plotted against each other, enabling $f_o(S_w^*)$ and $d_{cpw}(S_w^*)$ to be evaluated by fitting a straight line to the data. There are two other possible scenarios: in the case of no capillary pressure, a horizontal (i.e.

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zero-slope) line is to be expected, corresponding to the conventional Buckley-Leverett solution (Buckley & Leverett, 1942). This situation arises when the flowrates are relatively high; in the case of low flowrates, the effects of capillary pressure lead to a 'smearing' of the saturation profile, as noted by Dullien (1992). Another special case occurs if the saturation value S_w^* corresponds to a stabilised front (i.e. a 'step function' between the displacing and displaced phases), in which case the data would be grouped around a single point.

5.4 LB Simulation Methodology

LB simulations were carried out on the 3D X-ray microtomography (XMT) Bentheimer sandstone lattice as described in Section 3.4.3 using the same apparent mean pore velocity of 0.69 mm s⁻¹ as in the NMR experiments. The resultant velocity images were used to simulate displacement propagators at a variety of observation times using the DRW algorithm outlined in Section 3.4.1. The diffusion coefficient used for the propagator simulations was that of the glycerol/water solution, i.e. 4.8×10^{-10} m²s⁻¹.

Different pore environments for 'CO₂ analogue' entrapment were then considered, using the same methodology as outlined in Section 3.4.2. Thus utilising the known experimental CO₂ analogue saturation from experiments, pores in the simulation lattice were switched from being glycerol-water saturated to being occupied by hexane until the percentage value for the experimental CO₂ analogue saturation was reached for the following scenarios: Scenario 1 – the smallest pores fill with hexane preferentially,

Scenario 2 – the largest pores fill with hexane preferentially and,

Scenario 3 – random allocation of pores to be filled with hexane.

Figure 5.3(c) and (d) shows this pore allocation for the corresponding slices shown in Figure 5.3(a) and (b) respectively. LB flow fields were then recalculated treating hexane-occupied pores effectively as solids and the propagators re-simulated and compared directly with corresponding experimental measurements.



Figure 5.3 (a) Transverse and (b) axial slices extracted from the simulation lattice. Pore space is shown in beige. (c) and (d) show the partitioning of the pore space into individual pores in the same slices as above, prior to allocation of selected pores as being 'filled' by hexane.

5.5 Experimental Results and Discussion

5.5.1 Single-phase flow

100 µm bead pack

Figure 5.4(a) shows the free induction decay (FID) spectrum for the glycerol-water saturated bead pack, with FWHM typically ~100 Hz for this system. The spectrum contains two peaks, with considerable spectral overlap, due to the different chemical shift of the OH protons (found in both the water and glycerol) and CH₂ protons (found only in glycerol). The OH peak is much larger, due to its greater spin density, by a ratio of about 3 to 1. It should be noted that all the NMR spectra presented in this chapter were referenced to TMS as zero frequency using data from the Spectral Database for Organic Compounds (SDBSWeb: http://sdbs.db.aist.go.jp, National Institute of Advanced Industrial Science and Technology, accessed on 16 October 2014) and are shown plotted in a non-standard way with the ppm scale increasing from left to right.

The signal peaks were resolved by fitting a Voigt line-shape to each one, as shown in Figure 5.4(a). Propagators were then obtained for each of the fitted peaks. Figure 5.4(b) shows an example of a propagator at $\Delta = 500$ ms for each of the OH and CH₂ peaks. It appears that the propagator shape for the CH₂ peak is shifted towards the left (i.e. lower displacements) compared to the one for the OH peak. This is most probably an artefact due to the spectral overlap between the two peaks, with the dominance of the OH proton peak leading to difficulty in separating the CH₂ contribution; such an effect was also observed by Khrapitchev et al. (2002) in two-phase measurements of the flow of silicone oil and water in bead packs. Another possibility could be the presence of more water molecules undergoing surface relaxation near pore walls, perhaps due to a higher affinity for the surface than glycerol; removal of these spins from the OH peak propagator would lead to an enhancement in the measured mean displacement relative to the CH₂ peak. Figure 5.4(c) confirms that the discrepancy between the CH₂ and OH peak propagators exists at all the different observation times used. For this study, the mean displacements used were calculated for the OH peak, as the signal from this peak predominates. Figure 5.5 shows the evolution of the propagator shape with observation time for the OH peak. As expected, a more 'Gaussian' shape is observed at longer observation times. The ratios of measured to expected mean displacements, θ , for the propagators shown in Figure 5.5 were 1.07, 1.11, 1.10 and 1.11 for $\Delta = 250, 500, 750$ and 1000 ms respectively, which is consistent with previous studies (e.g. Hussain et al., 2011; Scheven et al., 2005b).

Bentheimer sandstone

The single-phase propagators acquired for the Bentheimer sandstone are shown in Figure 5.6. Unlike in the bead pack, there is no chemical resolution between the different proton peaks of the glycerol-water solution, as Bentheimer sandstone has a much broader NMR spectral line-width – around 2.5 times that of the bead pack. For the propagators shown in Figure 5.6, the relative amount of stagnant to flowing water decreases with time and the flowing peak shape becomes more 'Gaussian' at longer observation times, as expected. The θ values of these propagators were 0.97, 0.99, 1.06 and 1.18 for $\Delta = 100$, 250, 500 and 1000 ms respectively, which is consistent with previous studies (Scheven et al., 2005b; Mitchell et al., 2008).



Figure 5.4 (a) FID spectrum for 41 % glycerol-water solution in a 100 μ m bead packing (black line). The red and blue lines show the fitted peaks for the CH₂ (glycerol) and OH (glycerol and water) protons, respectively. (b) APGSTE NMR propagators at $\Delta = 500$ ms for the CH₂ (glycerol, dashed line) and OH (glycerol and water, solid line) proton peaks in (a), respectively. (c) Mean displacements of the propagators CH₂ (glycerol, squares) and OH (glycerol and water, diamonds) proton peaks, respectively, at various observation times. The solid line shows the expected mean displacement.



Figure 5.5 NMR propagators for glycerol-water solution flowing in a 100 μ m bead pack at Q = 6 ml min⁻¹ at various observation times.



Figure 5.6 NMR propagators for glycerol-water solution flowing in Bentheimer sandstone at $Q = 10 \text{ ml min}^{-1}$ at various observation times. The probability distributions have been normalised by plotting the dimensionless function $P\langle \zeta \rangle \times \langle \zeta \rangle_0$ against $\zeta / \langle \zeta \rangle_0$.

Portland carbonate

In the Portland carbonate, the NMR spectral line-width was around 1.5 times that of the bead pack; hence, the CH_2 and OH proton peaks were convoluted, but resolution by peak-fitting was still possible (Figure 5.7). The evolution of propagator shape with increasing observation time for the OH proton peak is shown in Figure 5.8(a); it is observed that the propagator shape, which consists of a stagnant fluid peak and a long tail, is fairly similar at all observation times.



Figure 5.7 APGSTE NMR spectrum of 41 % glycerol-water solution in Portland carbonate (----), along with the fitted peaks for the CH₂ (glycerol) (···) and OH (glycerol and water) (----) protons, respectively.



Figure 5.8 (a) NMR propagators acquired for glycerol-water solution flowing in Portland carbonate at $Q = 10 \text{ ml min}^{-1}$ at various observation times. The probability distributions have been normalised by plotting the dimensionless function $P\langle \zeta \rangle \times \langle \zeta \rangle_0$ against $\zeta / \langle \zeta \rangle_0$. (b) Propagators for the flow of pure water at $Q = 10 \text{ ml min}^{-1}$ at an observation time of $\Delta = 500 \text{ ms}$ for two different Portland carbonate core plug samples.

The values of θ (based on a porosity of 18.5 % for Portland carbonate as reported by Verganelakis et al. (2005)) for the propagators shown in Figure 5.8(a) were 0.41, 0.48 and 0.53 for $\Delta = 500$, 750 and 1000 ms respectively, which seem unusually low compared to previously reported literature values (Scheven et al., 2005a, 2005b). This indicates that the carbonate rock sample used here is extremely heterogeneous. In order to illustrate this, Figure 5.8(b) shows a comparison of displacement propagators acquired at $\Delta = 500$ ms for the flow of pure water (in order to allow a more direct comparison with previous studies) at Q = 10 ml min⁻¹ in two different Portland carbonate cores: 'Portland 1', which is the core sample used in this study, and 'Portland 2', which was used in a previous set of experiments. From the figure, it can be seen that the ratio of stagnant to flowing water is much greater in the Portland 1 sample, which suggests that considerable variation in pore size distribution can be found not only within a particular carbonate core plug itself, but also between different core plugs of Portland carbonate. It should also be noted that the θ values measured for Portland 2 were 1.16, 1.33, 1.32 and 1.41 for $\Delta = 125$, 250, 375 and 500 ms respectively at the above-mentioned flowrate. These values are consistent with Scheven et al. (2005a), where an asymptotic value of $\theta = 1.4$ was seen at long observation times.

One reason for the propagator shape observed for Portland 1 may be that the effect of internal field gradients (which affect fast-flowing spins, leading to suppression of the measured mean displacement) is large. However, the fact that the tails of the propagators in Figure 5.8(a) are virtually identical at all observation times also suggests that the fluid in the channels is exiting the sample during the observation times used. The resulting truncation of the propagators means that the mean displacements obtained are not quantitative. However, further investigation is required to determine the exact cause of this discrepancy.

5.5.2 Two-phase flow

100 µm bead pack

After acquiring single-phase propagator measurements for the flow of glycerol-water through the bead pack, the Mn-EDTA complex was added to the solution in order to reduce its T_1 prior to injection of the 'CO₂ analogue' hexane; this reduced the T_1 value in the bead pack from 790 ms to 25 ms. Following this, approximately 3 pore volumes (PV) of hexane was flowed through the core at 6 ml min⁻¹ until an equilibrium saturation was reached. The Mn-EDTA doped water solution was then flushed through again at 9 ml min⁻¹ to leave some residual oil in the core. Figure 5.9(a) shows FID spectra acquired without any significant T_1 weighting (RT = 10 s) for each stage of this process. In order to provide a quantitative measure of the relative saturation of the oil and water phases in the Bentheimer sandstone core, T_1 inversion nulling was used to remove the hexane signal, as detailed in Section 5.3.2. Figure 5.9(b) shows FID spectra acquired both with and without inversion nulling, from which it is evident that the nulling removes the hexane signal more or less completely without affecting the glycerol-water signal, as desired. Figure 5.9(c) shows 1D profiles of relative glycerol-water saturation in the axial direction; the profiles were obtained from inversion nulled 1D NMR profiles, acquired under no flow conditions once equilibrium was reached, that were normalised with respect to a profile of the initially glycerol-water saturated sample. The profile obtained after flooding with hexane shows that the equilibrium (irreducible) glycerol-water phase saturation, S_{wi} , averaged over the entire sample, was 55 ± 1 %. There was, however, considerable variation over the sample length, with the relative glycerol-water saturation from z = 0 to z = 20 mm staying virtually constant at ~0.2, before rising sharply to ~ 0.5 at z = 27 mm and increasing steadily across the rest of the sample length to ~ 0.9 at the outlet. In contrast, the subsequent flooding with glycerol-water resulted

in an even spread of residually trapped hexane along the length of the sample, with an S_{or} value of 11 ± 1 %.



Figure 5.9 (a) NMR FID spectra acquired in the 100 μ m bead pack for the initially glycerol-water saturated sample (—), after flooding with hexane at 6 ml min⁻¹ (---), and after flushing through with glycerol-water at 9 ml min⁻¹ (···). (b) NMR FID spectra for hexane/glycerol-water mixture in the 100 μ m bead pack, acquired without (—) and with (···) inversion nulling. (c) Normalised 1D NMR profiles showing relative saturation of glycerol-water in the sandstone core after flowing through hexane at 6 ml min⁻¹ (---), and then after subsequently flushing through with glycerol-water at 9 ml min⁻¹ (···). The initial glycerol-water saturation in the core is assumed to be 1 (—). The slice-selective APGSTE displacement propagators were acquired within the region between the vertical dashed lines, and the vertical dotted line shows the position of the 2D spin-echo images.

In addition to the 1D profiles, 2D spin-echo imaging with a short RT was also utilised, in order to further visualise the spatial distribution of the fluids in the sample via the large T_1 contrast between the two phases; such images may be expected to show qualitatively the

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regions with greater hexane content, which will have lower signal intensity than the glycerolwater saturated regions. This is confirmed in Figure 5.10, which shows a comparison of FID spectra acquired at RT values of 10 s and 125 ms respectively after flooding with hexane, with a decrease of 74 % (obtained by fitting peaks) in the amount of signal from the hexane peak without any significant signal reduction for the glycerol-water phase. Quantification of these images in terms of relative saturation would involve knowing the distribution of fluids in each image pixel (such as could be measured using CSI techniques, as outlined in section 5.2.2); however, in this case, only the overall distribution of fluids is known, from FID spectra such as those shown in Figure 5.10, where the hexane peak at an RT of 125 ms contributes 27 % to the overall signal.



Figure 5.10 NMR FID spectra acquired of the 100 μ m bead pack sample after flowing hexane through at 6 ml min⁻¹ with a RT of 10 s (—) and 125 ms (…).

Figure 5.11 shows a set of such 2D images in an x-y (transverse) slice of thickness 2 mm centred on the axial midpoint of the sample. Figure 5.11(a) shows the initially glycerol-water saturated sample, which has quite spatially homogeneous signal intensity throughout the cross-section, as expected. Figure 5.11(b) shows the sample after flooding the core with hexane, where it can be clearly seen that most of the hexane content in the slice occurs in a single large channel near the top of the sample. It is also worth noting that in a separate run of experiments, as shown in Figure 5.11(e), the large hexane channel was located in the centre of the cross-section—indicating that it does not necessarily have to be located at the top of the sample. There is an overall reduction in signal intensity across the rest of the cross-section as well, indicating that breakthrough is not just occurring at one place, although no other

large channels were formed. Figure 5.11(c) shows the sample after flushing with glycerolwater to leave residually trapped hexane; here, as in the initially glycerol-water saturated sample, the signal intensity also appears quite uniform throughout the cross-section, although lower than in Figure 5.11(a). This data, along with the 1D relative saturation profiles shown in Figure 5.9(c), suggests that the large hexane channel is swept away, leaving behind an even distribution of residually trapped hexane through the sample cross-section. Figure 5.11(d) shows radial average signal intensity profiles for each of the images in Figure 5.11(a)-(c), which confirm the qualitative observations made above.

The error in the inversion-nulled 1D profiles was estimated by comparing the cumulative signal intensity of profiles of the initially glycerol-water saturated system acquired with and without inversion nulling, as the profile obtained without inversion nulling was considered an accurate measure of the total amount of aqueous phase within the sample. The profiles obtained with inversion nulling, however, may still contain some signal from the nulled phase (i.e. hexane). The comparison showed that a profile with inversion nulling contained 1 % more signal than that acquired without; thus, this value was taken as a representative error for these profiles, which were then converted into relative saturation profiles as shown in Figure 5.9(c). For the radial profiles shown in Figure 5.11(d) and (f), the error bars represent the standard deviation from the average signal intensity at a particular radius. The discrepancy is significantly higher for the profiles extracted from the images shown in Figure 5.11(b) and (e) (19 % and 68 %, respectively, compared with 7 % and 10 % for the images in (a) and (c), respectively); thus, it is evident that there are significant variations in radial saturation which are not captured by the 1D profiles shown in Figure 5.9(c), particularly after flooding with hexane, where the sharp rise in glycerol-water saturation after z = 20 mm indicates the presence of a large hexane finger.

The results shown in Figure 5.9 and Figure 5.11 suggest that viscous fingering, which is an instability at the interface between two fluids, occurs at the injection flowrates (and hence capillary numbers) used here, which is likely due to the large viscosity ratio between the bulk and injected fluids (Saffman & Taylor, 1958). The onset of viscous fingering, however, also depends on other factors, such the permeability and wettability of the porous medium and the system geometry and dimensions (Peters et al., 1981); the latter dependence in particular has implications for the scaling-up of results from experiments on core plugs such as in the present study; however, the relatively high flowrates used here encourage capillary trapping

of CO_2 , which is the main focus of this study. A more detailed discussion of the flow regime in these experiments is given in section 5.5.3.



Figure 5.11 2D NMR spin-echo images of the 100 μ m bead pack sample in the *x-y* plane (slice thickness is 2 mm) through the sample axial midpoint (total sample length is 69 mm) showing the sample: (a) saturated with glycerol-water; (b) after flowing hexane through at 6 ml min⁻¹; (c) after flushing through with water at 9 ml min⁻¹. The images are 256 × 256 pixels in size with a FOV of 50 mm × 50 mm. (e) A plot of the average radial intensity of the images in (a), (b) and (c), represented by the —, --- and … lines respectively. (d) Similar to (b), but from a different experimental run. (e) A plot of the average radial intensity of the image in (d).

Propagators were also acquired after residual trapping, using the same experimental parameters as described earlier, for a glycerol-water flowrate of 6 ml min⁻¹. As before, the different peaks were resolved by fitting a Voigt profile in order to obtain chemically-resolved propagators, Figure 5.12(a). A sample hexane propagator is shown in Figure 5.12(b), along with the corresponding propagator from the OH proton peak. As expected, the hexane propagator is centred on zero displacement; however, a slight deviation from the Gaussian shape occurs, with an asymmetry towards negative displacements. This artefact is similar to

that seen by Khrapitchev et al. (2002) and is a result of the error due to de-convolution of the peaks.

Figure 5.13 shows the propagators for the OH proton peak both before and after trapping. A shift in the propagator shape towards higher displacements is clearly visible at all the observation times, indicating that the residually trapped hexane is reducing the amount of available porosity for water flow, as expected. By plotting the mean displacements of the propagators against observation time before and after residual hexane trapping, it is possible to estimate the change in mean pore velocity from the lines of best-fit (Figure 5.14), resulting in a S_{or} value of 9.0 %, which underestimates by 2 % the value obtained earlier from the 1D profiles. However, some errors may be introduced in the measurement due to the deconvolution of the hexane and water peaks, as well as due to relaxation effects. Nevertheless, there is reasonable agreement between the two methods.



Figure 5.12 (a) FID spectrum for 41 % glycerol-water solution with residual hexane trapping in a 100 μ m bead pack (black line). The red, green and blue lines show the fitted peaks for the CH (hexane), CH (glycerol) and OH (glycerol and water) protons, respectively. (b) APGSTE NMR propagators at $\Delta = 1000$ ms for the CH (hexane, dashed line) and OH (glycerol and water, solid line) proton peaks in (a), respectively.



Figure 5.13 ¹H APGSTE NMR displacement propagators for 41 wt% glycerol in water solution flowing at 6 ml min⁻¹ through a 100 µm bead pack before (solid line) and after (broken line) trapping residual hexane in the core, shown at observation times of: (a) 250 ms, (b) 500 ms, (c) 750 ms and (d) 1 s.



Figure 5.14 Mean displacements of APGSTE NMT propagators acquired before (diamonds) and after (squares) residual hexane trapping in a 100 µm bead pack.

Bentheimer sandstone

After flowing glycerol-water through the sandstone core plug and acquiring APGSTE NMR propagator measurements, the Mn-EDTA doped solution was flowed through, following which the core was flooded with around approximately 5 PV of hexane at 10 ml min⁻¹ until equilibrium saturation was reached. The Mn-EDTA doped glycerol-water solution was then flushed through again at 20 ml min⁻¹ to leave some residual oil in the core. Figure 5.15(a)shows FID spectra acquired without any significant T_1 weighting for each stage of this process. Figure 5.15(b) shows FID spectra acquired without and with inversion nulling. Figure 5.15(c) shows axial (z) profiles of relative water saturation in the sample after flooding with hexane at 10 ml min⁻¹ and following the subsequent flushing through of glycerol-water at 20 ml min⁻¹; these show that S_{wi} goes down to 38 ± 2 % after flooding hexane and increases after the subsequent flooding with water, thus resulting in a Sor of 20 ± 2 % overall. It was also observed that in the interval of a few minutes after the hexane flooding but prior to flushing through with glycerol-water, the profile also showed a small shift in position with higher glycerol-water occupancy towards the latter half of the sample, although the overall relative saturation remained unchanged. This shift may have been due to the buoyancy of the hexane. Figure 5.15(c) also shows that the relative glycerol-water saturation is greater towards the latter part of the sample following the hexane flood. After residual trapping however, the glycerol-water saturation is fairly consistently spread along the core with a slight decrease from inlet to outlet.

As was previously done for the bead pack, 2D spin-echo images were acquired using an RT of 125 ms, which was sufficiently high to avoid any significant T_1 weighting for the aqueous phase, but reduced the amount of hexane signal (in a FID spectrum obtained after equilibrium) by 65 %, as shown in Figure 5.16(d). Figure 5.16 also shows a series of spin-echo images of an *x*-*y* slice of thickness 2 mm centred on the axial midpoint of the sample before, Figure 5.16(a), and after, Figure 5.16(b), flooding the core with hexane, and after subsequently flushing through with glycerol-water solution, Figure 5.16(c). Figure 5.16(b) clearly shows that although the overall signal intensity appears reduced over most of the cross-section, distinct hexane channels or fingers are present over large regions of the cross-section, which, as in the case of the bead pack, is likely due to viscous fingering. Figure 5.16(c) shows that after flushing with water these channels are mostly saturated back to their previous signal intensity, suggesting that the fluid within them is swept out, whereas most of the residual hexane trapping appears to occur outside these regions. Figure 5.16(e)

shows a plot of the average radial intensity of the images in Figure 5.16(a)-(c), which confirms that most of the decrease in signal intensity after hexane flooding was from the middle of the cross-section, and that this area has also recovered the most intensity after subsequently flushing through with glycerol-water. As was seen earlier for the bead pack, the discrepancy between the average signal intensities shown in Figure 5.16(e) and the standard deviations, represented by the error bars, was much higher (76 %) for the image with the fingering, Figure 5.16(b) than without (20 % and 23 % for Figure 5.16(a) and (c), respectively), thus highlighting the shortcomings of the 1D profiles shown in Figure 5.15(c) in capturing the extent of the radial variation in saturation due to the hexane fingers.



Figure 5.15 (a) NMR FID spectra of Bentheimer sandstone: initially glycerol-water saturated (—), after flooding with hexane at 10 ml min⁻¹ (---), and after flooding with glycerol-water at 20 ml min⁻¹ (···). (b) NMR FID spectra of Bentheimer sandstone acquired without (—) and with (···) inversion nulling. (c) Normalised 1D NMR profiles showing relative saturation of glycerol-water in the sandstone core after flowing through hexane at 10 ml min⁻¹ (---), prior to flooding with glycerol-water (---), and after flooding with glycerol-water at 20 ml min⁻¹ (···). Slice-selective APGSTE displacement propagators were acquired within the region between the vertical dashed lines, and 2D spin-echo images at the vertical dotted line.



Figure 5.16 2D NMR spin-echo images of the Bentheimer sandstone core sample in the *x-y* plane (slice thickness is 2 mm) through the sample axial midpoint (total sample length is 69 mm) showing the sample: (a) saturated with glycerol-water; (b) after flowing hexane through at 6 ml min⁻¹; (c) after flushing through with water at 9 ml min⁻¹. The images are 256×256 pixels in size with an isotropic spatial resolution of 195 µm. (d) shows NMR FID spectra acquired of the sample after flowing hexane through at 10 ml min⁻¹ with a RT of 10 s (—) and 125 ms (…). (d) shows a plot of the average radial intensity of the images in (a), (b) and (c), represented by the —, — and … lines respectively.

Figure 5.17 shows the propagators acquired both before and after trapping; a shift in the propagator shape towards higher displacements is clearly visible particularly at the longer observation times; at $\Delta = 100$ ms the change in propagator shape appears negligible due to the dominance of the stagnant peak. By plotting the mean displacements of the propagators against observation time before and after residual hexane trapping, it is possible to estimate the change in mean pore velocity from the lines of best-fit (Figure 5.18), resulting in a *S*_{or} value of 22 ± 1 %, which is in good agreement with the value of 20 % obtained from the 1D profiles, Figure 5.15(b), in the slice selected for propagator acquisition.



Figure 5.17 APGSTE NMR displacement propagators for 41 wt% glycerol in water solution flowing at 10 ml min⁻¹ through Bentheimer sandstone core before (solid line) and after (broken line) trapping residual hexane in the core, shown at observation times of: (a) 100 ms (b) 250 ms (c) 500 ms (d) 1 s.



Figure 5.18 Mean displacements of APGSTE NMT propagators acquired before (squares) and after (diamonds) residual hexane trapping in a Bentheimer sandstone core plug.

Portland carbonate

For the Portland carbonate sample, the same procedure was followed as for the sandstone: single-phase APGSTE NMR propagators were acquired for the flow of glycerol water solution, followed by the injection of Mn^{2+} doped glycerol-water. After injection of the doped solution, it was observed that the T_1 of the fluid inside the pores was reduced from 596 ms to 14 ms. In order to ensure that equilibrium was reached between the Mn^{2+} ions and the rock matrix, the sample was left overnight; the following day, the measured T_1 value had increased to 71 ms indicating that some of the Mn^{2+} was adsorbed on the rock surface. The doped glycerol-water solution was flowed through the sample again until an equilibrium T_1 value of 18 ms was achieved. The T_2 of the solution was obtained using a two-component fit with values of 5 ms and 41 ms. The core was flooded with around 75 ml of hexane at 10 ml min⁻¹ (~5.8 PV) until equilibrium saturation was reached. Figure 5.19(a) shows FID spectra acquired before and after the hexane flood.

Figure 5.19(b) shows the FID spectra without and with inversion nulling, demonstrating the elimination of the oil peak. Figure 5.19(c) shows an example of the two-component T_2 fit for a T_2 preconditioned 1D profile with inversion nulling, in order to account for spatial variation in T_2 along the sample length. Figure 5.19(d) shows a 1D profile of the relative glycerol-water saturation in the core after flooding with hexane; the profile was normalised with respect to one acquired of the originally glycerol-water saturated sample (the initial saturation was assumed to be 1). The profile shows that the glycerol-water saturation across the sample is relatively homogeneous; this may be due to the fast-flowing channels in the rock getting occupied preferentially by the hexane. The equilibrium value of S_{wi} went down to $64 \pm 3 \%$ after flooding with hexane. Glycerol-water was then flushed through the sample at 20 ml min⁻¹ until steady state was reached.



Figure 5.19 (a) NMR FID spectra acquired in the Portland carbonate for the initially glycerol-water saturated sample (—), and after flooding with hexane at 10 ml min⁻¹ (---). (b) NMR FID spectra for hexane/glycerol-water mixture in the Bentheimer sandstone, acquired without (—) and with (…) inversion nulling. (c) Example of a two-component T_2 fit, for a data point selected at the centre of one of the T_2 -preconditioned 1D profile (d) Normalised 1D NMR profile showing relative saturation of glycerol-water in the carbonate core after flowing through hexane at 10 ml min⁻¹ (---). The initial water saturation in the core is assumed to be 1 (—). The slice-selective APGSTE displacement propagators were acquired within the region between the vertical dashed lines.

Figure 5.20(a) shows FID spectra acquired before and after flushing with glycerol-water (RT = 10 s); the spectra show that the amount of oil signal decreased by ~64 %, which corresponds to a S_{or} value of ~13 %. However, a T_2 -preconditioned 1D profile with inversion nulling (RT = 100 ms, τ_{null} = 450 ms) acquired after the glycerol-water flushing actually shows a decrease in signal intensity compared to one acquired before; Figure 5.20(b) shows a comparison of the (un-normalised) I_0 profiles. This decrease in signal intensity may be due to a change in the relaxation properties of the doped glycerol-water solution in the rock pores after flowing it through following the initial hexane flood, and means that the resulting 1D

profile is not quantitative. Further work will need to be done in order to identify the exact cause of this reduction in signal intensity.



Figure 5.20 (a) NMR FID spectra acquired in the Portland carbonate after flooding with hexane at 10 ml min⁻¹ (red dashed line), and after subsequently flushing through with glycerol-water at 20 ml min⁻¹ (green dotted line). (b) T_2 preconditioned 1D NMR profiles with inversion nulling showing I_0 value of glycerol-water in the sandstone core after flowing through hexane at 10 ml min⁻¹ (red dashed line), and after subsequently flushing through with water at 20 ml min⁻¹ (green dotted line).

In order to visualise the spatial distribution of the fluids in the core, 2D spin-echo images (slice thickness 2 mm) with T_2 preconditioning were acquired of the sample at different positions along the sample axis (z = 6 mm, 18 mm, 30 mm, 42 mm and 54 mm) before and after flooding with hexane, and after the subsequent flooding with glycerol-water. The images of the initially glycerol-water saturated rock, Figure 5.21(a)-(e), show that the distribution of porosity in the rock cross-section is quite heterogeneous, and varies along the sample axial length. In particular, dark regions of low porosity are present frequently throughout the rock. There are also some (though fewer) bright regions consisting of groups of adjacent pixels which may correspond to features such as cracks or fractures in the rock through which fluid flows preferentially.

Figure 5.21(f)-(j) shows the corresponding slices in (a)-(e) after flooding with hexane. The short recycle time used decreased hexane signal by ~ 81 % (obtained by comparing FID spectra acquired with RT values of 10 s and 100 ms, respectively). The overall signal intensity in these images has decreased, although no clear patterns can be detected as the decrease appears to be spread fairly evenly throughout the cross-section, with the bright regions seen earlier becoming dark as well, which indicates that hexane is occupying these

regions. Figure 5.21(k)-(o) shows the set of images acquired after re-flooding with glycerolwater. The overall signal intensity has increased, as expected, and some of the bright regions seen previously are visible again, suggesting that these regions are, at least partially, resaturated with the glycerol-water solution. This is consistent with the interpretation that these regions represent large voids in the rock through which fluid flows preferentially.

To quantitatively identify the presence of the high-porosity features in the rock, a gating procedure was used, illustrated in Figure 5.22, for the images shown in Figure 5.21(e) and (o). First, a suitable threshold was identified for the image in Figure 5.21(e), which was high enough to include the bright regions. This was found to be at $I_0 = 8.71 \times 10^5$, two standard deviations above the mean signal intensity as shown on the signal intensity histogram in Figure 5.22(a), with the corresponding gated image (all pixels intensities below the threshold were assigned a value of 0) shown in Figure 5.22(b). However, as the overall signal intensity in the images after re-flooding with glycerol-water is lower than that in the initially glycerolwater saturated sample due to the presence of some residual hexane, the same threshold cannot be used for the image in Figure 5.21(o). Instead, a threshold of $I_0 = 7.23 \times 10^5$, which is two standard deviations above the mean signal intensity for this image, was used. The signal intensity histogram of this image, along with the threshold intensity, is also shown in Figure 5.22(a), with the corresponding gated image shown in Figure 5.22(c). Thus, the pixels that are common to the gated images in Figure 5.22(b) and (c) are likely due to the presence of high-porosity features in the rock that are almost fully re-saturated with glycerol-water—as opposed to, e.g., uncorrelated noise. This procedure was repeated for the images at each position along the sample axis and the results are shown in Figure 5.23, from which it is evident that the most prominent features are present in the images at z = 6 mm and z = 54mm along the sample axis, although some bright spots occur in all the images.



Figure 5.21 2D NMR T_2 preconditioned spin-echo images (showing the I_0 signal intensity) of the Portland carbonate core sample in the *x-y* plane (slice thickness is 2 mm) at different positions along the *z*-direction (total sample length is 69 mm), showing the sample: (a)-(e) saturated with glycerol-water; (f)-(j) after flowing hexane through at 6 ml min⁻¹; (k)-(o) after flushing through with water at 9 ml min⁻¹. The images are 128 × 128 pixels in size with an isotropic spatial resolution of 491 µm.



Figure 5.22 (a) Signal intensity histograms for the images shown in Figure 5.21(e) (blue solid line) and (o) (red dashed line). The vertical black dashed lines indicate the thresholds used for image gating. (b) and (c) show the gated images corresponding to Figure 5.21(e) and (o), respectively.



Figure 5.23 Pixel maps showing the location of identified high-porosity regions for the images shown in Figure 5.21 at different positions along the sample axis. The orange area represents the rock cross-section and the pixels representing the high-porosity regions are shown in white.

Figure 5.24 shows the propagators acquired before and after residual hexane trapping for the flow of glycerol-water at 10 ml min⁻¹ through the Portland carbonate core sample. The propagators acquired after trapping are virtually identical at all observation times used and are even more heterogeneous than the ones acquired before the trapping. This suggests that the residually trapped hexane may be occupying part of the channels in the rock, thus reducing the available cross-sectional area for the fast-flowing glycerol-water. As a result, more of the flowing solution exited the sample in the observation time, which further truncated the propagator shape as compared to before the hexane trapping. However, as discussed previously in section 5.5.1, these propagator shapes are not consistent with previously reported measurements in Portland carbonate.



Figure 5.24 APGSTE NMR displacement propagators for 41 wt% glycerol in water solution flowing at 10 ml min⁻¹ through a Portland carbonate core before (solid line) and after (broken line) trapping residual hexane in the core, shown at observation times of: (a) 500 ms (b) 750 ms (c) 1 s.

5.5.3 Coreflood analysis

Bead pack 100 µm

Here, the coreflood analysis method described in Section 5.3.4 was applied to in-situ saturation data in order to gain further insight into the relative importance of viscous and capillary forces on the two-phase immiscible displacement. Figure 5.25(a) shows 1D saturation profiles along the z-(axial) of the relative saturation of the glycerol-water phase at different time points, following hexane injection into the initially glycerol-water saturated bead pack at 6 ml min⁻¹ until equilibrium was reached. Figure 5.25(b) shows the total relative saturation as a function of time, with four distinct regions labelled as A, B, C and D. In region A, the glycerol-water saturation decreases only slightly; this corresponds in Figure 5.25(a) to a saturation reduction mostly near the sample inlet, which indicates start-up effects. The glycerol-water saturation decreases at a constant rate, dS_w/dt , of 0.0049 s⁻¹ at around t = 35 s as fluid enters the sample (region B). This is as expected with no breakthrough and a constant injection rate, and corresponds in Figure 5.25(a) to the rapid, almost 'piston-like' displacement flow of hexane through the sample. The 2D image shown in Figure 5.11 acquired after stopping the hexane flow indicate that a single large hexane channel is present. In the region between $S_w = 0.2$ to $S_w = 0.65$ in Figure 5.25(a), the relative saturation front appears to be advancing more slowly, suggesting the presence of smaller flow channels which are not absorbed into the bulk channel. The end of region B corresponds to breakthrough, at around t = 87 s, following which dS_w/dt decreases gradually (region C), until an equilibrium saturation of $S_{wi} = 0.55$ is reached (region D). The shape of the saturation profile, however, does change slightly in region D, with some of the hexane appearing to migrate towards the sample outlet and being balanced by glycerol-water moving in the opposite direction. Overall, at equilibrium most of the hexane content (\sim 77 %) is in the first half of the sample.

The hexane/glycerol-water saturated sample was subsequently flushed through with glycerolwater in order to leave residual hexane saturation, S_{or} . Figure 5.26(a) shows normalised 1D profiles along the *z*-(axial) direction showing the relative saturation of the glycerol-water phase at different time points following hexane injection, while Figure 5.26(b) shows the total relative saturation as a function of time, with three distinct regions which are labelled as A, B, and C. In region A, the value of dS_w/dt is constant at 0.0073 s⁻¹, which corresponds to the large hexane channel(s) formed earlier being swept out rapidly. The end of region A 156 corresponds to breakthrough, which is followed by region B, where the relative glycerolwater saturation reaches a maximum of 0.91 before decreasing slightly, leaving a residual hexane trapping, $S_{or} = 0.13$, at t = 104 s. The residual hexane saturation is distributed evenly through the sample, as evidenced from the 1D profiles. The equilibrium glycerol-water saturation value obtained from this experiment, 0.87, was slightly (~2 %) less than the value of 0.89 measured after switching off the glycerol-water flow, indicating that the relaxation weighting of the 1D profiles increased under flow conditions.



Figure 5.25 (a) Evolution of relative glycerol-water saturation along the sample length (with inlet at z = 0) with time for hexane injected into an initially glycerol-water saturated bead pack at 6 ml min⁻¹; (b) total relative glycerol-water saturation in the sample as a function of time, with different regions marked as A (blue triangles), B (red circles), C (black diamonds) and D (green asterisks).



Figure 5.26 (a) Evolution of relative glycerol-water saturation along the sample length (with inlet at z = 0) with time for glycerol-water injected into a bead pack with a relative glycerol-water saturation of 0.55 initially, at 9 ml min⁻¹. (b) Total relative glycerol-water saturation in the sample as a function of time, with different regions marked as A (blue triangles), B (red circles), and C (green asterisks).

The coreflood analysis method described in Section 5.3.4 was subsequently applied to the insitu saturation data shown in Figure 5.25. Figure 5.27 shows the local glycerol-water Darcy (superficial) velocity, U_w , across the sample at the time-points corresponding to the ones shown in Figure 5.25(a); as expected, the velocities are highest during region B, when most of the glycerol-water is displaced, before gradually falling across the sample as equilibrium is reached (though not completely reaching zero, particularly around the middle of the sample). It can also be observed that in region A, the glycerol-water velocities across the sample actually decrease between t = 17 s and t = 26 s, before increasing again in region B. In order to solve the saturation equation, Equation (5.14), $U_o(z^*,t)$ was plotted against $\frac{\partial S_w}{\partial z}\Big|_{z^*,t}$ for

different values of S_w^* ; an example of this is shown in Figure 5.28. As the figure, shows, a horizontal line was obtained, which corresponds to the Buckley-Leverett solution. This indicates that once the initial breakthrough of hexane occurs into the sample, the large flow

channel that is formed is mainly driven by viscous forces. In contrast, in low capillary number displacement flow, the non-wetting oil phase tends to disintegrate into blobs of residual oil (Larson et al., 1981).



Figure 5.27 Evolution of local Darcy phase velocity of glycerol-water with time, for hexane injected into a glycerol-water saturated bead pack at 6 ml min⁻¹ (corresponding to a superficial velocity of 0.093 mm s⁻¹).



Figure 5.28 Data scatter showing the direct solution of the saturation equation, Equation (5.14), at $S_w^* = 0.55$ using the coreflood analysis method, for hexane injected into a glycerol-water saturated bead pack at 6 ml min⁻¹. The horizontal line shows the mean value of $U_o(z^*,t)$ for this data.

A comprehensive study on two-phase immiscible displacements was done by Lenormand et al. (1988) on porous media micromodels using various fluid pairs of different physical properties. They found that for drainage flow (i.e. the displacement of a wetting by a non-

wetting fluid), the observed fingering patterns in a porous medium depend on the capillary number (Ca) and the viscosity ratio (M, defined as the ratio of the non-wetting fluid viscosity to that of the wetting one) in the following manner: at high Ca and M values, viscous forces in the wetting fluid dominate, leading to a stable displacement front; at low M values and intermediate Ca values, viscous forces in the non-wetting fluid dominate, leading to viscous fingering patterns; and at low Ca and intermediate-to-high M values, capillary forces dominate, leading to capillary fingering. A 'regime diagram' showing the values at which the transitions occurred was produced by Lenormand et al. (1988), according to which the transition between the viscous and capillary dominated regimes occurs at Ca values of $\sim 10^{-5} - 10^{-6}$ for an M value of 0.075, as used in this work; in comparison, the value of Ca here is 1.6×10^{-6} . However, as acknowledged by Lenormand et al. (1988) the exact boundaries of the different regions depend on the pore-size distributions and size of the network, and as shown by the results presented here, capillary forces do not dominate at the flowrates used in this study. For this reason, coreflood analysis data from the experiments with the sandstone and carbonate rock cores are not presented in this thesis. It is also worth noting that in a previous study by Suekane et al. (2009) in which supercritical CO_2 was injected into an initially water saturated Berea sandstone core (i.e. a similar porous medium to that used in this work), the capillary numbers used were on the order of 10^{-9} ; in that case, the coreflood analysis demonstrated that the flow was in the regime where capillary effects were significant. Thus, in order to use the coreflood analysis technique of Goodfield et al. (2001), the experiments presented in this chapter will need to be repeated at lower flowrates.

5.6 LB Simulation Results and Discussion

Here, we compare the LB simulated propagators in the BN 300 lattice with the results obtained from NMR experiments in Bentheimer sandstone. A qualitative overlay of the experimental and simulated propagators for the glycerol-water saturated sample is shown in Figure 5.29. The simulated propagators show excellent agreement with the experimental propagators at the lower observation times, in this case $\Delta = 100$, 250 and 500 ms. At the highest observation time $\Delta = 1000$ ms, the simulated propagator fails to predict the higher displacements; however, the discrepancy between the simulated and expected mean

displacements is only 6 %. The results are consistent with those shown in Section 3.6.2 for ordinary brine flow in Bentheimer sandstone.



Figure 5.29 Comparison of experimental displacement propagators (black line) with LB simulated propagators in the BN 300 lattice (grey line) for glycerol-water flowing in sandstone. Propagators were obtained at observation times of (a) $\Delta = 100$ ms, (b) 250 ms, (c) 500 ms, and (d) 1000 ms.

In order to model the displacement propagators post-hexane entrapment, the pore space of the simulation mask was filled according to the scenarios described in Section 4.4. The pores were filled up to a level of 21 % of the total pore volume in order to match the experimentally measured value. The LB simulated propagators for the different scenarios are shown in Figure 5.30 overlaid with the experimentally obtained propagators after hexane entrapment; qualitatively, it appears that the simulated propagators for scenario 2 (large pores filled) show the best agreement with the experimental propagators. It is, however, difficult to provide a good quantitative comparison of the experimental and simulated propagators without taking into account the 'corrected' (i.e. upper bound) moments, as defined in Chapter 3, which are unavailable here due to the absence of an independent measure of the sample porosity after

entrapment. Nevertheless, a quantitative comparison of these results was made by interpolating the simulated propagators at the ζ -values measured in the experiments and calculating the corresponding resulting residual sum of squares (RSS), as shown in Figure 5.31. These RSS values do suggest that the simulated propagators for scenario 2 show the best agreement with the experimental propagators in general, except at the smallest observation time, $\Delta = 100$ ms, which is dominated by the stagnant fluid peak. One possible explanation for this is that scenario 2 may lead to the blocking of a large dead-end pore or pores, thus removing a significant number of molecules undergoing self-diffusion from the simulation.



Figure 5.30 Displacement propagators obtained using APGSTE NMR for the flow of glycerol-water in the Bentheimer sandstone post-hexane entrapment (solid line) and simulated on the BN 300 lattice with 21 % of the pore space assigned to be CO₂ analogue according to the three scenarios (scenario 1 – red dashed line; scenario 2 – blue dotted line; scenario 3 – green dash-dot line) outlined in the text. Propagators were obtained at observation times of (a) $\Delta = 100$ ms, (b) 250 ms, (c) 500 ms, and (d) 1000 ms.


Figure 5.31 Residual sum of squares (RSS) values between the experimental and simulated propagators shown in Figure 5.30 for the different simulation scenarios as outlined in the text (scenario 1 – triangles, scenario 2 – crosses; scenario 3 – circles), at various observation times Δ .

To provide a more quantitative comparison of the experimental data and the different simulation scenarios for CO_2 trapping, as was done in Chapter 3, the ratio of the standard deviation of the propagators after trapping (shown in Figure 5.30), σ_1 , to that of the propagators before trapping (shown in Figure 5.29), σ_{0} , was calculated for both simulation and experimental data. The resultant σ_1/σ_0 ratios are plotted in Figure 5.32; again, scenario 2 shows the best agreement with experiments, with scenario 3 (random pores filled) falling between scenarios 1 (small pores filled) and 2. This indicates that hexane, being the nonwetting phase, preferentially occupies the larger pores, as expected. However, there is still a discrepancy between the experimental and simulated data. This discrepancy is most likely due to the fact that while larger pores are preferentially filled, some smaller pores are filled as well. Additionally, it is likely that the hexane does not occupy the entire pore; this may be due to the wetting water-glycerol phase forming a film on the grain surfaces of the rock, thereby isolating the hexane in the larger pores. As a consequence of these sources of error, the standard deviations (i.e. rms width) of the simulated propagators after trapping (Figure 5.30) were consistently larger than those of the experimentally-measured propagators. This, in addition to the fact that at larger observation times the simulator tends to underpredict the rms width for the single-phase (i.e. pre-trapping) propagators, as discussed in Chapter 3, means that the σ_1/σ_0 value for the simulations is always higher than that obtained experimentally.



Figure 5.32 Ratio of standard deviations of displacement propagators before and after pore space modification by CO₂ entrapment for different observation times, Δ ; comparison between experiments (squares) and simulation scenarios (scenario 1 – triangles, scenario 2 – crosses; scenario 3 – circles) outlined in the text is shown.

5.7 Conclusions

Capillary trapping of the supercritical CO₂ analogue occurred in the pore space of three different porous media: a model porous medium (packed bed of 100 μ m glass ballotini), and core plugs of Bentheimer sandstone and Portland carbonate rock. Quantitative measurements of the relative saturations in the samples were obtained using T_1 inversion-nulled 1D spinecho profiles to suppress the signal from the oil phase. The use of 2D spin-echo images with a short recycle time for T_1 contrast allowed a qualitative measure of the spatial location of the two phases within the core, as well as providing an insight into the two-phase displacement mechanism occurring. A coreflood analysis method was used to interpret the in-situ saturation data, and indicated that at the capillary numbers used in the experiments the immiscible displacement was mainly dominated by viscous forces.

In addition, chemically-resolved APGSTE NMR propagator measurements were acquired before and after capillary trapping which provided another quantitative measure (in the bead pack and sandstone) of the ' CO_2 analogue' phase entrapment via the change in mean displacement. These two methods showed good agreement in estimating the amount of residually trapped ' CO_2 analogue'. For the Bentheimer sandstone, interpretation of the differences in the propagators without and with CO_2 entrapment was facilitated by LB flow and propagator simulations applied to a 3D XMT lattice of a real sandstone rock core.

Different scenarios for CO₂ entrapment were considered in the simulations with occupation of the largest pores producing best agreement with the experimental data. In the Portland carbonate, due to heterogeneity within the pore structure, the 1D profiles and 2D images acquired were corrected for T_2 weighting by 'pre-conditioning' the acquisitions with a CPMG echo train. Propagator measurements acquired provided an insight into the pore structure of the carbonate but were not considered quantitative due to the extreme heterogeneity of the rock. This heterogeneity was also confirmed by the qualitative 2D images which showed regions of high signal intensity likely corresponding to naturally-occurring fractures in the carbonate rock which are filled up by the displacing CO₂ analogue phase preferentially. Finally, it was shown that for similar experimental conditions in both rocks, the amount of residually trapped CO₂ analogue in the Bentheimer sandstone was significantly higher (21 %) as compared to the Portland carbonate (13 %), suggesting that the more homogeneous structure of the sandstone favours the formation of CO₂ ganglia within the pore space.

In this chapter, we have shown how the use of a combination of PFG NMR and MRI experimental methods can allow probing of the change in transport properties of an aqueous phase caused by the capillary trapping of an immiscible phase in a porous medium, as well as quantitatively measure the extent of this trapping. We have applied these techniques to real rock cores such as may be encountered in sub-surface aquifers. These experimental data were subsequently used in conjunction with lattice-Boltzmann simulation methods in order to gain insight into the pore-scale trapping mechanisms of CO_2 in such porous media. In future this simulation method may be extended to include more complex pore-filling scenarios than single-fluid pore occupancy and to more heterogeneous rocks such as Portland carbonate. In addition, the coreflood experiments may be repeated at lower flowrates (and hence much lower capillary numbers) in order to investigate the effect of capillary forces on the two-phase immiscible displacement of supercritical CO_2 and water.

5.8 References

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6 Gravity Currents in Two-Layered Porous Media

6.1 Introduction

In this chapter, the effect of permeability heterogeneity on the flow of miscible gravity currents (i.e. flow driven by hydrostatic pressure gradients due to density contrast) in porous media is investigated, using MRI techniques such as 2D spin-echo imaging and phase-shift velocity imaging, which allow for the quantification of the amount of mixing between the bulk and injected fluids. Specifically, we consider strong vertical permeability heterogeneity, which is relevant for flow in underground rock formations where layers of different rock types, of varying permeabilities, may be present. In particular, such conditions are highly relevant for the injection of CO_2 into the sub-surface for storage, where mixing plays an important role in determining the amount of CO₂ sequestered, as well as for enhanced oil recovery (EOR) processes such as water-alternating-gas (WAG) EOR, where crossflow (i.e. flow perpendicular to the bulk flow direction) effects due to permeability differences can cause the injected fluid to bypass the oil phase, thus severely affecting recovery performance (Rogers & Grigg, 2000). The gravity currents studied here are those between ordinary water and brine; such gravity currents also arise at the interface between freshwater and brine in coastal aquifers (Cooper et al., 1964), where the intrusion of seawater into these wells can result in the loss of precious water supply to the populations surrounding those areas.

In order to investigate the effects of permeability heterogeneity on the fluid flow, quantitative MRI spin-echo images were acquired in a dual-layered porous medium showing the timeevolution of injected gravity currents with fixed inlet flux. The results show that above a certain critical inlet flowrate, the injected gravity current overrides the layer it is flowing in favour of a higher-permeability layer. In addition, velocity maps were acquired of the system in steady state which provided insight into the position where override occurs as well as on the relative amount of flux in the two layers. The experimental data obtained here on a 3D porous medium was used to validate a theoretical model developed by Huppert et al. (2013) for the transition of the injected current from gravity-driven flow to preferential flow in high-permeability regions. It is shown here that the model, which was developed for a 2D system, predicts the experimental data reasonably well. Finally, some preliminary results from a 3D CFD model of the two-layer system are presented, which also showed good agreement with experiments.

6.2 Literature Review and Background

Gravity currents have long been of interest due to their relevance in natural and industrial processes. Pioneering work on understanding the fluid mechanics behind them was done several decades ago; a comprehensive review may be found in Huppert (2006). The formation of natural gravity currents between brine and freshwater due to the problem of seawater (i.e. 'lateral intrusion') or deep saline groundwater (i.e. 'upward intrusion') infiltration into coastal aquifers has been studied extensively. Much of the work done in this area has focused on the coastal regions of the United States, Mexico and Canada, as reviewed by Barlow & Reichard (2010). In addition, brine and freshwater come into contact in estuaries, i.e. bodies of water at the interface of rivers and seas, where a so-called 'salt wedge' may be formed by the layering of the less-dense river water on top of the seawater. The resultant velocity gradients at the interface of the salt wedge cause upward mixing of the seawater with the freshwater, as studied experimentally on a lab-scale by Grigg & Ivey (1997). A similar mixing process occurs when estuary water comes into contact with freshwater aquifers. This can lead to the transfer of nutrients between the water bodies, thus affecting the local quality of groundwater, as shown in the finite-element modelling study of Smith & Turner (2001). Apart from the natural processes outlined above, man-made applications involve the injection of less-dense fluids into confined saline aquifers, e.g. for freshwater storage or wastewater disposal (Gelhar et al., 1972). In addition, the injection of CO_2 into deep saline aquifers for sequestration is likely to cause some brine displacement as not all the CO_2 will dissolve. This displaced brine may subsequently seep into nearby shallow freshwater aquifers, causing groundwater contamination, as highlighted by Walter et al. (2012).

The effect of permeability variations on gravity currents was studied by Huppert & Woods (1995), who considered flow within shallow porous layers bounded by impermeable rocks, such as those found in sub-surface aquifers. More recently, Cinar et al. (2006) investigated the interplay of capillary, viscous and gravitational forces on multi-phase (isooctane-water

and isooctane-water/isopropanol) fluid displacements in a thin two-layered bead pack using relevant scaling parameters such as the Bond number (as defined in Chapter 4) to characterise the crossflow between the different phases for high- and low-IFT systems and various cell orientations. They then used two different models, a two-dimensional finite-difference simulator and a streamline simulator (Berenblyum et al., 2003) to simulate their experimental data, which showed broadly the same transitions between the different flow regimes as seen in experiments. In the context of CO_2 sequestration, Neufeld & Huppert (2009) developed a model for propagation of a CO_2 gravity plume in a porous medium bounded from above by a thin layer of lower permeability. They then extended the model to consider flow in multi-layered strata; a schematic of the process is shown in Figure 6.1. However, despite the fact that such layers are present in real oil and gas wells, as shown by time-lapse seismic imaging of industrial-scale CO_2 injection into the Sleipner gas field in Norway (Arts et al., 2004; Bickle et al., 2007), there is no 3D experimental data to validate the model.



Figure 6.1 Schematic illustration of a CO₂ plume rising in a reservoir with multiple layers. A constant flux of buoyant fluid is injected beneath the first horizon under which it spreads asymmetrically and through which it drains. The spatially integrated drainage through each layer is then input as a timedependant flux into the subsequent layer. At each layer the spread of the buoyant CO₂ is illustrated by the solid line, while the vertical dashed line indicates the lateral extent of the plume. Reproduced from Neufeld & Huppert (2009), Figure 11.

Calculation of critical override velocity

The work presented in this chapter builds on previous work done on a two-layered system by researchers at the Department of Applied Mathematics and Theoretical Physics (DAMTP) in Cambridge (Huppert et al., 2013), who found that injection of a dense fluid into the lower layer ($k_l < k_u$, where the subscripts *l* and *u* denote the lower and upper layers respectively) of a two-dimensional Hele-Shaw cell above a certain 'critical' inlet flowrate caused the gravity current in the lower layer to flip over to the high permeability layer, thus overriding the lower layer in spite of the density difference between the bulk and injected fluids. Huppert et al. performed experiments over a large range of permeability ratios Λ (= k_u / k_l) and found that the 'critical flux' Q_c at which the gravity current flips into the higher permeability layer correlates with the permeability ratio between the upper and lower layers, Λ , according to:

$$Q_{C} = c(\Lambda - 1)^{-n}, \tag{6.1}$$

where the values of the fitted constants c and n were found to be 0.93 and 0.34 respectively. This is illustrated in Figure 6.2, where the fitted line for Q_C clearly demarcates the boundary between the non-overriding and overriding regimes. The system was modelled by defining the non-dimensional flux Q (in a Hele-Shaw cell) as follows:

$$Q = \frac{q/H}{u_b},\tag{6.2}$$

where *q* is the dimensional flux (in $m^2 s^{-1}$) and *H* is the depth of the lower permeability layer. Here, u_b is the characteristic buoyancy velocity of the injected fluid:

$$u_b = \frac{k_l g'}{v},\tag{6.3}$$

where $g' \equiv g\Delta\rho/\rho$ is its effective gravity and *v* is the kinematic viscosity.

In addition, Huppert et al. (2013) found good agreement between experimentally measured values of permeability of glass bead packs and theoretical values predicted using the Cozeny-Karman correlation (Bear, 1988), which characterises the permeability, k, of a mono-disperse packing of spheres as:

$$k = \frac{d^2}{180} \frac{\phi^3}{(1-\phi)^2} \,, \tag{6.4}$$

where d is the bead size and ϕ is the porosity. In the current study therefore, the permeabilities of the different layers of glass beads were predicted using Equation (6.4), with

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porosity measured gravimetrically for each bead size. As the work in this study was conducted in a three-dimensional system, it was further assumed that the column side-length to particle diameter ratios, ranging from 19 to 62, were sufficiently high to ignore wall effects (i.e. a region of higher porosity at the wall corresponding to a lower packing fraction). The dense (i.e. having a specific gravity greater than 1), miscible fluid used in these experiments was KCl brine. KCl was chosen as it does not change the viscosity of water (i.e. 8.9×10^{-4} Pa·s under room conditions) at the concentrations used in this work (Kestin et al., 1981); thus, the flow in water-saturated porous media is driven only by density difference. The densities of the doped brine solutions and the DI water were measured gravimetrically as 1.007 g cm⁻³ and 1.015 g cm⁻³ (for the 2 wt% and 3 wt% solutions respectively), and 0.996 g cm⁻³ (for the water). The acceleration due to gravity, *g*, was taken as 9.81 m²s⁻¹; substituting the values of the other variables into Equations (6.3) allowed the value of u_b to be calculated. However, as the model described above is two-dimensional, the definition of *Q* in Equation (6.5) was modified to:

$$Q = \frac{q/H.W}{u_b},\tag{6.5}$$

where W is the width of the cell (= 37 mm), in order to be dimensionally consistent with an inlet volumetric flowrate q in ml min⁻¹.



Figure 6.2 Regime diagram separating overriding currents (diamonds) from non-overriding currents (triangles), plotted using data from Huppert et al. (2013). The dotted line shows the critical flux Q_c .

6.3 Experimental Methodology

6.3.1 Experimental setup

The porous media used for these experiments consisted of two distinct average particle sizes (of either glass beads or sand) layered one on top of the other in a rectangular box-shaped Perspex cell of square cross-section (inner sides 37 mm) and length 130 mm. The cell contained removable end caps and an 8.0 mm diameter hole in the top for pouring in the beads, which was sealed using a plastic screw (see Figure 6.3). It was originally packed under de-ionised (DI) water to prevent the formation of air bubbles; the lower layer was packed and consolidated by tapping the cell, before the beads in the upper layer were slowly poured in from the top and spread out by gently shaking the cell so as not to disturb the lower layer. However, this method did not allow a uniformly horizontal interface between the two layers to be generated; this is visible in Figure 6.3(a), where the interface shows a 'dip' in the middle of the cell. This issue was overcome in subsequent experiments by setting the lower layer in Polyethylene Glycol (PEG) (Sigma Aldrich), a waxy semi-solid at room temperature that melts at 25 °C and is water-soluble. The lower layer was filled under molten PEG with the cell in a water bath at 45 °C, before being refrigerated at 11 °C; this solidified the PEG and allowed the top layer to be packed under cold water without disturbing the bottom layer. The cell was then replaced in the water bath to re-melt the PEG and flushed with warm water until the PEG was completely removed. The cell was then allowed to cool to room temperature (~20 °C) before placing it in the NMR spectrometer. This method allowed a smooth horizontal interface to be generated between the two layers and is very reproducible. In this chapter we present the results obtained both using the PEG method for obtaining a horizontal interface between the two layers, as well as preliminary results obtained using a non-uniform interface.

Glass beads

Two different sets of bead sizes (referred to as Set 1 and Set 2) were used for these experiments; Set 1 consisted of 2.0 mm beads in the upper layer and 1.0 mm in the lower layer and Set 2 consisted of 1.0 mm in the upper and 0.6 mm in the lower layer. The corresponding values of Λ were 5.0 and 2.3 for Set 1 and Set 2, respectively. The

corresponding porosities and permeability values for the different beads sizes, calculated using Equation (6.4), are shown in Table 6.1.



Figure 6.3 Dual-permeability flow cell for the AV-85 viewed from: (a) side-on; (b) front-on.

 Table 6.1 Porosity and Permeability values for the different bead sizes used in the dual layers

 experiments. The porosities were measured gravimetrically and the permeabilities calculated using

 Equation (6.4).

<i>d</i> /mm	ϕ	k / μ m ²
2.0	0.420	4870
1.0	0.399	979
0.6	0.417	426

The experiments with the non-uniform and the uniform interface between the two layers were carried out with KCl concentrations of 3 wt% and 2 wt % for the injected fluid, respectively. The lower salt concentration was chosen for later experiments in order to minimise the effect of the paramagnetic salt on the tuning of the r.f. probe, which can lead to a lowering of the signal-to-noise ratio in the MR images. For the experiments with the non-uniform layer the value of *H* was taken as an average of the layer height at the start and middle of the cell; hence for these experiments the calculated q_c value is not exact, but is useful as an approximate value of the required critical inlet flowrate.

Sand

The cell was packed using the PEG method described in Section 6.3.1 and two different grades of crushed silica sand (David Ball Group plc) were used: sand B (particle size range of 0.6 mm to 1.18 mm) in the lower layer and sand C (0.3 mm to 0.6 mm) in the upper layer. The porosities of sand B and C were measured gravimetrically to be 0.395 and 0.390, respectively. It was shown by [huppert1995gravity] that a gravity current from a fixed-flux source spreading in a two-dimensional porous layer propagates according to the following similarity solution:

$$X_{N}(T) = \eta_{N} T^{\frac{2}{3}}, \tag{6.6}$$

where η_N is a constant with a value of 1.48, and the dimensionless groups X_N and T representing the front position of the current and time, respectively, are defined by:

$$X_N = \frac{x_N}{S_H} \text{ and } T = \frac{t}{S_T}.$$
(6.7)

The horizontal and temporal scaling parameters S_H and S_T are given by

$$S_{H} = \left(\frac{q}{\phi^{1-\alpha}u_{b}^{\alpha}}\right)^{1/(2-\alpha)} \text{ and } S_{T} = \left(\frac{q}{(u_{b}^{2}/\phi)}\right)^{1/(2-\alpha)}, \tag{6.8}$$

respectively. In the case of a fixed flux $\alpha = 1$, substituting into Equation (6.6), x_N may be written as

$$x_{N} = \eta_{N} \left(\frac{qkg'}{\phi^{2}\nu}\right)^{\frac{1}{3}} t^{\frac{2}{3}}.$$
(6.9)

Thus, by plotting x_N as a function of $t^{2/3}$ for a given gravity current, the permeability k of the porous medium may be determined from the slope of the best-fit line.

6.3.2 NMR measurements

For the NMR experiments, the cell was placed in a birdcage r.f. coil of length 195 mm and inner diameter 80 mm inside a Bruker AV-85 NMR Spectrometer with a resonant frequency of 85.18 MHz for the ¹H nucleus. Fluid was pumped through the sample using a Teledyne ISCO model 260D syringe pump with a pump controller.

In order to use suitable MRI techniques to visualise the ingress of fluid into the porous medium sample, a contrast agent was employed; this reduced the T_1 relaxation time of the brine and thus provided T_1 contrast between the bulk and injected fluids. In the experiments presented here the common contrast agent Gd³⁺, obtained in the form of Gadolinium (III) Chloride Hexahydrate (GdCl₃.6H₂O) crystals, was used. Gd³⁺ was preferred over other contrast agents such as Mn²⁺ as it reduces the T_2 relaxation time to about the same level as the T_1 , unlike Mn²⁺ which causes the T_2 value to fall much more rapidly than the T_1 , thus limiting the echo time (ET) and precluding the use of rapid imaging sequences such as RARE.

The brine solution was doped with 2.7 mM Gd³⁺ (0.1 wt% GdCl₃.6H₂O), which reduced its T_1 value to ~29 ms, in contrast with the measured value of 2.75 s before doping. However, when the doped solution was flowed through the cell the first time, it was found that once in contact with the glass beads the T_1 value of the solution increased after some time. This indicated that Gd³⁺ ions were adsorbing on the surface of the beads, thus reducing the concentration of Gd³⁺ in the bulk solution. In order to ensure that an equilibrium adsorption of Gd³⁺ on the surface of the beads was reached (thereby ensuring that the concentration of Gd^{3+} in the doped brine solution would not be reduced on contact with the beads), it was necessary to soak both bead sizes in a concentrated solution of GdCl₃ for at least 24 hours prior to the experiments. The beads were then washed with DI water prior to packing in the flow cell, which means that any effects on density of the bulk fluid due to the adsorbed GdCl₃ may be considered insignificant. The T_1 values of the bulk water in the initially watersaturated sample were ~ 1.2 s and ~ 250 ms in the upper and lower layers, respectively. While these values are significantly lower than the 'expected' bulk water T_1 value of ~2 s (measured in each bead size prior to soaking in GdCl₃), there was still sufficient T_1 contrast between the bulk and injected fluid for imaging purposes. In later experiments with the uniform two-layer

interface, the spin-echo images were made quantitative by calibrating the NMR signal intensity with the concentration of Gd^{3+} in the brine under room conditions. In order to do this, a series of images (with RT = 15 ms, the same used in experiments) were acquired for a uniformly saturated two-layer sample at different concentrations of Gd^{3+} . The images were normalised using a spin-echo image acquired without T_1 weighting, in order to correct for the effect of spatial variations of porosity in the sample on the distribution of signal intensities in the image. The average signal intensity at each concentration was then calculated from a group of pixels in the centre (relatively homogeneous r.f. region) of the image. Figure 6.4 shows the resulting calibration curve relating normalised signal intensity to Gd^{3+} concentration. Error bars were estimated from the standard deviation of the signal intensity.



Figure 6.4 Calibration curve relating normalised NMR spin-echo signal intensity to Gd³⁺ concentration, for dual layer sample with 2.0 mm beads in the upper layer and 1.0 mm beads in the lower layer.

The imaging technique used for these experiments was conventional 2D spin-echo imaging with a short Recycle Time (RT). Although the use of this pulse sequence does limit the speed of signal acquisition compared to 'fast' imaging techniques such as RARE and FLASH, the spin-echo pulse sequence is easy to use and robust, and the imaging timescales achieved were considered adequate for these experiments. The images acquired were 128 x 64 pixels in size with a field-of-view (FOV) of 100 mm in the *z*- (read) direction and 50 mm in the *y*- (phase) direction, giving an isotropic spatial resolution of 0.781 mm in the read and phase directions. The RT used was 15 ms corresponding to a time delay of 3.88 s between successive image acquisitions.

Phase shift images of the sample were acquired at steady-state using a velocity encoding pulse sequence (see Section 2.2.8). These images were 128 x 32 pixels in size with a field-of-view of 100 mm in the read (*z*-) and 50 mm in the phase (*y*-, *x*-) directions, giving a spatial resolution of 0.781 mm in the read and 1.56 mm in the phase directions. Velocity was encoded in both the axial flow (*z*-) direction and the vertical (*y*-) direction for each slice orientation. The observation time, Δ , used was 12 ms and the gradient application time, δ , was 5 ms. The velocity encoding gradient, *g*, was varied from -10.7 to 10.7 G cm⁻¹ and the RT used was 100 ms, resulting in a total acquisition time of 45 s. The resulting velocity maps were obtained by subtracting phase shift images for the system with no flow from those of the flowing system in order to account for zero-offset (see Section 2.2.8 for more details). All experiments were repeated twice to ensure reproducibility.

6.3.3 Experiments performed

In the imaging experiments, fluid was injected into the lower layer of the cell at a constant volumetric flowrate using a Teledyne Isco 260D syringe pump, through the inlet shown in Figure 6.3. Fluid entered the sample through 1/8" outer diameter tubing which is separated from the packing by a nylon mesh with 10 µm holes. Image acquisition commenced after switching the flow on. After acquiring a time-series of images at a particular flowrate, the system was flushed through with de-ionised (DI) water in order to restore the cell to its initial water-saturated state before repeating the experiment. A range of different inlet flowrates were used for each system.

6.4 Simulation Methodology

The simulation work described in this section was performed by Dr Ruina Xu and coresearchers at Tsinghua University and is preliminary work aimed at providing a limited comparison with some of the experimental results presented here. The 3D model was developed using the commercial CFD package ANSYS® Fluent. The model used the finite volume method with the SIMPLE velocity-pressure coupling algorithm (Patankar & Spalding, 1972) and second-order discretization for the advection terms and transient terms. The simulation domain was based on the flow cell described in Section 6.3.1 and used a hexahedral mesh with 434760 nodes, Figure 6.5, which was refined near the interface of the two layers. The simulations considered the systems of glass beads, with the porosities and permeabilities of the different layers set to match the values in Table 6.1.



Figure 6.5 Simulation mesh for CFD model of the two-layer system in ANSYS® Fluent.

For modelling purposes, the displacement process between the bulk and injected fluids was treated as KCl mass transfer in a single aqueous phase. As the flow rates considered are relatively small, the convection-dispersion equation (CDE) was used to describe the mass transfer process, while the Navier-Stokes equations were used to describe the flow process. Three assumptions were made for the calculation of buoyance: (1) viscous dissipation in the flow was neglected; (2) all fluid properties were assumed constant except for density and viscosity; (3) it was assumed that density only changes in the buoyance term of the momentum equation, while remaining constant in the other terms. The KCl solution density, ρ , varies with the solute concentration, c, according to:

$$\rho = \rho_0 + 6.4233c_{\perp} \tag{6.10}$$

where ρ_0 is the density of pure water. The viscosity, μ , can also, like ρ , be written as a function of *c* by fitting the data obtained from Lide (2004):

$$\mu = (10039945 - 12.8756c + 12.0825c^2 - 5.105c^3)/10^6.$$
(6.11)

As the buoyance term in the y-direction varies with concentration, the effect of buoyance was taken into account by defining the effective pressure, p_{eff} , thus:

$$p_{\text{eff}} = p + \rho_0 g y. \tag{6.12}$$

The momentum equations in porous media may then be expressed, in the x-, y-, and z-directions respectively, as

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$$\frac{\partial \rho_0 u}{\partial t} + \nabla \bullet \left(\rho_0 u U\right) = -\frac{\partial p_{eff}}{\partial x} + \nabla \bullet \left(\mu_{eff} \nabla u\right) - \frac{\mu}{k} u , \qquad (6.13)$$

$$\frac{\partial \rho_0 v}{\partial t} + \nabla \bullet \left(\rho_0 v U \right) = -\frac{\partial p_{eff}}{\partial y} + \nabla \bullet \left(\mu_{eff} \nabla v \right) - \frac{\mu}{k} v - 6.4233 gc, \text{ and}$$
(6.14)

$$\frac{\partial \rho_0 w}{\partial t} + \nabla \bullet \left(\rho_0 w U \right) = -\frac{\partial p_{eff}}{\partial z} + \nabla \bullet \left(\mu_{eff} \nabla w \right) - \frac{\mu}{k} w, \tag{6.15}$$

where μ_{eff} is the Brinkman effective viscosity (Brinkman, 1949) and k is the permeability of porous media. In addition, the CDE is written as

$$\frac{\partial c}{\partial t} + \nabla \bullet (cU) = \nabla \bullet (D\nabla c), \tag{6.16}$$

where D is the effective diffusivity tensor of KCl in water saturated porous media, including both the effects of molecular diffusion and dynamic dispersion. For simplicity, the longitudinal and transverse dispersivity were set as constants, at 1 mm and 0.1 mm respectively.

6.5 Results and Discussion

6.5.1 Glass beads, Set 1

Uniform interface

In this set of experiments, the cell was packed with Set 1 of the glass beads ($\Lambda = 5.0$) using the method described in Section 6.3.1 whereby the lower layer was set in PEG in order to provide a uniformly horizontal interface between the two layers, as illustrated in the MRI image shown in Figure 6.6. 2 wt% KCl brine doped with 2.7 mM Gd³⁺ was injected into the lower layer at flowrates of 1, 2, and 10 ml min⁻¹ and a time-series of spin-echo images was acquired at each flowrate, which were converted into concentration maps, as shown in Figure 6.7, using the calibration curve determined earlier (Figure 6.4). The error in the concentrations was estimated to be \pm 7.5 % using the relative standard deviation in signal intensity of an image of the sample fully saturated with 2.7 mM Gd³⁺. However, in the concentration maps it can also be observed that some speckling occurs in the upper layer, corresponding to voxels where the concentration appears to be unusually high; this is an artefact related to the low local porosity in some of the voxels, and may be improved by spatially averaging the signal intensities in the particular regions where speckling occurs. From Figure 6.7 it appears that at q = 1 ml min⁻¹ the injected current stays in the lower layer, whereas at q = 2 ml min⁻¹ some fluid breaks through into the upper layer, suggesting that the critical flowrate, q_c , for this system occurs at around 2 ml min⁻¹, which shows reasonable agreement with the value of 2.47 ml min⁻¹ predicted using the correlation of Huppert et al. (2013). The discrepancies which do exist between the work presented here and that of Huppert et al. (2013) are likely due to differences in geometry and position of the fluid inlet between the two systems. Furthermore, at q = 10 ml min⁻¹, it appears that some of the brine flowing in the top layer falls back into the lower layer (as can be seen in the frame at t = 147 s in Figure 6.7(a)); this phenomenon, known as Rayleigh-Taylor fingering, arises due to the unstable stratification of a dense fluid overlaying a lighter fluid.



Figure 6.6 Spin-echo MRI image (slice thickness 10 mm) in the *y*-*z* plane, taken through the centre of a two-layer sample with 2.0 mm beads in the upper layer and 1.0 mm beads in the lower layer.



Figure 6.7 Time-series of concentration maps obtained from calibrating the signal intensity of spin echo MRI images taken in the *y*-*z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a dense gravity current consisting of 2 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a) 1 (b) 2 and (c) 10 ml min⁻¹ into the lower layer of an initially water-saturated two-layer system. The upper and lower layers consisted of 2.0 mm and 1.0 mm beads, respectively. Flow is from left to right and the total sample length is 130 mm. The red broken line shows the position of the interface between the two layers. Injection starts at t = 0.

In order to further investigate the longer-term behaviour of the overriding gravity current, the sample was shifted in the r.f. coil so that the imaging field-of-view included the latter half of the flow cell. The experiment with KCl brine injected at 10 ml min⁻¹ was then repeated with the new, downstream, imaging region. Figure 6.8(a) shows a frame extracted from the time-series of images in which Rayleigh-Taylor fingers can be clearly seen; to further illustrate this observation, 1D profiles were showing the cumulative Gd^{3+} concentration in the lower layer were extracted from the time-series (e.g. Figure 6.8(b) shows a profile extracted from the area highlighted by the red box in Figure 6.8(a)). Figure 6.8(c) shows the profiles as a function of time, whereby the presence of two 'fingers' can be clearly seen.



Figure 6.8 (a) Concentration map obtained from calibrating the signal intensity of a spin echo MRI image taken in the *y-z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a dense gravity current consisting of 2 wt% KCl brine doped with 2.7 mM Gd³⁺ at 10 ml min⁻¹ into the lower permeability layer of an initially water-saturated two-layer system. The upper and lower layers consisted of 2.0 mm and 1.0 mm beads, respectively. Flow is from left to right and the total sample length is 130 mm. (b) 1D profile extracted from the region highlighted by the red box in (a). (c) Profiles of cumulative Gd³⁺ concentration in the lower layer along the sample length as a function of time. Rayleigh-Taylor fingers falling from the upper to lower layer are circled in red.

In addition to the mainly qualitative interpretations discussed so far, the MRI data shown in Figure 6.7 may also be used to obtain quantitative information relating to the displacement and mixing of the two fluids. As an example, consider the image shown in Figure 6.9(a) extracted from the time-series for the experiment at q = 10 ml min⁻¹. The overall extent of the injected brine current in each layer may be determined by the number of pixels with intensity above that of the initial water-saturated sample. The threshold values of Gd³⁺ concentration, determined using a histogram of intensities in the image at t = 0 in Figure 6.7(c), were 0.42 mM and 0.64 mM for the lower and upper layers, respectively. However, due to dispersion, the interface between the bulk water and injected brine is not sharp, but consists

of a 'mixing zone' (Galeati et al., 1992). This is illustrated in Figure 6.9(b), which shows a zprofile through the lower layer at y = 4.7 mm; as the profile shows, the average Gd³⁺ concentration in the brine current, $[Gd^{3+}]^{inj}_{avg}$, is close to the injected value, $[Gd^{3+}]^{inj}_{0}$, of 2.7 mM until around z = 18.7 mm, which is the start of the mixing zone. Hence, the relative amount of mixing between the injected brine and the bulk water, normalised by $[Gd^{3+}]^{inj}_{0}$, may be expressed as:

Relative mixing (%) =
$$\frac{[Gd^{3+}]_{0}^{inj} - [Gd^{3+}]_{avg}^{inj}}{[Gd^{3+}]_{0}^{inj}} \times 100, \qquad (6.17)$$

i.e., the change in concentration of the injected brine current. Thus, in the limit of pure displacement flow, the relative mixing is zero; else, if mixing occurs, the relative mixing value will vary between 0 and 100 %.



Figure 6.9 (a) Concentration map taken from the time-series shown in Figure 6.7(c), showing the injection of a dense gravity current consisting of 2 wt% KCl brine doped with 2.7 mM Gd³⁺ at 10 ml min⁻¹ into the lower permeability layer of an initially water-saturated two-layer system. The red broken line shows the position of the interface between the two layers. (b) 1D profile extracted from the position indicated by the white broken line in (a). The vertical dashed lines indicate the boundaries of the mixing zone between the injected and bulk fluids.

Figure 6.10 shows both the overall displacement of the bulk water by injected brine current as a percentage of the image field-of-view, as well as the relative mixing, in each layer as a function of time at the different flowrates used. At q = 1 ml min⁻¹ (Figure 6.10(a) and (d)), flow is mostly concentrated in the lower layer, although at ~400 s after injection some fluid starts to enter the upper layer. The relative mixing value in the lower layer decreases with time before approaching a steady value of 42%. In comparison, at q = 2 ml min⁻¹ (Figure 6.10(b) and (e)), which is closer to the critical flowrate, the injected fluid starts to

enter the upper layer at ~100 s, and the relative mixing in the lower layer decreases faster than before, reaching a steady value of 20 %; in both cases, however, the relative mixing is higher in the upper layer, and follows the same trend as that in the lower layer. At the highest flowrate, q = 10 ml min⁻¹ (Figure 6.10(c) and (f)), which is well above q_c , the injected fluid starts flowing in the upper layer almost immediately after injection. Here also, the relative mixing behaviour appears different from the previous two cases, reaching a minimum value of 15 % in the lower layer before overtaking the mixing in the upper layer at t = 116 s to reach a steady value of 32 %. This enhanced mixing in the lower layer may be attributed to the Rayleigh-Taylor fingering seen earlier in Figure 6.7 and Figure 6.8.



Figure 6.10 Displacement, (a)-(c), and relative mixing, (d)-(f), in the lower (blue solid line) and upper (red dashed line) layers of the two-layer system shown in Figure 6.7 for injection of a dense gravity current consisting of 2 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a),(d) 1 (b),(e) 2 and (c),(f) 10 ml min⁻¹ into the lower layer of the initially water-saturated system. Injection starts at t = 0.

The spin-echo images presented here allowed the critical flux governing the transition between the overriding and non-overriding current regimes to be determined. However, these images do not provide information about the flux entering the upper layer, which would allow calculation of the relative distribution of the injected fluid in the porous medium, nor about the position where the override occurs; such information may be of interest for applications such as the geological sequestration of CO_2 . For further characterization of the two-layer system therefore, net phase-shift velocity images—which can quantify the velocities of the fluid near the interface between the two layers—were acquired, as described in Section 6.3.2. To provide an appreciable phase shift for the technique to work, an injected brine flowrate of 10 ml min⁻¹ was used. However, as the acquisition time for the velocity images was relatively long, the images could only be acquired after a steady-state was reached whereby both layers were saturated with the doped brine. Sample slices were acquired in the y-z and z-x planes; a slice thickness of 10 mm was used as this thickness allowed the velocity to be averaged over several bead diameters and ensured an adequate signal-to-noise ratio. The y-z slice was chosen through the centre of the sample and the z-xslice was chosen such that it included the interface between the two layers. The resultant velocity images are shown in Figure 6.11(a) and (b) for the y-z and x-z planes, respectively. The error in the velocity images was estimated as ~0.011 mm s⁻¹ based on the standard deviation in a phase map with no flow.

Figure 6.11(a) shows that the fluid velocities are higher close to the inlet, and that downstream of the inlet the average velocity in the upper layer, 0.30 mm s⁻¹, is higher than that in the lower layer, 0.10 mm s⁻¹. It is also evident that wall effects are significant in the upper layer due to the relatively large bead size, thus creating a region of higher permeability near the top of the cell through which fluid flows preferentially. If the fluid inlet is assumed to be an ideal point source, the velocities may be expected to follow a radially-dependant profile, with the velocity at a hemispherical surface at a distance *r* away from the source given by

$$\mathbf{u} = \frac{q}{2\pi r^2 \phi} \,\hat{\mathbf{r}} \,. \tag{6.18}$$

Using this simple source flow estimate, the expected velocities through the *x-y* slice shown in Figure 6.11(b) may be calculated; these are shown in Figure 6.11(c), with a comparison between experimental and predicted width-averaged vertical velocities along the sample length shown in Figure 6.11(d). As the figure shows, the source estimate under-predicts the width-averaged velocities by factor of about 2, as the upward velocities in Figure 6.11(b) do not follow a radial profile but are spread evenly across the sample width. In addition, wall effects are also present, as indicated by the higher velocities near the edges of the image,

which increases the observed velocities further. As a result, the vertical flux through the twolayer interface was calculated from Figure 6.11(b) to be 7.0 ml min⁻¹ (cf. the predicted flux of 3.5 ml min⁻¹), which means that over half of the fluid entering the sample goes into the upper layer.



Figure 6.11 2D velocity images (slice thickness 10 mm) of the two-layer sample shown in Figure 6.7, with 2 wt% KCl brine doped with 2.7 mM Gd³⁺ injected into the lower layer at 10 ml min⁻¹, in slices through the: (a) *y*-*z* plane, showing the *z*- (flow direction) velocity; (b) *x*-*z* plane showing the *y*- (upward) velocity. The position of the fluid inlet and the location of the *x*-*z* slice for the velocity image shown in (b) are indicated in red in (a). (c) Predicted velocities through the slice shown in (b) using a simple source estimate. (d) Width averaged *y*-velocities along the sample axis, showing a comparison between experimental (red line) and predicted (blue line) values.

Non-uniform interface

In these experiments, 3 wt% KCl brine was injected into the lower layer at flowrates of 2.5, 5, 10 and 20 ml min⁻¹ and time-series of spin-echo images were acquired at each flowrate, as shown in Figure 6.12. The images were not acquired through the centre of the sample but at an offset of 11 mm in order to select a slice with a relatively even distribution of the two layers. The acquired images were normalised using a phantom sample of identical dimensions to the test cell but filled with water, in order to correct for inhomogeneity in the r.f. field. The images at t = 0 show the initially water-saturated sample at the start of each experiment. For the experiment at 2.5 ml min⁻¹ it was observed that the injected gravity current stayed in the lower layer due to its higher density compared to the bulk fluid, thus indicating that q was below the critical value. At 5 ml min⁻¹ it appeared that the current had started to break through into the upper layer, thus indicating that Q was near the critical

value. At 10 ml min⁻¹ and 20 ml min⁻¹ the fluid is clearly flowing preferentially in the upper layer, indicating that $q > q_c$. Thus the critical flux for this system appears to be close to the value of 4.62 ± 1.45 ml min⁻¹ predicted using the correlation of Huppert et al. (2013). The corresponding displacement curves are shown in Figure 6.13, for threshold normalised signal intensity values of 0.09 and 0.13 in the lower and upper layers respectively. These curves are consistent with the ones shown earlier for the uniform interface (Figure 6.7), which suggests that the tilt of the interface does not have a significant effect on the overriding behaviour of the current. However, as the signal intensity of these images was not calibrated to Gd³⁺ concentration, the corresponding relative mixing curves could not be calculated.



Figure 6.12 Time-series of spin echo MRI images taken in the *y*-*z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a dense gravity current consisting of 3 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a) 2.5 (b) 5 (c) 10 and (d) 20 ml min⁻¹ into the lower layer of an initially water-saturated two-layer system. The upper and lower layers consisted of 2.0 mm and 1.0 mm beads, respectively. Flow is from left to right and the total sample length is 130 mm. The red broken line shows the position of the interface between the two layers. Injection starts at *t* = 0.



Figure 6.13 Displacement in the lower (blue solid line) and upper (red dashed line) layers of the two-layer system shown in Figure 6.12 for injection of a dense gravity current consisting of 3 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a) 2.5 (b) 5 (c) 10 and (d) 20 ml min⁻¹ into the lower layer of the initially water-saturated system. Injection starts at t = 0.

6.5.2 Glass beads, Set 2

Uniform interface

A similar set of experiments to those outlined in the previous section for Set 1 were also performed for Set 2 ($\Lambda = 2.3$), whereby 2 wt% KCl brine was injected into the lower layer at flowrates of 0.5, 1, 2, and 10 ml min⁻¹ and a time-series of spin-echo images was acquired at each flowrate. These images were then converted into concentration maps, as shown in Figure 6.14. The 'bright spots' in the images, which can be seen in Figure 6.14, are attributed to background noise present in the vicinity of the NMR spectrometer when the measurements were carried out. The effect of this noise was to produce a regular interference pattern in the **k**-space data (perhaps characteristic of the presence of electronic equipment such as a pump in the vicinity of the spectrometer); however, we were unable to determine its source. Nevertheless, The images show that the critical velocity for this system appears to be close to 1 ml min⁻¹, which is over-predicted by the value of 2.13 ml min⁻¹ from Huppert et al. (2013)'s two-layer correlation.

The corresponding displacement and relative mixing curves for this system are shown in Figure 6.15, for threshold Gd3+ concentration values of 0.23 mM and 0.27 mM in the lower and upper layers, respectively. At q = 0.5 ml min-1, i.e. below q_c , the injected current in the lower layer is driven mainly by displacement flow, reaching a steady relative mixing value of 14 % at ~600 s after injection, when approximately 30 % of the lower layer is occupied by brine. However, as the flowrate is increased to 1 ml min⁻¹, which is close to the relative mixing appears to be much higher, decreasing only gradually to a steady value of 22 % in the

lower layer at around ~ 1200 s after injection, which suggests the presence of a large mixing zone; this is supported qualitatively by the images shown in Figure 6.14(b) and (c). At this flowrate, relative mixing in the upper layer is higher than that in the lower layer, but follows the same trend. However, as the flowrate is increased further, the mixing in the lower layer starts to overtake that in the upper layer, which is consistent with the results shown previously in Figure 6.10 for Set 1.



Figure 6.14 Time-series of concentration maps obtained from calibrating the signal intensity of spin echo MRI images taken in the *y*-*z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a dense gravity current consisting of 2 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a) 0.5 (b) 1 (c) 2 and (d) 10 ml min⁻¹ into the lower layer of an initially water-saturated two-layer system. The upper and lower layers consisted of 1.0 mm and 0.6 mm beads, respectively. Flow is from left to right and the total sample length is 130 mm. The red broken line shows the position of the interface between the two layers. Injection starts at t = 0.



Figure 6.15 Displacement, (a)-(d), and relative mixing, (e)-(h), in the lower (blue solid line) and upper (red dashed line) layers of the two-layer system shown in Figure 6.14 for injection of a dense gravity current consisting of 2 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a),(e) 0.5 (b),(f) 1 (c),(g) 2 and (d),(h) 10 ml min⁻¹ into the lower layer of the initially water-saturated system. Injection starts at t = 0.

As was done previously for Set 1 (Section 6.5.1), velocity maps were acquired at a flowrate of 10 ml min⁻¹ once steady-state was reached (shown in Figure 6.16(a) and (b) for slices through the *y*-*z* and *x*-*z* planes, respectively). Figure 6.16(a) shows that downstream of the inlet the average velocity in the upper layer, 0.47 mm s⁻¹ is higher than that in the lower layer, 0.19 mm s⁻¹. Here also, the width-averaged vertical velocities from Figure 6.16(b) were compared with the source estimate shown in Figure 6.16(c); the result, Figure 6.16(d), shows that the observed width-averaged velocities are higher than the predicted velocities, although the discrepancy between the two is not as large as for Set 1, this may be due to wall effects not being as prominent here as was the case with the larger 2.0 mm beads in the upper layer. However, similar to Set 1, the *y*-velocities are spread evenly across the sample width and do not correspond with the expected radial profile. The flux entering the upper layer was calculated from Figure 6.16(b) to be 4.2 ml min⁻¹ (cf. the predicted flux of 3.1 ml min⁻¹); hence, less than half of the fluid entering the sample goes into the upper layer.



Figure 6.16 2D velocity images (slice thickness 10 mm) of the two-layer sample shown in Figure 6.14, with 2 wt% KCl brine doped with 2.7 mM Gd³⁺ injected into the lower layer at 10 ml min⁻¹, in slices through the: (a) *y*-*z* plane, showing the *z*- (flow direction) velocity; (b) *x*-*z* plane showing the *y*- (upward) velocity. The position of the fluid inlet and the location of the *x*-*z* slice for the velocity image shown in (b) are indicated in red in (a). (c) Predicted velocities through the slice shown in (b) using a simple source estimate. (d) Width averaged *y*-velocities along the sample axis, showing a comparison between experimental (red line) and predicted (blue line) values.

Non-uniform interface

In these experiments, 3 wt% KCl brine was injected into the lower layer at flowrates of 1, 5, 10 and 20 ml min⁻¹ (Figure 6.17). The images show that the critical inlet velocity for this system appears to be between 1 and 5 ml min⁻¹, which is consistent with the value of 2.13 ± 0.40 ml min⁻¹ predicted using the correlation of (Huppert et al., 2013). Thus it appears that the non-uniform interface between the two layers does not have a significant effect on the critical velocity. The corresponding displacement curves are shown in Figure 6.18, for threshold normalised signal intensity values of 0.08 and 0.10 in the lower and upper layers respectively; in Figure 6.18(b), it can be observed that above q_c , displacement in the upper layer starts sooner after injection with increasing inlet flux, as was the case for the corresponding two-layer system with a uniform interface (Figure 6.15).



Figure 6.17 Time-series of spin echo MRI images taken in the *y*-*z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a dense gravity current consisting of 3 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a) 1 (b) 5 (c) 10 and (d) 20 ml min⁻¹ into the lower layer of an initially water-saturated two-layer system. The upper and lower layers consisted of 1.0 mm and 0.6 mm beads, respectively. Flow is from left to right and the total sample length is 130 mm. The red broken line shows the position of the interface between the two layers. Injection starts at *t* = 0.



Figure 6.18 Displacement in the lower (blue solid line) and upper (red dashed line) layers of the two-layer system shown in Figure 6.17 for injection of a dense gravity current consisting of 3 wt% KCl brine doped with 2.7 mM Gd³⁺ at flowrates of (a) 1 (b) 5 (c) 10 and (d) 20 ml min⁻¹ into the lower layer of the initially water-saturated system. Injection starts at t = 0.

6.5.3 Two-layer sand pack

The experiments performed so far have utilised layers of different glass bead sizes to construct the dual layered porous medium. However, in a real porous medium such as a saline aquifer in which CO₂ would be injected for sequestration purposes, the pore size distribution would be much more heterogeneous. Therefore, as a first step towards more accurately representing the structure of rock in a saline aquifer, a two-layered sand pack was used. The sand permeabilities were measured experimentally using a fixed flowrate of DI water into an initially brine-saturated sample consisting of a single type of sand. The values of the front position of the resulting gravity current, x_N , were determined from a time-series of MRI images, taken for an inlet flowrate of 1 ml min⁻¹; x_N was then plotted against $t^{2/3}$, as illustrated in Figure 6.19, and the value of *k* was calculated as described in Section 6.3.1. The values of permeability were calculated to be 5790 µm² and 577 µm² for sand B and C respectively, resulting in a A value for this system of 10.0.

As noted by Huppert et al. (2013), the theoretical model discussed in Section 6.2 applies both to the injection of a dense fluid into the lower layer of a two-layer system with $k_l < k_u$, as considered thus far, and to the injection of a buoyant fluid into the upper layer with $k_u < k_l$, as might be case for CO₂ injected into, e.g., a depleted oil or gas well. Therefore, in order to effectively reverse the inlet position, the sand pack was initially saturated with 3 wt% KCl brine and a current of DI water was injected into the lower layer, which was made up of the more permeable sand B, while the upper layer was made up of sand C. The DI water was injected into the cell at flowrates of 0.5, 1 and 5 ml min⁻¹, and time-series of spin echo images were acquired as previously. The images were then converted into concentration maps, shown in Figure 6.20. The corresponding displacement and relative mixing curves are shown in Figure 6.21, for threshold Gd³⁺ concentration values of 1.62 mM and 1.66 mM in the lower and upper layers, respectively, below which pixels were considered to be part of the injected water current. Here, the mixing was normalised using the initial concentration of the bulk fluid, $[Gd^{3+}]_0^{bulk}$, as the initial concentration of the injected fluid was zero.



Figure 6.19 (a) 2D spin-echo MRI image taken in the *y*-*z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a gravity current consisting of DI water into a uniform porous medium consisting of sand B saturated with 3 wt% KCl brine doped with 2.7 mM Gd³⁺, at a flowrate of 1 ml min⁻¹. The front position x_N of the current was extracted for a time-series of images and plotted against $t^{2/3}$ for: (b) sand B; (c) sand C. The experimental data points are shown as circles and the best-fit line is indicated by the solid line.

As Figure 6.21 shows, the displacement behaviour for this system is somewhat different to that seen in the experiments with the glass beads. At the slowest flowrate of 0.5 ml min⁻¹, Figure 6.20(a), the injected current mainly flows preferentially in the upper layer due to buoyancy effects, indicating $q < q_c$. There is however a small preference for the high permeability lower layer immediately following injection, as can be seen in Figure 6.21(a); this may be due to the inlet position being closer to this layer and is unlike the behaviour seen in the glass beads, where the injected current stayed entirely in the low-permeability layer for flowrates below q_c . Similarly, the relative mixing in the upper layer is initially higher, Figure 6.21(d) but is overtaken by that in the lower layer as the flow in the upper layer starts to dominate. As the flowrate is increased to 1 ml min⁻¹, Figure 6.20(b), the injected current immediately shows a preference for the lower layer, although mixing in the two layers remains close initially, indicating a q value just above q_c . At longer times, however 196

(t > ~1400 s), mixing in the upper layer starts to dominate, Figure 6.21(e), due to the instability of the underlying current. This is supported by Figure 6.20(b), where the presence of Rayleigh-Taylor fingers can be seen in the frame shown at t = 22 m 26 s, leading to mixing between the currents in each layer. At the highest flowrate of 5 ml min⁻¹, Figure 6.20(c), the transition to an underlying current is evident at all times, as the injected current clearly bypasses the upper layer and flows almost entirely along the high permeability layer. In addition, the mixing in the upper layer, Figure 6.21(f), is higher as expected. Here also, the correlation of (Huppert et al., 2013) slightly over-predicts the value of q_c as 1.9 ml min⁻¹. These preliminary results on a two-layer sand pack indicate that changing the inlet position may have an effect on the transitional behaviour of the injected gravity current, although further experiments are needed to quantify this effect.



Figure 6.20 Time-series of concentration maps obtained from calibrating the signal intensity of spin echo MRI images taken in the *y*-*z* plane (slice thickness 3 mm) through the centre of a sample of width 37 mm, showing the injection of a gravity current consisting of water at flowrates of (a) 0.5 (b) 1 and (c) 5 ml min⁻¹ into the lower layer of a two-layer system initially saturated with 3 wt% KCl brine doped with 2.7 mM Gd³⁺. The upper and lower layers consisted of sand B and sand C, respectively. Flow is from left to right and the total sample length is 130 mm. The red broken line shows the position of the interface between the two layers. Injection starts at t = 0.



Figure 6.21 Displacement, (a)-(c), and relative mixing, (d)-(f), in the lower (blue solid line) and upper (red dashed line) layers of the two-layer system shown in Figure 6.20 for injection of a less-dense gravity current consisting of water at flowrates of (a),(d) 0.5 (b),(e) 1 and (c),(f) 5 ml min⁻¹ into the lower layer of a two-layer system initially saturated with 3 wt% KCl brine doped with 2.7 mM Gd³⁺. Injection starts at t = 0.

6.5.4 Simulation results

The results of the CFD simulation model described in Section 6.4 are shown in Figure 6.22 and Figure 6.23, alongside the corresponding MRI data from Figure 6.7 and Figure 6.14, respectively. The figures provide a qualitative comparison of the experiments and simulations and the results show good agreement between the two methods in terms of predicting the override of the injected brine current into the upper layer. However, it is also apparent that the model does not take into account the effect of pore size distribution or heterogeneity of the porous media; this does not affect the results greatly in the case of the mono-disperse glass bead packs but may prove significant when considering flow in more non-ideal systems such as sand packs and rock cores. Future simulation work would thus involve the incorporation in the model of geometrical parameters such as surface area to pore volume
ratio, as well as quantitative validation of the fluid mixing and longer-term stability of the overriding gravity current.



Figure 6.22 Time-series of concentration maps obtained from a 3D CFD model (set 'S'), shown side by side with the corresponding MRI experimental data (set 'E') in the *y*-*z* plane through the centre of a rectangular flow cell of width 37 mm, showing the injection of a dense gravity current consisting of 2 wt% KCl brine at flowrates of (a) 1 (b) 2 and (c) 10 ml min⁻¹ into the lower layer of an initially water-saturated two-layer system. The upper and lower layers are modelled as packing of mono-disperse glass beads of 2.0 mm and 1.0 mm respectively. The flow in the images shown is from left to right and the red broken line shows the position of the interface between the two layers. In the colour scale shown for experimental data, a Gd³⁺ concentration of 2.7 mM corresponds to 2 wt% KCl. Injection starts at t = 0.



Figure 6.23 Time-series of concentration maps obtained from a 3D CFD model (set 'S'), shown side by side with the corresponding MRI experimental data (set 'E') in the *y*-*z* plane through the centre of a rectangular flow cell of width 37 mm, showing the injection of a dense gravity current consisting of 2 wt% KCl brine at flowrates of (a) 0.5 (b) 1 (c) 2 and (c) 10 ml min⁻¹ into the lower layer of an initially water-saturated two-layer system. The upper and lower layers are modelled as packing of mono-disperse glass beads of 1.0 mm and 0.6 mm respectively. The flow in the images shown is from left to right and the red broken line shows the position of the interface between the two layers. In the colour scale shown for experimental data, a Gd³⁺ concentration of 2.7 mM corresponds to 2 wt% KCl. Injection starts at t = 0.

6.6 Conclusions

In this chapter, we have demonstrated the applicability of MRI techniques to visualise the flow of a dense gravity current injected into a porous medium with vertical permeability heterogeneity. We observed that at a non-dimensional flux greater than some critical value the injected current did not simply progress along the lower permeability layer due to buoyancy driven flow as expected, but overrode this layer to flow preferentially in the upper, higher permeability layer. Spin-echo NMR images were acquired for brine injected into the

lower layer of an initially water-saturated dual-layered bead pack at various flowrates. Two different sets of bead sizes were used, with a different permeability ratio between the two layers. The results showed reasonably good agreement with a correlation obtained by Huppert et al. (2013) for a corresponding two-dimensional system. The spin-echo images were made quantitative by calibrating the NMR signal intensity to show the concentration of an NMR contrast agent added to the injected fluid.

Phase shift velocity images were also acquired of the flowing system at steady-state, at flowrates above the critical flowrate. These images, acquired both transverse to and through the interface between the two layers, allowed calculation of the flux entering the upper layer, and also showed that the upward velocities across the interface are not consistent with a simple source flow estimate. In addition the longer-term behaviour of an overriding current was observed and it was found that Rayleigh-Taylor fingering occurs due to the presence of a denser fluid overlaying the lighter fluid in the lower layer. This is an important mechanism leading to enhanced mixing between the two layers and indicates the overriding current is ultimately a transient state. As a first step towards investigating a more complex porous medium, spin echo images were acquired of gravity current flow in a two-layer sand pack, the permeability of which was measured using MRI techniques. The results obtained from the sand pack indicate that the position of the inlet may have an effect on the mixing behaviour of injected gravity currents.

The experimental approach used here may be extended in future work to more realistic systems in the context of CO₂ sequestration, such as rocks of different permeabilities and immiscible two-phase fluid mixtures. Other questions of interest, such as the effect of the two-layer interface orientation on Rayleigh-Taylor fingering may also be investigated. Ultimately, the experimental data may be used to validate 3D models of gravity current flow in reservoirs with spatial permeability variations, and at conditions more relevant to subsurface aquifers. A first step towards this aim was taken by showing limited comparison with a 3D CFD model developed by a collaborating institution, which showed good agreement with the experimental data.

6.7 References

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7 Immiscible Gravity Currents in Porous Media

7.1 Introduction

In previous chapters we have mainly considered the flow of different (miscible or immiscible) liquid phases in porous media. However, gas/liquid flow is also relevant for CO_2 sequestration in the subsurface as the injected CO_2 may be present in the gas phase, alongside oil and water, in shallow reservoirs such as depleted oil and natural gas wells (Metz, 2005). Against this backdrop, two-phase gravity current models have been developed (e.g. Golding et al., 2011), which may be capable of predicting the long-term effects of different trapping mechanisms on CO_2 storage. Here, a first attempt is made to investigate the effect of particle-and pore-size distributions on the gas/liquid interface using quantitative MRI techniques, such as T_2 -preconditioned 2D RARE and 2D spin-echo images, with a view to providing experimental data for the validation of such models. In order to do this, displacement flow was visualised in different porous media initially saturated with water, after injection with a non-wetting gas phase (air).

7.2 Background

In the geological sequestration of CO_2 , two-phase gravity currents occur between the injected gas- or supercritical-phase CO_2 and the denser reservoir brine. The injected CO_2 rises as a plume due to buoyancy until it reaches a flow barrier such as a layer of impermeable caprock, upon which it spreads laterally. Once injection stops, residual CO_2 is trapped in the pore space of the rock as the spreading current recedes. The extent of vertical and lateral spreading of the CO_2 current, therefore, determines the amount of reservoir volume contacted by it and hence the amount of CO_2 trapped. Previous studies by Farcas and Woods (2009) and MacMinn and Juanes (2009) have proposed two-phase models which seek to quantify the proportion of CO_2 trapped by taking into account the shape of the post-injection current and the competition between drainage and capillary retention, respectively. These studies, as well as many other models reported in the literature (e.g. Huppert and Woods, 1995; Lyle et al., 2005; Hesse et al., 2007; Gasda et al., 2009; Juanes et al., 2010) use an approximation whereby the contacting fluids are fully saturated. Such 'sharp-interface' models are

applicable for immiscible flows in porous media only where capillary forces are negligible compared to gravitational and viscous forces. In the context of CO_2 sequestration, the use of sharp-interface models has been justified in previous studies through highlighting the density contrast (Gasda et al., 2009) and relative mobility (Juanes et al., 2010) of the injected CO_2 phase and the resident brine. However, Bickle et al. (2007), in their study of time-lapse seismic reflection images obtained from the CO_2 injection at Sleipner gas field found that the whole-reservoir and individual CO_2 layer permeability values obtained using a traditional sharp-interface model to fit the data greatly underestimated measured permeability values of lab-scale core samples taken from the reservoir. They suggested that a possible explanation for this discrepancy could be due to the model not taking into account capillary forces, which cause a spatially varying zone of partial CO_2 saturation at the interface between the two fluids, thus altering the relative permeability of the rock.

Moreover, as noted by Golding et al. (2011), recent experimental studies on sand packs (Pentland et al., 2011; 2010; Al Mansoori et al., 2010) which aim to replicate conditions relevant to CO₂ sequestration have shown that the amount of residually trapped non-wetting phase (in this case either octane, air or supercritical CO₂, with brine as the wetting phase) depends on the initial non-wetting phase saturation. The experiments were performed in the capillary-controlled regime and thus showed that capillary forces played a significant role in determining the relative phase saturations. In addition, the aforementioned studies also showed that the pore structure has a significant effect on the amount trapped, as it was observed that above a certain initial saturation limit (which varied depending on the non-wetting phase) no further increase was seen in residual trapping in the unconsolidated sand, which was attributed to displacement of the non-wetting phase from smaller pores. As Pentland et al. (2010) themselves highlighted, this was in contrast with previous studies of gas-liquid systems in highly consolidated media such as rock cores with a wide pore size distribution, where the non-wetting phase can become trapped in relatively isolated small pores at high initial saturations, consequently leading to higher amounts of capillary trapping.

Against this backdrop, Golding et al. (2011) proposed a gravity current model which extended existing two-phase flow models by taking into account the vertical equilibrium between capillary forces and gravity in a current of non-wetting fluid spreading horizontally against an impermeable barrier (e.g. a layer of caprock), in a porous medium initially saturated with a denser, wetting fluid. By assuming a semi-infinite porous medium (i.e. large

aspect ratio of the spreading current) and thus neglecting the velocity of the wetting phase, they derived a time-dependent model for the spreading current thickness and saturation profile. They further used the model to predict the capillary trapping of CO₂ in the subsurface under relevant conditions and showed that the estimates of CO₂ trapping obtained by accounting for capillarity can be up to 50 % higher compared to traditional sharp-interface models, which predict a constant amount of trapped CO₂. Golding et al. subsequently extended their developed framework to consider axisymmetric currents with constant flux (Golding et al., 2013) and found that, just as in the case of the equivalent single-phase flow configuration, the front of the current propagates as $t^{1/2}$. They also showed that effects of capillary forces on the propagation of and relative phase saturation within the current are a strong function of the Bond number (Bo) between the fluids and the pore-size distribution parameter (Λ) of the porous medium.

From the above discussion, it is evident that theoretical models can play an important role in predicting the amount of CO_2 trapped at various time-scales in large-scale sequestration projects, thus reducing the risk and uncertainty inherent in such projects. However, there remains a shortage of 3D experimental data at a range of conditions for validation of such models. MRI techniques, being phase- and species-selective and able to image transient processes non-invasively (unlike traditional core flooding measurements, for example), can be used to provide such data.

7.3 Experimental Methodology

The flow cell used for these experiments consisted of a rectangular box-shaped Perspex cell of square cross-section (inner sides 37 mm) and length 130 mm, as described in Chapter 6. Air entered the sample through 1/8" outer diameter tubing, located 5.6 mm from the top of the cell in the centre of the sample in the *x*-direction, onto a grooved surface for fluid distribution through the sample cross-section. The air inlet was separated from the cell packing by a 10 µm nylon mesh. The cell also contained a threaded 8.0 mm diameter hole in the top for ease of packing. The hole was originally sealed using a brass screw, which was subsequently replaced by a plastic one. The cell was placed in a birdcage r.f. coil of length

195 mm and inner diameter 80 mm inside the AV-85 NMR Spectrometer. All experiments were done using ¹H NMR and therefore signal was obtained only from the protons in water.

The packing for the flow cell consisted of either borosilicate glass ballotini (QA Equipment ltd) or silica sand (David Ball Group plc). Three different grades of sand were obtained, classified according to particle size as sand B (0.6–1.18 mm), sand C (0.3–0.6 mm) and sand D (0.15–0.3 mm). Three different packings were used (with the porosity, ϕ , of each measured gravimetrically):

i) $100 \pm 20 \,\mu\text{m}$ ballotini ($\phi = 0.385$);

ii) sand B ($\phi = 0.395$);

iii) mixture of sand B, C, and D, with equal (dry) weight fraction of each ($\phi = 0.349$).

Packings i) and ii) were used in order to provide a relatively narrow pore size distribution, but with a different average particle size in each case, and packing iii) was used in order to provide a heterogeneous pore size distribution.

Air was injected into the sample at a constant flowrate using an Omega FMA 3200 Series mass flow controller with an operating range of 100–1000 ml min⁻¹. The inlet pressure of the air was maintained at 2 barg using a two-stage regulator. A non-return valve was used to prevent water from entering the mass flow controller due to back-flow. A schematic of the flow setup used is shown in Figure 7.1. Air was used as the gas phase due both to its easy availability and to the ease of imaging the air/water system. The range of flowrates used in this work was limited by the available equipment. All experiments were conducted at room temperature (~20 °C).



Figure 7.1 Schematic of the flow setup for the air/water system in the AV-85 spectrometer.

NMR measurements

In order to visualise the drainage of the water from the porous medium sample using suitable MRI techniques, an NMR contrast agent was utilised to reduce the T_1 relaxation time of the bulk water and thus enable the use of short recycle times (RT) for imaging. For the experiments presented in this section, the common contrast agent Cu²⁺ (in the form of Copper (II) chloride dihydrate crystals, Sigma-Aldrich) was used. Cu²⁺ was preferred over other contrast agents such as Mn^{2+} as it reduces the T_2 relaxation time to about the same level as the T_1 , unlike Mn²⁺ which causes the T_2 value to fall much more rapidly than the T_1 , thus limiting the echo time (ET) and precluding the use of rapid imaging sequences such as RARE. Cu^{2+} was also preferred over another common contrast agent, Gd^{3+} as it does not cause the T_2 value to fall as rapidly at low concentrations as Gd³⁺, which would also preclude the use of RARE; this does however limit the RT that can be used and thus the time-resolution of successive image acquisitions. The water solution was doped with 1.0 wt% of $CuCl_2.2H_2O_1$ which reduced its T_1 value in the packing to ~200 ms, in contrast with the measured value of ~ 2 s before doping. In order to ensure that an equilibrium adsorption of Cu²⁺ on the surface of the beads was reached, thereby ensuring that the concentration of Cu²⁺ in the doped brine solution would not be reduced on contact with the beads, both the glass beads and the silica sand were soaked in a concentrated solution of CuCl₂ for at least 24 hours prior to the experiments; they were then washed with de-ionised (DI) water and packed in the flow cell under water, to prevent the formation of air bubbles therein.

The imaging pulse sequences used for these experiments were a T_2 -preconditioned RARE pulse sequence, used in order to remove T_2 weighting (Chen et al., 2010), and a conventional 2D spin-echo imaging pulse sequence. A CPMG pulse train was used for T_2 preconditioning as this reduces signal loss due to molecular diffusion unlike the Hahn spin-echo (Section 2.2.5). The RT was lowered as much as possible whilst still being at least 3 times as large as T_1 , in order to recover >95% of the signal between acquisitions and thus keep T_1 weighting negligible. RARE was used as this allows a relatively fast time resolution between image acquisitions in order to monitor the in-situ progress of the air current through the sample. The T_2 preconditioning was added in order to extract quantitative information on the relative saturations of air and water in the sample. The conventional spin-echo imaging pulse sequence, which has higher SNR and is quantitative as significant T_1 and T_2 weighting effects are not present, was used once the system reached steady-state as acquisition time is not constrained then.

Experiments performed

Air was injected into the initially-water saturated cell at a constant volumetric flowrate of 100 ml min⁻¹, which was the lowest flowrate possible with the available setup. A sample slice of thickness 3 mm was selected in the in the y-z plane; for the experiments with the 100 μ m ballotini the selected slice was at an offset of 14.2 mm from the centre of the sample (the reason for which is explained in Section 7.4), but for the ones with sand the imaged slices were selected through the centre of the sample. The RARE images acquired were 128 x 64 pixels in size with a field-of-view (FOV) of 100 mm in the z- (read) direction and 50 mm in the y- (phase) direction, giving an isotropic spatial resolution of 0.781 mm. The RT used for the experiments with 100 µm ballotini was 1.2 s (which also corresponds to the time between successive image acquisitions) and images were acquired with 3 different T_2 weightings (corresponding to a CPMG train with *n* echoes preceding the RARE sequence, where n = 2, 32 and 128) before repeating the sequence. The temporal resolution of the I_0 images is therefore $3 \times RT$. The echo spacing (i.e. $2 \times \tau$) used was 2 ms. Once steady state was reached the flow was stopped and a spin-echo image with 128×64 pixels and a FOV of 120 mm in the read and 50 mm in the phase directions (spatial resolution 0.938 mm and 0.781 mm respectively) was acquired with an RT of 1.2 s and 4 signal averages, giving a total acquisition time of 5 min 7 sec. The RT was later reduced to 1 s in subsequent experiments as the T_1 value was slightly lower for the sand samples, resulting in a total acquisition time of 4 min 16 s for the spin echo images. Each experiment was repeated thrice to ensure reproducibility.

7.4 Results and Discussion

Figure 7.2 shows an example of the fitting done for the T_2 -preconditioned RARE images. A series of T_2 weighted images of the initially water-saturated porous medium are shown for the packing of sand B in Figure 7.2(a)-(c). Figure 7.2(d) shows a plot of signal intensity with echo time for three different image pixels located on a profile through the centre of the images shown in Figure 7.2(a)-(c) in the y-direction, along with the corresponding fitted

exponential decay curves. Figure 7.2(e) shows the resulting I_0 map obtained by extrapolating the fitted curves to t = 0.



Figure 7.2 (a)-(c) Consecutive T_2 -preconditioned RARE images with different amounts of T_2 weighting, for a packing of Sand B in the initially water-saturated cell. (d) Signal intensity decay curves at of each of the points labelled A, B, C in (a) with a single-component T_2 fit; (e) Resulting I_0 map.

100 µm Ballotini

Figure 7.3 shows the resultant time series of images for the system with flow. The images were normalised using an image of the initially water-saturated sample in order to express the signal intensity in terms of relative water saturation, where the initial saturation was assumed to be 1. The error in the fitted values of the I_0 images was estimated to be 7 % based on the relative standard deviation of a sample of image pixels in a series of images of a water-saturated sample with no flow. It can also be observed that there are some pixels showing a large variation in intensity towards the upper right corner of the images; these are artefacts due to the presence of the brass screw in the centre of the cell roof, which distorts the local r.f. magnetic field. The artefact gets more prominent closer to the centre of the sample, hence the offset of the chosen sample slice away from the centre. The screw was subsequently replaced with a plastic one for the experiments with sand, which eliminated these artefacts.

Figure 7.3 shows that the air flow through the sample is plug-like, leaving 'bands' of high water saturation perpendicular to the flow direction in its wake. The water saturation decreases rapidly immediately after the air current enters the sample, corresponding to the image at t = 32.4 s; thereafter, the reduction is more gradual until equilibrium is reached at around t = 238 s. After equilibrium was reached, a spin-echo image of the sample was acquired.



Figure 7.3 Time series of saturation maps showing flow of air at 100 ml min⁻¹ into an initially watersaturated 100 µm bead pack. A slice thickness of 3 mm was used, at an offset of 14.2 mm from the centre of the sample.

In order to see how far down the sample the air/water front had progressed, the sample was shifted down the r.f. coil so that the latter half was within the imaging region, and another spin-echo image was acquired. The two images were combined to form a composite image which was normalised using an image acquired before starting the flow in order to produce a saturation map, as shown in Figure 7.4(a). A 1D profile of the average water saturation along the sample length, extracted from the image in Figure 7.4(a), is shown in Figure 7.4(b). The profile shows that the relative water saturation in the sample does not fall below 0.4 and that the saturation increases gradually along the sample length; this increase is punctuated by spikes in intensity which correspond to the 'bands' seen in the 2D images. These bands may

be due to capillarity, as the capillary force is inversely proportional to the mean radius of curvature between the two fluids, which is smaller for smaller bead sizes.



Figure 7.4 (a) Composite calibrated spin-echo image showing the relative water saturation in a 100 μm bead pack taken at equilibrium after flowing air through. A slice thickness of 3 mm was used, at an offset of 14.2 mm from the centre of the sample. (b) Average water saturation along the sample axis.

Sand B, 0.6 mm – 1.18 mm

Air was injected into the sample at 100 ml min⁻¹; the resulting time-series of images is shown in Figure 7.5. The error in the fitted values of the I_0 images was estimated to be 9 %. As the brass screw used earlier in the top of the cell was replaced by a plastic one, the image slice shown was taken through the centre of the sample. The image at t = 0 shows the initially water saturated sample; as air subsequently enters the sample, water is displaced parallel to the direction of the air current. The air/water interface moves mainly downward in the ydirection until equilibrium is reached. It can also be observed that at longer times the air-rich regions images shown in Figure 7.5 appear speckled; this is due to errors in the T_2 fitting as the signal-to-noise ratio becomes low in the mainly air saturated regions. Figure 7.6(b) shows a saturation profile of the sample in the y-direction at z = 51 mm, taken from a calibrated spin-echo image acquired at equilibrium, Figure 7.6(a). The interface between the two fluids is fairly sharp, indicating that the particle size range of the sand is not large enough to cause a saturation 'transition zone' at the air flowrates used.



Figure 7.5 Time series of saturation maps showing flow of air at 100 ml min⁻¹ into an initially watersaturated packing of sand B (0.6 mm - 1.18 mm). The sample field of view shown in the *z*-direction is 75.8 mm and in the *y*-direction is 35.2 mm. A slice thickness of 3 mm was used, through the centre of the sample.



Figure 7.6 (a) Spin-echo image showing the relative water saturation in a packing of sand B taken at equilibrium after flowing air through at 100 ml min⁻¹. A slice thickness of 3 mm was used, through the centre of the sample. (b) Average water saturation along the sample axis. (b) Profile of water saturation at z = 51 mm at equilibrium, taken from the image in (a) at the position shown by the dashed line.

Mixture of sand B, C, and D

For the final set of experiments, a mixture of sand of different particle sizes was used, as detailed in Section 7.3 in order to get a much broader pore size distribution, and thereby

obtain a smoother air/water interface due to capillary forces. Figure 7.7 shows the resultant time series of images for injection of air at 100 ml min⁻¹ into the sample; the slice shown was taken through the centre of the sample in the yz plane. The error in the fitted values of the I_0 images was estimated to be 12 %. The images show that the injected air current displaces water in both the downward and horizontal directions, corresponding to scenario which is in between the behaviour seen with the 100 µm ballotini and sand B. As Figure 7.7 also shows, there are some small red patches in the earlier images in the time series; these are artefacts caused by the change in water saturation being more rapid than the time resolution of the T_2 preconditioned RARE sequence, thus causing errors in the T_2 fitting. Although the air/water interface is not as uniform as previously, Figure 7.8(b) shows the saturation profile of the sample in the y-direction at z = 20 mm, in a region where the interface is relatively horizontal. The profile is taken from a calibrated spin-echo image acquired at equilibrium, Figure 7.8(a), and shows that the interface between the fluids is not as sharp as it was for the packing of only sand B, as expected. Figure 7.8(c) shows a photograph of the initially water-saturated sample, which indicates that the packing is not homogeneous; although care was taken to mix the different sand sizes well, some particle segregation may have occurred while packing the cell due to the large difference in size between the smallest (150 μ m) and largest (1.18 mm) particles. The 'bands' of higher water saturation transverse to the flow direction therefore most probably correspond to the regions where smaller particles are mainly present, and are similar to those seen for the 100 μ m beads.

In order to provide a more direct comparison between the three sets of images shown in Figure 7.3, Figure 7.5, and Figure 7.7, the total relative water saturation as a function of time for each set is shown plotted in Figure 7.9. The curve for the 100 μ m beads shows an initial sharp drop in relative water saturation followed by a plateau from round t = 14 s to t = 58 s; thereafter, the relative water saturation decreases gradually before reaching a steady value of ~0.49 at around t = 210 s. This behaviour can be explained as the (relatively few) larger pores getting filled up first, followed by an increase in the capillary pressure at the air/water interface until it exceeds the entry pressure for the smaller pores, whereupon these fill up until an irreducible water saturation is reached. The curve for sand B, on the other hand, shows a gradual decrease in relative water saturation from the beginning, reaching an irreducible value of ~0.40 at around t = 310 s. This indicates that the pores are large enough that viscous forces and gravity separation dominate at all times. Finally, the curve for the mixture of sand B, C, and D shows an initial sharp drop in relative water saturation before

reaching a constant value of ~0.50 at around t = 100 s; again, this is likely due to the larger pores being filled up first but the capillary pressure being insufficient for entry into the smaller pores. Thus, these results show qualitatively the effect that average particle size and pore size distribution of different porous media has on the air/water interface. To enable a more quantitative comparison to be made, further information would be required in addition to the saturation values obtained from the MRI data, such as measurements of capillary pressure and pore size distribution.



Figure 7.7 Time series of saturation maps showing flow of air at 100 ml min⁻¹ into an initially watersaturated packing of sand B, C and D. The sample field of view shown in the *z*-direction is 75.8 mm and in the *y*-direction is 35.2 mm. A slice thickness of 3 mm was used, through the centre of the sample.



Figure 7.8 (a) Spin-echo image showing the relative water saturation in a packing of a mixture of sand B, C, and D taken at equilibrium after flowing air through at 100 ml min⁻¹. A slice thickness of 3 mm was used, through the centre of the sample. (b) Average water saturation along the sample axis. (b) Profile of water saturation at z = 20 mm at equilibrium, taken from the image in (a) at the position shown by the dashed line. (c) Photograph of the initially water-saturated cell.



Figure 7.9 Relative water saturation curves as a function of time for air flowing at 100 ml min⁻¹ through initially water saturated packings of 100 μm glass beads (blue solid line), sand B (green dashed line) and a mixture of sand B, C and D (red dashed-dotted line). The curves were extracted from the MRI images shown in Figure 7.3, Figure 7.5, and Figure 7.7 respectively.

7.5 Conclusions

 T_2 -preconditioned 2D RARE images were acquired of the flow of air into different initially water-saturated porous media (consisting of a packing of 100 µm glass ballotini, and two different sand mixtures with a narrow and a broad particle size distribution, respectively), thus allowing the transient behaviour of the air/water interface to be monitored. The steadystate air/water interface was also measured using a conventional spin-echo imaging sequence, which confirmed that the RARE images were quantitative. The results indicated that for the more homogeneous media, the average particle size has a considerable effect on the progression of the air current through the sample. For the sand with the broad particle size distribution, the observed behaviour was in between that for the two relatively homogeneous cases. These results suggest that two-phase theoretical models of gravity currents in porous media (as outlined in Section 7.2) could be validated using experimental data such as that presented here. Future studies would extend this work by conducting experiments under a wide range of conditions such different temperatures, pressures and flowrates, as well as by using different pairs of fluids and consolidated porous media such as real sandstone and carbonate rock cores, in order to provide better data for model validation to enable accurate prediction of the long-term storage behaviour of CO₂, trapped in the gas- or supercriticalphase alongside one or more immiscible fluid phases.

7.6 References

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8 Conclusions and Future Work

The work presented in this thesis involved the investigation of single- and two-phase miscible and immiscible flow in porous media such as bead packs and rock cores, with applications mainly towards the geological sequestration of CO₂ as well as freshwater/brine flow in aquifers. The work presented here was mainly based on nuclear magnetic resonance (NMR) experimental techniques, with lattice-Boltzmann (LB) numerical simulations used where applicable. Throughout the dissertation, various fluid and porous medium configurations are considered: e.g., Chapters 3, 4 and 5 are mainly focused on the capillary trapping of CO₂ and analogue fluids in porous media initially saturated with an aqueous phase, Chapter 6 is focused on the flow of miscible gravity currents in porous media with layers of different permeability, and Chapter 7 is focused on gas-liquid displacement flow in porous media of varying pore size distribution. Hence, a summary of the main findings is presented in Section 8.1 on a chapter-by-chapter basis, followed by the conclusions that may be drawn from this work as a whole in Section 8.2. Finally, in Section 8.3, suggestions are made for future work that may be undertaken, both in the short- and the long-term, in order to build upon the work presented here.

8.1 Summary

Chapter 3 – APGSTE NMR propagators were acquired for brine flowing in two different porous media: a packed bed of 100 μ m glass ballotini, and a core plug of Bentheimer sandstone. It was shown that using a slice-selective APGSTE NMR pulse sequence for acquisition of displacement propagators eliminates artefacts associated with entry and exit effects, thus enabling more accurate measurements in samples which are homogeneous on the scale of the sample size (i.e. 10^{-2} m). The experimentally measured propagators were simulated successfully using LB techniques, with low-order moment analysis showing favourable comparison between experiments and simulation. For the Bentheimer sandstone, two different 3D simulation masks were used – a morphologically thinned image of a bead pack acquired using MRI, and an X-ray microtomography (XMT) image of a real sandstone core. The results showed that while the real sandstone image is preferred, the 'artificial' morphologically thinned image may be used in the absence of real rock data. Following this, capillary trapping of CO₂ gas occurred in the pore space of the bead pack through flowing

carbonated brine and the extent and spatial distribution of this trapping was quantified using NMR and magnetic resonance imaging (MRI) techniques. LB simulations were then conducted using different trapping scenarios in order to identify the pore morphology where the CO_2 was likely to be trapped. The simulations indicated that CO_2 was preferentially trapped in the larger pores, which is consistent with a non-wetting fluid phase flowing in conjunction with a wetting aqueous phase.

Chapter 4 – MRI techniques were successfully used for analysis of droplets of immiscible fluids in a continuous phase in order to measure the interfacial tension (IFT) between the different fluids. The IFT measurements were validated for systems of hexane and heptane droplets in water, for which literature data was available. However, the true utility of this technique lies in its application to systems for which conventional optical imaging techniques cannot be used. This was demonstrated for refractive-index-matched fluids (i.e. hexane and heptane with solutions of glycerol in water) and fluids with an opaque continuous phase (i.e. water in crude oil). The IFT measurements were subsequently used to select a pair of analogue fluids with matching Bond number and viscosity ratio to the supercritical CO₂/water system, for use in the existing low-pressure NMR setup.

Chapter 5 – The supercritical CO_2 /water analogue system identified in Chapter 4 was used for coreflood experiments in three different porous media: a packed bed of 100 µm glass ballotini, and core plugs of Bentheimer sandstone and Portland carbonate rock. Capillary trapping of the CO₂ analogue (hexane) was encouraged in the pore space for all three media and NMR techniques such as T_1 inversion-nulled 1D spin-echo profiles, 2D spin-echo images, and chemically-resolved APGSTE NMR propagator measurements were used to quantify the extent and spatial distribution of the different fluid phases within the samples, with the 1D profiles and propagator measurements showing good agreement in estimating the amount of residually trapped hexane in the case of the bead pack and the Bentheimer sandstone. In the heterogeneous Portland carbonate rock, however, propagators were not able to provide quantitative measurement and so T_2 'pre-conditioned' 1D profiles and 2D images were used to map the relative phase saturations. The 2D images clearly revealed the presence of naturally-occurring fractures in the sandstone which were filled up with the displacing hexane phase preferentially. It was also shown that the amount of hexane trapped residually in the Bentheimer sandstone was significantly higher (21 %) as compared to the Portland carbonate (13 %), suggesting that the relatively homogeneous structure of the sandstone

favours greater capillary trapping within the pore space. Finally, LB simulation techniques, as applied in Chapter 3, were used to interpret the differences in the propagators before and after hexane entrapment for the Bentheimer sandstone using the XMT simulation mask. Different scenarios for hexane entrapment were considered, with the results showing likely occupation of the largest pores by the non-wetting hexane phase.

Chapter 6 – Quantitative MRI techniques were used to visualise the flow of miscible gravity currents of brine and water in two-layered porous media (consisting of glass bead and sand packs) with a different permeability in each layer. It was observed that at inlet flowrates greater than some critical value, the injected current overrode buoyancy effects to flow preferentially in the higher permeability layer. These results showed reasonably good agreement with a correlation obtained by Huppert et al. (2013) for the critical flowrate of a corresponding two-dimensional system (Hele-Shaw cell) using qualitative optical imaging techniques. This work, however, demonstrates the additional utility of MRI techniques (compared to, e.g., optical imaging techniques such as those employed by Huppert et al.) in being able to provide quantitative data on the mixing between the two fluids as well as on the steady-state velocities and the flux of injected fluid in each layer for a 3D realistic porous medium. Finally, such experimental data may be used to validate detailed reservoir simulators; as a first step towards this limited comparison was shown with a 3D CFD model, which showed good agreement with the experimental data.

Chapter 7 – Quantitative MRI techniques were used to visualise the transient and steady-state behaviour of air injected into different initially water-saturated porous media (consisting of a glass bead pack of 100 μ m average particle size, and two different sand mixtures with a narrow and a broad particle size distribution, respectively). The results indicated that for the narrow distributions, the particle size has a considerable effect on the progression of the air current through the sample, whereas the sand with the broad particle size distribution showed behaviour which was in between that observed for the two different glass bead sizes. These results represent a first step towards acquiring experimental data that could be used to validate two-phase theoretical models of gravity currents in porous media.

8.2 Conclusions

As stated in Chapter 1, the main aim behind the work presented in this thesis was to use NMR and MRI techniques combined with LB-based simulations to gain an insight into CO₂ trapping mechanisms at the pore-scale. It was shown in Chapter 3 that CO₂ exsolved under room conditions occupies the largest pores, which is similar to the behaviour of a non-wetting fluid introduced by drainage and is consistent with other literature studies (e.g. Fry et al. (1997); Enouy et al. (2011)). However, a recent study by Zuo & Benson (2014) showed that this may not be the case under reservoir conditions (50 °C, 41.4 bar), as under these conditions CO₂ coming out of solution was distributed independently of the pore morphology and was trapped in a much greater proportion than CO_2 introduced by drainage. Thus, in order to fully understand such processes it is important for experimental studies relating to CO₂ sequestration to be carried out under more realistic conditions, as is increasingly being done using various techniques such as MRI (Song et al., 2012), micro X-ray CT imaging (Perrin & Benson, 2010) and traditional coreflooding methods (Pentland et al., 2011), each of which have their own advantages and limitations. In addition, Chapter 3 also included propagator simulations on Bentheimer sandstone, which showed that the best agreement with experiments was reached at high flowrates and low observation times; thus, it is reasonable to expect good agreement at low flowrates and long observation times, i.e., over the range of displacements which are relevant to flow in subsurface aquifers but which occur over flow conditions which are out of the reach of NMR propagator measurements. Furthermore, comparison with pore network models derived from the same sample (Hussain et al., 2013) showed that the LB-based method was more robust in terms of predicting the propagator second and third moments and more able to capture the centimetre-scale heterogeneities of the sandstone. More recently, Bijeljic et al. (2013b) successfully simulated single-phase propagators in Portland carbonate using a similar CFD-based platform, subsequently extending their approach to include six other carbonate rocks of varying heterogeneity Bijeljic et al. (2013a).

In Chapter 4, it was demonstrated that MRI can be used to measure the interfacial tension of systems which are inaccessible to conventional optical imaging techniques; such an application may be of use in niche systems, particularly in petrophysics, and is likely to become more practical with advances in the capabilities of more readily available and

affordable low-field 'benchtop' NMR systems (Hussain et al., 2014). The supercritical CO₂/water analogue system thus verified using NMR was used to compare capillary trapping in two different rocks types, Bentheimer sandstone and Portland carbonate; the sandstone showed greater entrapment due to its more homogeneous pore space, which has more suitable sites for ganglion formation, whereas in the case of carbonate the non-wetting phase likely occupies large, low-tortuosity pores and is partially swept out after secondary imbibition with the aqueous phase. This study highlights the differences in capillary trapping between different rock types due to varying degrees of permeability heterogeneity; such variations may also be present within rocks of the same type, as demonstrated by Krevor et al. (2011), who showed that the presence of a low-permeability region in a Mount Simon sandstone core acted as a 'capillary barrier' increasing the amount of trapping compared to more homogeneous sections of the rock. On the reservoir scale, Saadatpoor et al. (2010) used the term 'local capillary trapping' to denote the effect of small-scale $(10^{-2}-10^{1} \text{ m})$ heterogeneities which can cause large deviations in the expected amount of trapping in rocks which normally may be expected to follow a single drainage curve. Hence, this area represents an important topic in ongoing studies of CO_2 sequestration, as highlighted by recent experimental and modelling studies (Perrin & Benson, 2010; Shi et al., 2011; Green & Ennis-King, 2010).

The work presented in Chapter 6 is relevant to the problem of saltwater intrusion into freshwater bodies, which may potentially arise as a consequence of the displacement of brine by CO₂ injection into saline aquifers; in general, however, the work presented in Chapters 6 and 7 aims to demonstrate the utility of quantitative MRI techniques in providing useful experimental data for validation of simulations, as it is recognised that experimental studies on lab-scale samples are by themselves not adequate for the description of fluid behaviour in vast geological rock formations. Therefore, in the absence of field-scale experiments, an approach is needed that can be up-scaled. Simulations can play such a role, provided that they can capture accurately what is happening at the pore scale—which is where experimental validation can be useful. Currently, a promising area in modelling CO₂ sequestration, as reviewed in a recent article by Huppert & Neufeld (2014), is the development of 'hybrid models' that build upon relatively simple, 'sharp-interface' models by taking into account vertical gravity-capillary equilibrium in order to resolve the saturation distribution at the interface of the two fluid phases (e.g. Golding et al. (2011, 2013)), yet are computationally much less expensive than full-scale numerical simulations of multi-phase flow. In particular, such models may be used in conjunction with seismic data from field-scale demonstration CCS projects (as shown by, e.g., Bickle et al. (2007) and Boait et al. (2012)) in order to predict various aspects of CO_2 flow in the sub-surface such as buoyant propagation, leakage, and trapping via mechanisms such as solubility and residual trapping.

8.3 Future Work

In the short-term, the experimental work presented in Chapter 5 may be continued by repeating the coreflood experiments at much lower flowrates, in order to be in the capillarycontrolled regime and hence enable the correlation of Goodfield et al. (2001) to be applied with meaningful results. In addition, the simulation work may be extended to include more complex pore-filling scenarios than single-fluid pore occupancy and to more heterogeneous rocks such as Portland carbonate. This latter step may necessitate the use of larger LB simulation masks in order to accurately capture the pore-scale heterogeneity of the carbonate and hence may be more computationally expensive, thus requiring the use of parallel computing methods such as multicore computing or cluster computing, which have not been employed in this work so far. Future LB simulations would also be conducted using multiple relaxation time (MRT) LB code, e.g. as implemented by Thomas Pintelon at the MRRC (Pintelon, 2010; Pintelon et al., 2012). MRT LB, which was originally proposed by d'Humières (1994), overcomes several limitations of the single relaxation time (SRT) LBGK algorithm (described in Section 2.3.2) which was used in this work, such as a fixed Prandtl number (Pr, i.e. the ratio between kinematic viscosity and thermal diffusivity) of 1, and a fixed ratio between the kinematic and bulk viscosities. Furthermore, Lallemand & Luo (2000) showed that the addition of extra relaxation times allows the MRT model to be tuned for stability over a broad range of conditions, unlike the SRT model which becomes unstable as $1/\tau$ (where τ is the LGBK relaxation parameter) becomes too large. In addition, the propagator simulation (DRW) algorithm used in this work may be modified to include the effects of surface relaxation, such as was previously attempted by Harris (2005), thus enabling more accurate comparison with the experimentally acquired NMR propagators.

For the work presented in Chapter 6, future experiments may include investigation of the effect of changing the orientation of the two-layer interface (e.g., by changing the angle of the interfacial plane with respect to the axial flow direction) on the longer term behaviour

(Rayleigh-Taylor fingering) of the overriding gravity current. In addition, the use of immiscible fluid phases, such as the supercritical CO₂ analogue system identified in Chapter 4, may also be considered. Furthermore, the 3D CFD model presented in Chapter 6 may be developed further and validated for a broader range of conditions. Similarly, the immiscible gas/liquid displacement flow work presented in Chapter 7 may also be extended through the use of a greater variety of experimental conditions, such as different fluids, a wider range of flowrates and pore size distributions, and through a more quantitative analysis of the acquired experimental data.

In the long-term, the main focus of this work should be an extension to more realistic conditions for CO_2 sequestration. The experimental work presented in this thesis employed either model porous media, such as glass bead and sand packs, or core plug samples of two different rock types—relatively homogeneous sandstone, and heterogeneous carbonate. In addition, the work was performed under ambient temperature and low pressure (i.e. < 4 bar) conditions, using gas-phase CO_2 or analogue fluids where applicable. The use of simpler porous media and process conditions allowed the development of experimental and simulation protocols, which in future may be directly extended to systems that more realistically represent the conditions in sub-surface, such as: higher temperatures, larger pressures and pressure drops, and more realistic porous media, e.g. a greater variety of rock core soft varying porosity and permeability. It is worth noting, however, that the size of rock core samples that can be used with NMR is necessarily limited by the spectrometer size.

In addition, one of the main goals for future work should be the study of supercritical CO₂ in a two- or possibly three-phase mixture (with water and oil being the other phases), as this configuration most accurately represents the conditions at the sub-surface depths at which bulk-phase CO₂ would likely be stored. The limited amount of work done so far on the transport properties of supercritical CO₂ in porous media and related systems using NMR suggests that there is plenty of scope for further research in this area. However, as the critical pressure of CO₂ is 73.9 bar, the apparatus used in NMR experiments needs to be able to withstand such pressures. The necessity of avoiding metallic materials of construction inside the magnet makes this a challenging, but not impossible, task. In addition, supercritical CO₂ is highly corrosive, particularly in the presence of water and other impurities (Sim et al., 2013), which additionally poses challenges for other components such as tubing and seals. Previously, Thurecht et al. (2005, 2006) used a high pressure polyether ether ketone (PEEK)

NMR cell based on the design of Wallen et al. (2000) to study the swelling of network and semi-crystalline polymers in the presence of supercritical CO₂. More recently, the immiscible two-phase flow of supercritical CO_2 and water in Berea sandstone, and of supercritical CO_2 and an oil phase (*n*-decane) in glass bead packs were investigated by Suekane et al. (2009) and Liu et al. (2011) respectively, using simple 2D MRI techniques. These studies did not directly image the CO₂ but inferred its presence through the lack of ¹H NMR signal. Another research possibility therefore is that of using ¹³C NMR to directly image the CO₂—as supercritical CO_2 , being of a similar density to liquids, does not suffer from the same inherent low signal issues as gas-phase CO_2 would. In systems where CO_2 exists in conjunction with an oil phase, the greater chemical shift resolution of the ${}^{13}C$ spectrum compared to ${}^{1}H$ could allow species-specific measurements. In addition, the relatively long T_1 of ¹³C allows the use of PFG NMR techniques over extended timescales (tens of seconds) compared to ¹H NMR, as shown by Akpa et al. (2007). However, the use of ¹³C NMR does suffer from certain inherent signal-to-noise deficiencies compared to ¹H NMR, mainly due to the low natural abundance of ${}^{13}C$ (~1.1 %), its lower gyromagnetic ratio (~1/4 that of ${}^{1}H$), and coupling effects with neighbouring ¹H nuclei which cause splitting of the signal peaks. These deficiencies can be overcome to some extent by using experimental techniques such as broad band ¹H decoupling and polarization transfer techniques such as INEPT (Morris & Freeman, 1979) and DEPT (Doddrell et al., 1982). In addition, ¹³C-enriched compounds may be used, though these are often not preferred due to their high cost.

8.4 References

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