Developing High Spatial Resolution MRI Methods for Characterisation of Porous Materials

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Preface

The work presented in this thesis was carried out at the Magnetic Resonance Research Centre and Department of Chemical Engineering and Biotechnology, University of Cambridge, between October 2016 and September 2020. This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University of similar institution except as declared in the Preface and specified in the text. This thesis does not exceed the prescribed word limit for the Engineering Degree Committee (65,000 words and 150 figures).

Kaspars Karlsons
November 2020
Acknowledgements

Firstly, I would like to thank my supervisor, Professor Lynn Gladden, for giving me the opportunity to study at the Magnetic Resonance Research Centre (MRRC). Her continued support, guidance, and encouragement have helped me to overcome many obstacles over the past four years. It has been a privilege to work in her group at the MRRC! I would like to also thank Dr Andy Sederman and Dr Mick Mantle for their help and invaluable advice on a day-to-day basis. Their guidance and expertise on magnetic resonance and chemical engineering have helped me to solve many problems, both practical and theoretical, during my PhD.

Thanks are also due to all other members of MRRC, past and present, who have helped me in this work. Most of all, I would like to thank Dr Daan de Kort, a former postdoctoral researcher at the MRRC, for his guidance and support over the last four years. We both worked on Digital Rock projects, which involved a lot of collaborative work, so many ideas of this work were inspired by conversations with Daan. Flow MRI experiments in Chapter 6 were carried out in close collaboration with him; some aspects of the work in Chapter 6 were entirely carried out by Daan, which include the development of MRI methods for the acquisition of 3D under-sampled spatially-resolved propagators, as well as the acquisition, processing, and analysis of the under-sampled spatially-resolved propagator data. In addition, I would like to thank Daan for his expertise during the pulse sequence development and implementation stages, his assistance in measuring the spectral linewidths of water-saturated porous rocks (Chapter 4) and compiling an overview of commercially-available MRI hardware technologies (Chapter 4), and for his assistance in constructing the flow loops (Chapters 6–8). Daan’s passion and enthusiasm for science motivated me to work harder! I would also like to particularly thank the following people: Dr Nick Ramskill for his guidance in performing compressed sensing data reconstructions, Dr Adeline Klotz for her guidance in velocity image processing, Dr Muhammad Asadullah Javed for providing the MRI velocity data of the packed bed discussed in Chapter 6, and Dr Isabelle Bush and Sean Smith for useful discussions on petrophysics. A special thanks also goes to Georgia Roussou for sharing her knowledge on chemically-selective MR; the work presented in Chapter 8 was largely inspired by her success in applying the chemically-selective MR techniques in spatially-resolved propagator measurements.
In addition, I must thank several people, past and present, at the Department of Chemical Engineering and Biotechnology for their help. I wish to thank Dr Daniel Markl for his assistance with µCT image acquisitions (Chapters 5–7) and reconstructions and for teaching the basics of digital image analysis, Mohammed Al-Sharabi for his help with µCT image acquisitions (Chapter 5), and Zlatko Saracevic for conducting MIP measurements.

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I am extremely grateful for funding and financial support I have received during these last few years. For this, I acknowledge Shell, my wife Marita, my grandfather Gunärs, and my parents.

Finally, I would like to thank my friends, my parents, my brother, and the rest of my family for their support and encouragement over the last four years. I would like to make a special mention and thank again my late grandfather Gunärs for his continued support and financial assistance during my studies. And lastly, I wish to thank my beautiful and loving wife Marita for being so supportive and patient. Without her unconditional love and unending support and encouragement this journey would have been much more difficult!
Abstract

In this thesis, high-resolution, quantitative 3D magnetic resonance imaging (MRI) methods are demonstrated to study the microstructure of, and fluid transport processes in porous rocks. A particular motivation of this work is to provide pore-scale, quantitative, spatially-resolved structural and flow information of rocks to aid the development of Digital Rock (DR) technology – a tool based on pore-scale imaging and modelling that plays an increasingly important role in the oil and gas industry and the deployment of carbon capture and storage technologies.

To be able to study pore-scale characteristics of rocks, the spatial resolution of 3D MRI was increased by 1–2 orders of magnitude (relative to routine MRI acquisitions), up to as high as $17.6 \, \mu m$, using sensitive MRI equipment in combination with rapid and under-sampled MRI pulse sequences and compressed sensing data reconstruction techniques; $17.6 \, \mu m$ is the highest spatial resolution reported for MRI images of rocks. To this end, a novel MR data under-sampling approach was developed using input from X-ray micro-computed tomography (µCT) data to derive optimal sampling schemes for acquiring high-resolution 3D MRI images of rocks. This approach was used to speed up the acquisition of structural and flow MRI images.

Quantitative, spatially-resolved under-sampled 3D flow MRI methods, namely velocity mapping and spatially-resolved propagators, were developed and applied to study structure-flow correlations for a single-phase flow through a Ketton limestone rock. 3D velocity maps acquired at $35 \, \mu m$ spatial resolution revealed that the flow in Ketton is highly heterogeneous with $\sim 10\%$ of the pores carrying more than $50\%$ of the flow. Structure-flow correlations were found between the local pore velocity and the size and topology of the pores. Co-registration of MRI and µCT data was used to identify complex flow patterns in the rock. By analysing 3D spatially-resolved propagators, each containing 331,776 local propagators, as a function of observation time, pore-scale flow dispersion was observed.

Single-phase fluid flow velocity fields in Ketton and Estaillades limestone core plugs were computed using pore-scale lattice Boltzmann method (LBM) simulations, performed directly on the µCT images of the pore space of rocks, and then benchmarked to 3D MRI velocity maps acquired at $35 \, \mu m$ spatial resolution for flow of water through the same rock samples. For Ketton rock, good quantitative and qualitative agreement was found between the simulated and MRI velocity fields. For Estaillades rock, which presents a more heterogeneous case with
many microstructural features below the spatial resolution of the µCT image, many complex flow patterns were qualitatively reproduced by the simulation, although some local differences between the LBM and MRI velocity maps were observed.

Novel, chemically-selective under-sampled 3D MRI techniques were demonstrated to acquire quantitative, high-resolution images of oil and water fluid phases in Estaillades core plugs at the end of spontaneous and forced imbibition experiments. The high spatial resolution (35 µm) and quantitative nature of the MRI images acquired enabled oil- and water-containing microstructures to be identified and local oil and water saturations to be quantified. Disconnected oil clusters were observed in some large pores at the end of forced imbibition. Using a novel, high-resolution, chemically-selective 3D velocity mapping method, the remaining oil was confirmed to be stagnant. The flow of water in the rock was highly localised and distant from where the remaining oil was located, thus limiting the ability to recover more oil.
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Nomenclature

Roman Symbols

\( A \)  cross-sectional area of a pore
\( B_0 \)  external (static) magnetic field
\( \Delta B_0 \)  inhomogeneities of the static magnetic field
\( B_1 \)  applied (r.f.) magnetic field
\( C_1; C_2 \)  constants used for the calculation of SSIM
\( d_b \)  pore body size (diameter)
\( d_t \)  pore throat size (diameter)
\( D \)  self-diffusion coefficient
\( E \)  energy
\( \Delta E \)  energy difference
\( g \)  applied pulsed field gradient (displacement-encoding gradient pulse)
\( g_i \)  difference in applied PFG strengths between two \( q \)-images
\( g_n \)  acceleration due to gravity
\( G \)  applied magnetic field gradients
\( G_0 \)  background (internal) gradient strength
\( G_{\text{max}} \)  maximum gradient strength
\( G_{\text{phase}} \)  phase-encoding gradient
\( G_{\text{read}} \)  frequency-encoding (read-out) gradient
\( G_{\text{slice}} \)  slice gradient
\( h \)  Planck’s constant
\( \hbar \)  reduced Planck’s constant
\( h_c \)  contrast factor
\( I \)  spin quantum number
\( I_c \)  colour intensity
\( I_o \)  integrated signal intensities of oil (dodecane)
\( I_w \)  integrated signal intensities of water
\( J \)  regularisation functional
<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$k$</td>
<td>number of Bregman iterations (superscript)</td>
</tr>
<tr>
<td>$k$</td>
<td>reciprocal space vector</td>
</tr>
<tr>
<td>$\Delta k$</td>
<td>increment (resolution) in $k$-space</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$k_{\text{FOV}}$</td>
<td>extent of $k$-space</td>
</tr>
<tr>
<td>$k_{\text{max}}$</td>
<td>maximum $k$-space coordinate</td>
</tr>
<tr>
<td>$K_p$</td>
<td>permeability</td>
</tr>
<tr>
<td>$l_c$</td>
<td>characteristic length scale</td>
</tr>
<tr>
<td>$\Delta l$</td>
<td>pixel width</td>
</tr>
<tr>
<td>$\Delta l_{\text{relax}}$</td>
<td>$T_2^*$-limited pixel size</td>
</tr>
<tr>
<td>$m$</td>
<td>magnetic quantum number</td>
</tr>
<tr>
<td>$m$</td>
<td>complex image (matrix)</td>
</tr>
<tr>
<td>$m_{\text{CS}}$</td>
<td>reconstructed image (matrix)</td>
</tr>
<tr>
<td>$m_{\text{FS}}$</td>
<td>fully-sampled image (matrix)</td>
</tr>
<tr>
<td>$M$</td>
<td>magnetisation vector</td>
</tr>
<tr>
<td>$M_0$</td>
<td>equilibrium magnetisation vector</td>
</tr>
<tr>
<td>$M_{x,y}$</td>
<td>transverse component of the magnetisation vector (in the $xy$-plane)</td>
</tr>
<tr>
<td>$M_z$</td>
<td>longitudinal component of the magnetisation vector</td>
</tr>
<tr>
<td>$n$</td>
<td>number of $k$-space samples</td>
</tr>
<tr>
<td>$N$</td>
<td>number of pixels (data points)</td>
</tr>
<tr>
<td>$N_\alpha$</td>
<td>number of spins in the $\alpha$ (low) energy state</td>
</tr>
<tr>
<td>$N_\beta$</td>
<td>number of spins in the $\beta$ (high) energy state</td>
</tr>
<tr>
<td>$N_p(i)/N_p^{\text{tot}}$</td>
<td>fraction of the number of pores</td>
</tr>
<tr>
<td>$N_{\text{phase}}$</td>
<td>number of phase-encoding increments</td>
</tr>
<tr>
<td>$N_{\text{RF}}$</td>
<td>RARE factor</td>
</tr>
<tr>
<td>$N_s$</td>
<td>number of scans</td>
</tr>
<tr>
<td>$N_{\text{vox}}$</td>
<td>number of voxels in an image</td>
</tr>
<tr>
<td>$p$</td>
<td>power of polynomial (superscript)</td>
</tr>
<tr>
<td>$p_f$</td>
<td>fluid pressure</td>
</tr>
<tr>
<td>$P$</td>
<td>spin angular momentum</td>
</tr>
<tr>
<td>$Pe$</td>
<td>Péclet number</td>
</tr>
<tr>
<td>$\bar{P}(\mathbf{R}, \Delta)$</td>
<td>probability distribution of molecular displacements</td>
</tr>
<tr>
<td>$\mathbf{q}$</td>
<td>reciprocal space vector of the space of dynamic displacements</td>
</tr>
<tr>
<td>$\mathbf{q}_d$</td>
<td>Darcy velocity</td>
</tr>
<tr>
<td>$Q_z$</td>
<td>flow rate in the $z$-direction</td>
</tr>
<tr>
<td>$r$</td>
<td>position vector</td>
</tr>
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Nomenclature

$r'$ position vector after an observation time

$r_A$ adjustable normalised radius

$r_N$ normalised distance from the origin to the corner of k-space

$\mathbf{R}$ displacement vector

$Re$ Reynolds number

$Re_l$ local Reynolds number

$S$ NMR signal detected in the xy-plane

$S_o$ relative oil saturation

$S_p/V_p$ surface-to-volume ratio of pore space

$S_w$ relative water saturation

$t$ time

$\Delta t$ time increment (interval)

$t_d$ dwell time

$\tau_e$ echo time

$\tau_{e, eff}$ effective echo time

$\tau_{exp}$ experimental time

$\tau_p$ pulse duration

$\tau_{pe}$ phase-encoding time

$\tau_{RD}$ recycle delay

$\tau_{store}$ longitudinal storage time

$T$ temperature

$T_1$ spin-lattice or longitudinal relaxation time

$T_{1,2b}$ bulk ($T_1$ or $T_2$) relaxation time

$T_2$ spin-spin or transverse relaxation time

$T_{2^*}$ transverse relaxation time in an inhomogeneous magnetic field

$\nu$ velocity

$\mathbf{v}$ velocity field vector

$\nu_i$ interstitial flow velocity

$\nu_z, \nu_x, \nu_y$ $z$, $x$- and $y$-velocity components

$\nu^m_z$ mean $z$-velocity within a pore

$\bar{\nu}^m_z$ average mean $z$-velocity within a pore

$\nu^\text{sum}_z(i)/\nu^\text{sum, tot}_z$ fraction of total flow in the $z$-direction

$V$ volume of fluid

$V_p(i)/V_p^\text{tot}$ fraction of the volume of pores

$x, y, z$ Cartesian coordinates

$y$ under-sampled k-space data (matrix)
\[ \Delta z \quad \text{slice thickness (in selective slice excitation)} \]

**Greek Symbols**

- \( \alpha \): regularisation parameter
- \( \Delta \): observation time (flow MRI)
- \( \Delta_{\text{PSNR}} \): difference in PSNR values
- \( \Delta_{\text{SSIM}} \): difference in SSIM values
- \( \delta \): PFG pulse duration (flow MRI)
- \( \delta_c \): chemical shift
- \( \varepsilon \): normally-distributed noise
- \( \mathcal{F}_u \): under-sampled Fourier transform operator
- \( \gamma \): gyromagnetic ratio
- \( \mu \): magnetic moment
- \( \mu \): mean of fluid displacement
- \( \mu_{\text{global}} \): mean of fluid displacement of a global propagator
- \( \mu_{\text{CN}} \): mean coordination number
- \( \mu_f \): dynamic (fluid) viscosity
- \( \mu_m \): mean of image intensity
- \( \mu_s \): mean (true) signal intensity
- \( \nabla \): vector differential operator
- \( \nu \): nucleus resonance frequency
- \( \nu_0 \): Larmor frequency
- \( \nu_f \): kinematic viscosity of fluid
- \( \nu_{\text{ref}} \): reference frequency
- \( \omega \): angular frequency
- \( \omega_0 \): Larmor (angular) frequency
- \( \omega_1 \): r.f. (angular) frequency
- \( \Delta \omega \): offset frequency
- \( \Delta \omega_{\text{bw}} \): (soft) pulse bandwidth
- \( \phi \): phase
- \( \phi_{\text{net}} \): net difference in phase shift
- \( \phi_R \): receiver phase
- \( \phi_{\text{res}} \): residual phase shift
- \( \phi_g \): gravimetric porosity
- \( \phi_{\mu\text{CT}} \): porosity determined from \( \mu \text{CT} \) images
- \( \rho \): (fluid) mass density
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<tr>
<td>( \rho_{1,2} )</td>
<td>surface relaxivity associated with ( T_1 ) or ( T_2 )</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>spin density</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>standard deviation of fluid displacement</td>
</tr>
<tr>
<td>( \sigma_{\text{global}} )</td>
<td>standard deviation of fluid displacement of a global propagator</td>
</tr>
<tr>
<td>( \sigma_m )</td>
<td>standard deviation of image intensity</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>standard deviation of noise</td>
</tr>
<tr>
<td>( \Delta \chi )</td>
<td>magnetic susceptibility differences</td>
</tr>
<tr>
<td>( \tau )</td>
<td>time delay</td>
</tr>
<tr>
<td>( \tau_e )</td>
<td>half echo time</td>
</tr>
<tr>
<td>( \theta )</td>
<td>flip angle</td>
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**Acronyms / Abbreviations**

- 1D, 2D, 3D: one-, two-, or three-dimensional
- µCT: (X-ray) micro-computed tomography
- µCT-VDS: µCT-based variable density sampling
- APGSTE: alternating pulsed gradient stimulated echo (pulse sequence)
- AVDS: adapted variable density sampling
- BGK: Bhatnagar-Gross-Krook (model)
- BTR: body-to-throat ratio
- CCS: carbon capture and storage
- cdf: cumulative density function
- CFD: computational fluid dynamics
- CND: coordination number distribution
- CPMG: Carr-Purcel-Meiboom-Gill (pulse sequence)
- CPU: central processing unit
- CS: compressed sensing
- CT: computer tomography
- CUDA: compute unified device architecture
- CYCLOPS: cyclically ordered phase sequence
- DNP: dynamic nuclear polarisation
- DR: Digital Rock
- eLBM: energy-based lattice Boltzmann method
- EOR: enhanced oil recovery
- EPI: echo planar imaging (pulse sequence)
- FEP: fluorinated ethylene propylene
- FID: free induction decay
FLASH  fast low angle shot imaging (pulse sequence)
FOV    field-of-view
FWHM  full width at half maximum
GPGPU general-purpose graphics processing unit
HI     hydrogen index
LBM    lattice Boltzmann method
LSSIM  local structural similarity index
MIP    mercury intrusion porosimetry
MRI    magnetic resonance imaging
MR     magnetic resonance
MRT-LBM multiple-relaxation-time lattice Boltzmann method
NMR    nuclear magnetic resonance
OOMFIP Object Oriented Mathematics for Inverse Problems
pdf    probability density function
PESV   phase encoding start value
PFG    pulsed field gradient (pulse sequence)
PGSE   pulsed gradient spin echo (pulse sequence)
PNM    pore network model
PSD    pore size distribution
PSNR   peak signal-to-noise ratio
r.f.   radio frequency
RAM    random-access memory
RARE   rapid acquisition with relaxation enhancement (pulse sequence)
REV    representative elementary volume
r.m.s. root-mean-square (distance)
SNR    signal-to-noise ratio
SPI    single point imaging (pulse sequence)
SPRITE single point ramped imaging with $T_1$ enhancement (pulse sequence)
SSIM   structural similarity index
SW     spectral width
TV     total variation
WET    water suppression enhanced through $T_1$ effects (pulse sequence)
Chapter 1

Introduction

1.1 Digital Rock Technology

Despite encouraging advances in renewable energy technologies, oil remains to be the primary energy source, providing approximately 33% of global energy consumption [1]. However, the average oilfield recovery factor worldwide is only approximately 30% of the initial oil in place, which means that about two thirds of the oil remains trapped in the reservoir [2]. Due to growing global energy demand, and at the same time an urgent need to relieve pressure on the environment, improved oil recovery technologies, such as enhanced oil recovery (EOR), may be part of a future in which oil is produced in a more sustainable and environmentally-friendly way. Using such technologies, more oil can be recovered from the reservoirs thus reducing the need for additional drilling. For instance, EOR relies on the injection of brine, polymers, or surfactants to recover the trapped or bypassed oil that has remained in the reservoir after primary (e.g., pressure depletion) and secondary (e.g., water flooding) recoveries. Using EOR, recovery factors of more than 50% can be achieved [2, 3].

The oil production efficiency of a reservoir relies on an accurate estimation of the petrophysical properties of rock formations within the reservoir. The main difficulty in accurately determining these properties is that most reservoirs are not uniform and contain rock formations which are highly heterogeneous. The traditional laboratory approaches to characterize sedimentary rocks are based on quantifying macroscopic petrophysical properties of representative reservoir rock samples (rock core plugs), such as porosity, permeability, and wettability. Although the macroscopic rock measurements are useful, they neglect the pore-scale characteristics of the rock microstructure (distribution of the pores and grains), which are a key factor underlying the efficiency of oil recovery processes.

Driven by the development of powerful, high-resolution three-dimensional (3D) imaging and modelling capabilities, so called Digital Rock (DR) technology is emerging as a powerful
Figure 1.1 A typical workflow of Digital Rock (DR) technology. First, high-resolution projection images of a rock sample are acquired using X-ray micro-computed tomography (µCT), which is the primary tool in DR technology used for acquiring images of the rock matrix. Three-dimensional (3D) images are then reconstructed from these projections obtained at different angular positions, corrected for the artefacts, and denoised. The result is a grayscale image of the rock matrix, where the intensities correspond to the local X-ray absorption within the rock material. By segmenting the image into the pore space and rock grains, the corresponding pore space image can be obtained. Lastly, rock properties are computed on the basis of the pore space image, e.g., flow and transport properties can be calculated using the lattice Boltzmann method (LBM). A representative pore network model (PNM) can be extracted from the pore space image, which can also be used to compute petrophysical rock properties. In DR technology, magnetic resonance imaging (MRI) serves as a tool for the development and validation of PNMs and DR simulators.
physical processes (e.g., flow and transport) are simulated on the extracted pore space images to determine the rock petrophysical properties. The method, in which the rock properties are computed directly from the segmented pore space image, is generally referred to as direct modelling [6]. The most popular approach within this category of simulations is the lattice Boltzmann method (LBM) [6, 9, 10], which is extensively used to compute fluid flow and transport properties in different pore geometries. The main advantages of LBM are that it is relatively easy to code and it is well suited for simulating complex fluid flow, such as single- and multi-phase flow through complex pore geometries, such as the pore space of porous rocks [6]. Despite these advantages, LBM has been recognised as a computationally demanding method.

Note that the segmented pore space images can also be used to compute elastic and electrical properties of rocks [5, 11]. An alternative approach is to extract a topologically representative pore network model (PNM) [12, 13] from the underlying pore space image and then semi-analytically compute the petrophysical properties through this PNM. Because the complex pore geometries of rocks are now represented by simpler PNMs, pore network modelling enables computations to be performed on a much larger scale compared to the direct modelling approaches [6]. Network modelling, of course, relies on an accurate representation of the pore space geometry and topology, which can be challenging to determine in some rocks, such as many carbonates, where the pore size of many pores is smaller than the achievable image resolution. However, the key aspect of network modelling is to identify which characteristics of the pore space (e.g., the connected porosity of macropores) need to be captured so that the relevant petrophysical properties can be representatively and accurately computed. For example, for a single-phase flow in some rocks, a PNM of the main macropore network might be sufficient to accurately simulate the flow, because in many rocks the small pores that are below the image resolution contribute very little to the overall flow behaviour in the system.

The aim of DR technology is to complement, or even possibly replace, the relatively slow conventional, laboratory-based petrophysical measurements of rocks. It has the potential to deliver fast and cheap core analysis. The overall objective, of course, is to up-scale the use of DR technology to build models of reservoirs, which can then be used to predict and evaluate reservoir prediction potentials and improved oil recovery scenarios.

1.2 MRI – a Tool for the Development of Digital Rock Simulators

As mentioned above, DR technology can provide a fast and cost-effective way to obtain petrophysical rock properties through simulations based on µCT images of rocks. It remains
necessary, however, to validate, calibrate, and initialise these simulations on the basis of experimental data acquired on physical rock samples and to develop improved, more representative PNM s. X-ray computed tomography (CT) has been extensively used to study multi-phase displacement processes in rocks both on the core scale [14] using medical CT and on the pore scale using X-ray µCT [8, 15, 16]. X-ray µCT is particularly useful because it can image fluid displacements in rocks at spatial resolutions of a few microns, although it is limited to relatively small sample sizes with diameters of 4–6.5 mm. For example, Berg et al. [15] used synchrotron-based, high-speed µCT to directly monitor pore-scale displacement processes in a Berea sandstone during drainage and imbibition experiments. This was the first time when dynamic pore-scale displacement events were imaged at a temporal resolution matching their actual occurrence using µCT. However, obtaining high-resolution µCT images of fluids in rocks can be problematic because a doping agent is often required to obtain sufficient contrast between material phases of similar densities (e.g., oil and water), which can potentially alter the properties of the system. Furthermore, µCT is mainly used to produce snapshot images of the moving fluid interface between two fluid phases.

Magnetic resonance (MR) is another well-established tool used for the characterisation of porous materials, including porous rock core plugs, because it provides a direct and non-invasive way to obtain quantitative chemical, structural, and transport information of fluids within optically opaque materials [17–20]. In the petrophysics community, nuclear magnetic resonance (NMR) experiments are widely exploited in well-logging and special core analysis (SCAL) measurements in the laboratory [21–23]. These NMR experiments traditionally include relatively simple, bulk measurements of relaxation time and self-diffusion coefficient. Although these data can be used to determine porosity, relative oil and aqueous phase saturations, and pore size distribution of rocks, they do not provide much insight into the spatial distribution of these properties. Furthermore, one needs to be careful when interpreting such data, because very often the fluid saturation along core plugs is not uniform due to structural heterogeneities, capillary end effects, or viscous instabilities, which can be significant in short rock samples, such as those used in the laboratory [24, 25]. To provide sensitivity to these petrophysical heterogeneities, spatial dimensions can be incorporated with magnetic resonance imaging (MRI).

The strength of MRI lies in the fact that it can spatially resolve fluid properties in 3D using a range of different non-invasive contrast mechanisms, based on, for example, fluid type via the MR chemical shift [26], wetting properties via MR relaxation time constants [27], and fluid mobility via MR measurements of molecular self-diffusivity, flow dispersion, and velocity [18, 28, 29]. These properties make it an ideal tool for the development of DR simulators (Fig. 1.1). In contrast to µCT, MRI can directly measure and spatially resolve
velocities and probability distributions of displacements of moving molecules within a fluid phase [18, 30] (note that, in principle, µCT can be used to construct flow fields using particle tracking velocimetry [31, 32]). In addition, chemical sensitivity can be implemented in MRI experiments to discriminate between oil and water phases without the need for doping [26]. Despite these benefits, the spatial resolution of routine MRI acquisitions is limited to several hundred microns due to the relatively low sensitivity of the magnetic resonance method. Therefore, there exists a strong incentive to increase the spatial resolution of MRI acquisitions by 1–2 orders of magnitude to be able to explore petrophysical rock properties at spatial resolutions much closer to that of the relevant pore scale. To achieve this, three key aspects need to be considered: (1) MRI hardware, (2) pulse sequences suitable for high-resolution imaging, and (3) data under-sampling and reconstruction techniques. With respect to the MRI hardware, sensitive radio frequency (r.f.) coils and high magnetic field strengths are a prerequisite for high signal-to-noise ratio (SNR) in MRI, and strong magnetic field gradients are needed to achieve high voxel resolution. A plethora of different MRI pulse sequences are available, however, not all are well suited for high-resolution MRI acquisitions. The default form and settings of pulse sequences are also rarely directly usable. Instead, they often need to be modified to suit the particular application. Fast MRI pulse sequences [33, 34] are good candidates for high-resolution imaging because they significantly reduce the acquisition time of images (from weeks to days). The time-savings achieved using the fast imaging techniques can then be invested either to enhance the SNR of MRI by signal averaging or to reduce the voxel size, thus improving the spatial resolution of MRI. The choice of MRI hardware and pulse sequence also limits the type of rocks that can be studied at high spatial resolution; this is mainly related to the presence of magnetic susceptibility induced internal gradients, the strength of which is determined by the amount paramagnetic species in rocks [35]. Lastly, the acquisitions of 3D MRI can be further sped up by combining the rapid pulse sequences, or other pulse sequences suitable for high-resolution imaging, with MRI data under-sampling and compressed sensing (CS) techniques [36], which can reduce the total image acquisition time to a few hours, which is comparable to scan times of 3D X-ray µCT. This is achieved by acquiring only a subset of the data that would be acquired in conventional MRI. The images are then reconstructed from the under-sampled data using a non-linear optimisation scheme, in which prior knowledge about the images is used to obtain an optimal reconstruction. Rather than viewing CS as a strategy to reduce data acquisition times at a given resolution, it can be seen as a tool to acquire images at higher spatial resolutions, at which the acquisition times would otherwise be prohibitively long.
1.3 Aim and Scope of This Thesis

The primary aim of this thesis is to develop high spatial resolution MRI methods for characterisation of porous sedimentary rocks. In particular, the main motivation is to use MR techniques to acquire high spatial resolution MRI images of rock core plugs and the fluids within them to better understand structure-flow relationships and to aid the development and validation of DR flow simulators that are used to predict complex single- and multi-phase fluid flow in rocks. The strategy for achieving this aim was a multi-step process which involved the procurement of sensitive MRI equipment, identification and development of pulse sequences suitable for high-resolution imaging, and optimisation of MRI data under-sampling and CS reconstruction techniques. Combining all of these factors enabled pore-scale structural and flow images of rocks to be acquired at resolutions of up to 17.6 µm and 35 µm, respectively; these are the highest spatial resolutions reported for MRI structural and flow images of rock samples. µCT data of rocks were also extensively used to complement the information obtained from MRI and even develop new MRI data sampling methods. In addition, the synergy of high-resolution MRI and µCT was exploited to gain a deeper understanding of structure-flow correlations in rocks and to benchmark single-phase LBM simulations.

The experiments in this thesis have been performed on a millimeter scale at spatial resolutions that are in most cases compatible with what can be achieved using state-of-the-art direct, µCT-based DR simulations. The objective of this work was not to study larger scale systems (centimetre and larger), which is, of course, essential for up-scaling purposes of DR technology, but to provide tools for the development of simulators at micrometre to millimetre scale. Using the high-resolution MRI methods and data presented in this thesis, we can now gain a deeper understanding of structure-transport relationships in rocks at pore-scale resolution during single- and multi-phase core flood experiments and provide useful input to and validation of DR simulators. Although the methods have been demonstrated in application to imaging of porous sedimentary rocks, they are entirely generic and can be used to achieve high spatial resolution MRI images of any system.

1.4 Outline of Thesis Chapters

This thesis is structured as follows:

Chapter 1 provides background information on DR technology and the imaging techniques that contribute to the development of this technology. The benefits for using MRI in DR technology are also highlighted. The aim and outline of this thesis are stated.
Chapter 2 describes the basic principles of NMR, MRI, and MR flow imaging relevant to this work.

Chapter 3 gives an introduction to digital image processing techniques that were used to process and analyse the acquired high-resolution MRI and µCT images.

Chapter 4 serves as a foundation for Chapters 5–8. This chapter discusses the main considerations for high-resolution MRI of porous rocks. It also introduces the concepts of MRI data under-sampling and CS data reconstruction techniques.

Chapter 5 presents a novel MRI data under-sampling approach which uses input from high-resolution 3D X-ray µCT data for acquiring high spatial resolution (up to 17.6 µm) 3D MRI images of rocks. The work presented in this chapter has been included in the following publication: K. Karlsons, D.W. de Kort, A.J. Sederman, M.D. Mantle, H. de Jong, M. Appel, and L.F. Gladden. Identification of sampling patterns for high-resolution compressed sensing MRI of porous materials: ‘learning’ from X-ray micro-computed tomography data. *J. Microsc.*, 276:63–81, 2019.

Chapter 6 demonstrates the application of the new MRI data sampling methodology and MRI flow imaging techniques developed for high-resolution imaging to investigate structure-flow relationships in a porous carbonate rock sample. Using image co-registration and simultaneous visualisation of MRI and µCT images made it possible to correlate local flow properties with the microstructure of the rock matrix. The work presented in this chapter has been included in the following publication: K. Karlsons, D.W. de Kort, A.J. Sederman, M.D. Mantle, J.J. Freeman, M. Appel, and L.F. Gladden. Characterising pore-scale structure-flow correlations in sedimentary rocks using magnetic resonance imaging. *Phys. Rev. E*, 103:023104, 2021.

Chapter 7 benchmarks single-phase LBM flow simulations, run on segmented 3D µCT images of carbonate rocks, against high resolution MRI flow fields acquired on the same rock samples. The work presented in this chapter has been submitted for publication: K. Karlsons, D.W. de Kort, F.O. Alpak, J. Dietderich, J.J. Freeman, M. Appel, M.D. Mantle, A.J. Sederman, L.F. Gladden. Integrating pore-scale flow-MRI and X-ray µCT for validation of numerical flow simulations.

Chapter 8 describes the development and application of chemically-selective high-resolution MRI methods for imaging multi-phase systems (oil and water). Chemically-selective structural and velocity images of oil/water systems in carbonate rocks are shown.

Chapter 9 summarises the main conclusions of this thesis and provides an outlook for possible future research areas.
Chapter 2

NMR and MRI Theory

2.1 Introduction

NMR is a physical phenomenon by which some nuclei can absorb and re-emit electromagnetic radiation at a specific resonant frequency when placed in a magnetic field. NMR was first described in 1938 by Isidor Isaac Rabi [37], who measured NMR in molecular beams of lithium chloride (LiCl) and observed the resonance/absorption peaks of Li and Cl. The first successful measurements of NMR in condensed matter were carried out almost simultaneously in 1946 by Felix Bloch [38] and Edward Purcell [39]. With the discovery of chemical shift [40], that is the variation of NMR resonant frequencies in different electronic environments within a molecule, NMR rapidly developed as one of the most versatile spectroscopic tools for structural and chemical analysis of molecules. In 1973, Lauterbur [41] and Mansfield and Grannell [42] used the principles of NMR to obtain the first magnetic resonance images of objects – a form of a magnetic resonance experiment known as MRI. Since its discovery, MRI has become a fundamental imaging tool in radiology used to non-invasively diagnose diseases and to monitor treatment. Relatively recently, it has also gained popularity in fields like chemical engineering, the pharmaceutical industry, and petrophysics.

This chapter provides an introduction to the basic theory and standard experimental techniques of NMR and MRI pertinent to this thesis. For a more detailed explanation of NMR and MRI principles, the reader is referred to the literature [43–46].
2.2 Basic Principles of NMR

2.2.1 Nuclear Spin and the Zeeman Effect

An NMR experiment is a detailed manipulation of a spin system. Spin is a quantum mechanical property carried by elementary particles. The atomic nucleus consists of protons and neutrons, both of which are spin-1/2 particles. The spin of a nucleus is determined by combining the spins of neutrons and protons it is comprised of. The nuclear spin is quantified by the spin quantum number, \( I \). Nuclei which have an even number of both protons and neutrons have \( I = 0 \) (e.g., \(^{12}\text{C}, \(^{16}\text{O}\)) and are termed “NMR silent”. If a nucleus contains an odd number of both protons and neutrons, \( I \) is an integer number greater than zero. However, if the sum of protons and neutrons is odd, nuclei have a half-integer spin. The most commonly used nuclei in NMR are \(^1\text{H}\) and \(^{13}\text{C}\), which both have the spin quantum number of \( I = 1/2 \). NMR-active nuclei possess a spin angular momentum, \( P \), which is quantised and is related to the spin quantum number \( I \) via:

\[
P = \hbar[I(I + 1)]^{1/2},
\]

where \( \hbar \) is the reduced Planck’s constant, \( \hbar = \frac{\hbar}{2\pi} \). Nuclei with non-zero spin also possess the magnetic moment, \( \mu \), which is proportional to \( P \) as:

\[
\mu = \gamma P.
\]

The constant of proportionality, \( \gamma \), is called the gyromagnetic ratio and is a characteristic of a particular nucleus. The \(^1\text{H}\) nucleus has the highest known value of \( \gamma \) of \( 2.675 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1} \). All data in this thesis were acquired using \(^1\text{H}\) NMR.

Nuclei can exist in different spin states. In the absence of an external magnetic field, the spin states are degenerate. However, if an external magnetic field of strength \( B_0 \) is applied, for example, along the z-direction, the degeneracy is broken, and the nucleus develops \((2I + 1)\) different energy level states; these are characterised by the magnetic quantum number, \( m \), which can take the values \(-I \ldots, 0, \ldots +I\). This splitting between the nuclear spin states is known as the Zeeman effect. The energy of each state, resulting from the interaction of the magnetic moment and the external magnetic field, is written as:
2.2 Basic Principles of NMR

For a spin-1/2 nucleus, such as $^1$H, two energy levels are formed, namely the $\alpha$-state ($m = +1/2$) and $\beta$-state ($m = -1/2$), which correspond to the angular momentum of the nuclear spin aligning parallel or antiparallel to the main magnetic field, respectively. A transition between the energy states can be induced by the absorption or emission of electromagnetic radiation (photon) of the energy, $\Delta E$, given by:

$$\Delta E = h\nu_0 = \hbar\gamma B_0,$$  \hspace{1cm} (2.4)

where $\nu_0$ is the resonance frequency of the nucleus under study. The Zeeman effect for a spin-1/2 nucleus is shown in Fig. 2.1.

2.2.2 The Bloch Vector Model

Although quantum mechanics can be used to understand some aspects of NMR, it cannot efficiently describe how the NMR experiments work. To develop understanding of NMR experiments, the Bloch vector (semi-classical) model is used.

For a macroscopic sample of spin-1/2 nuclei placed in an external magnetic field of strength $B_0$ at thermal equilibrium, the nuclear spins will populate the two states according to the Boltzmann distribution, expressed as:

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{h\gamma B_0}{k_B T}\right).$$  \hspace{1cm} (2.5)
Diagram of the Bloch vector model for spin-1/2 nuclei. At equilibrium, the net magnetisation vector, $M_0$, is aligned along the direction of the applied magnetic field, $B_0$. The red arrow indicates the direction of precession.

$N_\beta$ and $N_\alpha$ correspond to the number of spins in states $\beta$ and $\alpha$, $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$), and $T$ is the absolute temperature (K). Only a small excess of spins are expected to be found in the lower energy state ($\alpha$-state), e.g., for $^1\text{H}$ at 300 K and 7 T magnetic field strength, the population ratio is 0.99995. This is the main reason for the inherently low sensitivity of NMR compared to other spectroscopic techniques, such as infrared spectroscopy.

Using a semi-classical description, an ensemble of independent spin-1/2 nuclei can be represented as two cones (one in each state) in which the spins precess, which is illustrated in Fig. 2.2. The vector sum of all the individual magnetic moments, $\mu$, in the sample, which is proportional to the difference in population between the spin states, results in the net magnetic moment or bulk magnetisation, $M$ (denoted as $M_0$ at thermal equilibrium), parallel to the applied external magnetic field. By equating the torque, which is exerted on $M$ by $B$, to the rate of change of angular momentum, $\frac{dM}{dt}$, the following equation is obtained:

$$\frac{dM}{dt} = \gamma M \times B.$$  \hspace{1cm} (2.6)

The solution to Eq. 2.6 corresponds to a precession of the magnetisation around the direction of the applied magnetic field $B$ of strength $B_0$ with an angular frequency (in rad s$^{-1}$):

$$\omega_0 = \gamma B_0,$$  \hspace{1cm} (2.7)

or in the frequency units of Hz:
2.2 Basic Principles of NMR

\[ \nu_0 = \frac{\gamma}{2\pi} B_0. \] (2.8)

This precession frequency is known as the Larmor frequency, and is the fundamental frequency at which the NMR signal is excited and detected.

2.2.3 Resonance and Spin Excitation

To excite nuclear spins into their higher energy state, the energy is supplied in the form of a radio frequency (r.f.) “pulse”, i.e., a sinusoidal r.f. current is applied to the sample using a transmitter coil. In a more classical description, this means that a linearly polarised magnetic field, denoted \( B_1 \), rotating at the Larmor frequency, is applied perpendicular (in the xy-plane) to the main magnetic field, \( B_0 \) – this is the *resonance* phenomenon employed in NMR. The application of \( B_1 \) disrupts the bulk magnetisation vector from its equilibrium state, \( M_0 \), and causes \( M \) to precess simultaneously around \( B_0 \) at \( \omega_0 \) and around \( B_1 \) at \( \omega_1 \). In order to simplify the complex motion of precessing magnetisation under these conditions, the concept of the rotating frame of reference is used. The rotating frame is a new coordinate system, which rotates with angular frequency \( \omega_1 \) about the z-axis of the laboratory frame (xyz). The result is that in the rotating frame the precession of \( M \) around \( B_0 \) is no longer occurring, and the \( B_1 \) field appears static, such that \( M \) precesses only about \( B_1 \). In the subsequent part of this document, all the vector model diagrams will be represented in the rotating frame of reference.

To manipulate the magnetisation vector in a pulsed NMR experiment, short bursts of resonant r.f. pulses, \( B_1 \), are applied perpendicular to the main magnetic field, \( B_0 \). Under the

![Figure 2.3](image)

**Figure 2.3** Representation of the magnetisation in the rotating frame of reference. (a) The equilibrium net magnetisation vector can be flipped into the xy-plane by applying a \( B_1 \) field perpendicular to the main field, \( B_0 \). (b) A 90° pulse with angular frequency, \( \omega_1 \), and duration, \( t_p \), applied along the x-axis rotates the magnetisation vector onto the y-axis. (c) A 180° pulse with the same \( \omega_1 \), but twice the duration, \( 2 \times t_p \), applied along the x-axis rotates the magnetisation vector from the positive to negative z-direction.
resonance condition, i.e., $\omega_0 = \omega_1$, the flip angle, $\theta$, by which the magnetisation vector is rotated from its equilibrium position is determined by the duration, $t_p$, and the amplitude, $B_1$, of the applied field $B_1$, expressed as:

$$\theta = \omega_1 t_p = \gamma B_1 t_p.$$  \hfill (2.9)

A $B_1$ field with the correct amplitude and duration will rotate the magnetisation vector by $90^\circ$, i.e., from the $z$-axis into the $xy$-plane; this r.f. pulse is called a $90^\circ$ or $\pi/2$ pulse. Doubling the duration of the pulse would result in a $180^\circ$ rotation from the $+z$ to $-z$ direction, which is referred to as a $180^\circ$ or $\pi$ pulse. Figure 2.3 illustrates the effect of the r.f. pulses on the magnetisation vector. The pulse duration is inversely proportional to the range of frequencies (excitation bandwidth) it can excite. Therefore, if a short $90^\circ$ pulse (typically a few microseconds) is used, the entire range of Larmor frequencies in the sample under study would be excited at once. These pulses with a broad excitation profile are usually referred to as hard or non-selective pulses. On the contrary, the use of a longer $90^\circ$ pulse with smaller magnitude $B_1$ (flip angle determined by the product $\gamma B_1 t_p$) would affect only a narrow range of the NMR frequency spectrum. These pulses are referred to as soft or selective pulses. An NMR experiment consists of single or multiple r.f. pulses, which is collectively called a “pulse sequence”.

### 2.2.4 Signal Detection

After the application of a $90^\circ$ pulse (on resonance), the magnetisation vector is flipped into the $xy$-plane, forming a transverse magnetisation component, $M_{x,y}$. Due to the precession of the transverse magnetisation, $M_{x,y}$, an oscillating r.f. current is induced in the receiver coils (positioned in the $xy$-plane) at the Larmor frequency. The decaying signal intensity, $S(t)$, which is directly proportional to the precessing magnetisation, is known as a free induction decay (FID). The induced signal is complex and therefore contains both real ($x$) and imaginary ($y$) components. In order to detect both components of the signal, a process known as quadrature detection is used. During this process, the NMR signal is split into two parts and mixed with two reference signals $90^\circ$ out of phase with each other (heterodyning). This enables the real ($x$) and imaginary ($y$) parts of the signal to be be detected separately, which can be expressed as:

$$S(t) = S_x(t) + iS_y(t).$$  \hfill (2.10)
2.2 Basic Principles of NMR

Figure 2.4 Schematic of the pulse-acquire NMR experiment. (a) The time domain signal (FID) is acquired immediately following a 90° pulse. (b) The resultant NMR spectrum after Fourier transformation (FT).

Mixing together the induced NMR signal with the reference signal oscillating at $\omega_{\text{ref}}$ is equivalent to viewing the magnetisation in the rotating frame of reference. The heterodyne signal at offset, $\Delta\omega = \omega_0 - \omega_{\text{ref}}$, is written as:

$$S(t) = S_0 \exp(i\phi_R) \exp(i\Delta\omega t), \quad (2.11)$$

where $S_0$ is the signal amplitude immediately following the pulse ($\propto M_0$), and $\phi_R$ is the arbitrary receiver phase. In order to be stored in the computer memory, the FID signal is digitally sampled by a digitiser over a frequency range termed the spectral width (SW). The time between the digitally sampled points is called the dwell time, $t_d$, which is expressed as $t_d = \frac{1}{\text{SW}}$. According to Nyquist sampling theorem [47], SW must be at least twice the frequency of the signal in a sample in order to faithfully reproduce the signal. The phase-corrected Fourier transformation of $S(t)$ yields a pattern of peaks of the sample resonant frequencies, known as an NMR spectrum:

$$S(\omega) = \int_{-\infty}^{\infty} S(t) \exp(i\omega t) \, dt. \quad (2.12)$$

A schematic of a simple “pulse-acquire” NMR pulse sequence along with the resulting NMR spectrum is shown in Fig. 2.4. The intensity of the acquired NMR signal is directly proportional to the spin density in the sample. In an NMR spectrum, this means that the area under each peak is proportional to the number of nuclei that each peak represents.
2.2.5 Relaxation Processes

After the application of an r.f. pulse, the nuclear spin ensemble has excess energy, i.e., nuclear spins are excited to a higher energy state. To return to thermal equilibrium, excited spins redistribute the excess energy via relaxation processes. The dominant mechanism that causes spin relaxation arises from dipole-dipole interactions. Two relaxation processes are typically studied in NMR – spin-lattice relaxation and spin-spin relaxation.

2.2.5.1 Spin-Lattice Relaxation

Spin-lattice relaxation, also referred to as longitudinal relaxation, describes the recovery of longitudinal magnetisation, $M_z$, to its equilibrium value. It involves the exchange of energy between the spin ensemble and its surroundings (the lattice). Assuming an exponential behaviour of spin-lattice relaxation, it is defined as:

$$\frac{dM_z}{dt} = -\left( \frac{M_z - M_0}{T_1} \right),$$  \hspace{1cm} (2.13)

where $T_1$ is the spin-lattice relaxation time. Applying the initial condition $M_z(t = 0) = M_z(0)$ gives the solution to Eq. 2.13 as:

$$M_z(t) = M_z(0)\exp\left( -\frac{t}{T_1} \right) + M_0 \left[ 1 - \exp\left( -\frac{t}{T_1} \right) \right].$$  \hspace{1cm} (2.14)

The relaxation time constant $T_1$ represents the time at which 63% of the original, equilibrium magnetisation, $M_0$, is recovered. $T_1$ is sensitive to the molecular tumbling rate in a system. As molecules tumble, the nuclear spins, which reside in the molecules, reorient, thus generating fluctuations in the local magnetic field. These fluctuations are detected by neighbouring nuclear spins, encouraging them to relax. $T_1$ is the shortest when the molecular tumbling rate is approximately equal to the Larmor frequency. In general, the molecular motion, hence the value of $T_1$, depends on factors like viscosity, temperature, and molecule size. For example, solids, macro-molecules, and bound water molecules rotate slowly so have short $T_1$ values relative to mobile liquids (free water molecules); $T_1$ of bulk liquids is on the order of a few seconds. $T_1$ is also an important parameter to consider in MR experiments, because it determines the value of recycle delay ($t_{RD}$), which is the time between successive signal averaging scans. A short $t_{RD}$ is experimentally advantageous; if after the excitation pulse the magnetisation reaches its equilibrium value faster (shorter $T_1$), the shorter the value of $t_{RD}$ that can be used, thus shortening MR experimental times. However, for quantitative measurements, a sufficiently long
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Figure 2.5 Schematic of the inversion recovery pulse sequence used to measure $T_1$. $\tau$ is a variable time delay.

$T_1$ is typically measured using the inversion recovery [48] pulse sequence, shown in Fig. 2.5. In this experiment, a $180^\circ$ pulse is first used to flip the equilibrium magnetisation vector, $M_0$, from the positive $z$-axis onto the negative $z$-axis – this is the inversion step. A $90^\circ$ pulse is then applied after a time delay, $\tau$, which rotates the magnetisation into the $xy$-plane enabling its detection. The experiment is repeated for different $\tau$ values. To determine $T_1$, a plot of $M_z$ as a function of $\tau$ is fitted to the following equation:

$$M_z(\tau) = M_0 \left[ 1 - 2\exp \left( -\frac{\tau}{T_1} \right) \right]. \quad (2.15)$$

To allow the system to reach its equilibrium state, a $t_{RD} = 5 \times T_1$ is used between successive scans.

2.2.5.2 Spin-Spin Relaxation

Spin-spin relaxation, also known as transverse relaxation, represents decay of the magnetisation in the $xy$-plane, $M_{x,y}$, via loss of phase coherence (dephasing). As the name implies, it is the process whereby nuclear spins interact with each other and re-establish thermal equilibrium among themselves. As the spins interact with each other, it causes the magnetisation vector to dephase, leading to a change in $M_{x,y}$, defined as (assuming exponential behaviour):

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2}. \quad (2.16)$$
The solution to Eq. 2.16 is given by:

\[ M_{x,y}(t) = M_{x,y}(0) \exp \left( -\frac{t}{T_2} \right), \tag{2.17} \]

where \( M_{x,y}(0) \) is the initial magnitude of transverse magnetisation, and \( T_2 \) is the spin-spin relaxation time. Similarly to \( T_1 \), \( T_2 \) is also affected by the molecular tumbling rate. In fact, any mechanism that causes \( T_1 \) relaxation will also cause \( T_2 \) relaxation (non-secular part of \( T_2 \) relaxation). The secular part of \( T_2 \) relaxation is related to relatively slow magnetic field fluctuations that arise from slow molecular motions. Hence, bound water molecules and solids have short \( T_2 \) values. Because of the secular contribution to \( T_2 \), it has been found that \( T_2 \leq T_1 \) [43]. Practically, \( T_2 \) is an important experimental parameter to consider, because it determines how long the magnetisation vector associated with the sample exists in the \( xy \)-plane, hence limiting the amount of time in which the spin system can be manipulated in a pulse sequence. Thus, a long \( T_2 \) is generally desired.

The dephasing of the magnetisation is not only caused by spin-spin (dipolar) interactions, characterised by \( T_2 \), but also the time independent inhomogeneity effects, such as variations in the external magnetic field, \( \Delta B_0 \). The time constant \( T_2^* \) characterises \( M_{x,y} \) decay in the presence of magnetic field inhomogeneities, defined by:

\[ \frac{1}{T_2^*} \approx \frac{1}{T_2} + \gamma \Delta B_0. \tag{2.18} \]

\( T_2^* \) can be determined by measuring the full width at half maximum (FWHM) of an NMR spectrum (for a single peak) obtained using a pulse-acquire experiment:

\[ T_2^* = \frac{1}{\pi \text{FWHM}}. \tag{2.19} \]

The effects of inhomogeneities in the \( B_0 \) field can be made reversible (removed) by the use of a spin echo [49], which is described in more detail in Section 2.2.6.1. This enables the irreversible component of \( M_{x,y} \) decay, namely \( T_2 \), to be directly measured. The value of \( T_2 \) is typically determined using the Carr-Purcell-Meiboom-Gill (CPMG) [50, 51] pulse sequence, which is based on spin echoes. The CPMG sequence is illustrated in Fig. 2.6. First, a 90° r.f. pulse is used to flip the magnetisation in the \( xy \)-plane. A 180° pulse is then applied a time \( \tau_e \) after the initial 90° excitation pulse to form a spin echo, which is composed of two back-to-back FIDs. The maximum of the spin echo is reached a time \( t_e = 2 \times \tau_e \) after the 90° pulse; \( t_e \) is
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Figure 2.6 Schematic of the CPMG pulse sequence used to measure $T_2$. The first echo forms a time $t_e = 2\tau_e$ after the $90^\circ$ excitation pulse and a time $\tau_e$ after the first $180^\circ$ refocusing pulse; $t_e$ is the echo time. The repeated application of $180^\circ$ refocusing pulses generates a train of echoes, which decays exponentially with $T_2$.

known as the echo time. By repeatedly applying $180^\circ$ refocusing r.f. pulses at regular time intervals of $t_e$, a train of echoes is formed. The maxima of the echo train decays exponentially due to $T_2$ relaxation, as defined by Eq. 2.17. It is noted that $T_2$ is also sensitive to molecular diffusion, and, for accurate measurements of $T_2$, short interecho spacings, $t_e$, are preferable to reduce signal attenuation due to diffusion effects.

2.2.5.3 Relaxation in Porous Media

It is well known that fluids confined in porous media undergo enhanced relaxation. This enhanced relaxation of spins within fluid molecules is caused by a change in molecular mobility and dipolar coupling with paramagnetic species and other surface sites (diamagnetic surfaces) on the grain surfaces [17, 52]. The relaxation of nuclear spins in the pore space of porous medium can be described by the following equation [53]:

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2b}} + \rho_{1,2} \frac{S_p}{V_p}, \quad (2.20)$$

where $T_{1,2}$ ($T_1$ or $T_2$) is the observed relaxation time, $T_{1,2b}$ is the bulk relaxation time, $\rho_{1,2}$ is surface relaxivity (i.e., the strength of the surface to cause relaxation of spins), and $\frac{S_p}{V_p}$ is the surface-to-volume ratio of the pore network; the $\rho_{1,2} \frac{S_p}{V_p}$ term represents the relaxation of fluid molecules adsorbed on the surface. NMR relaxation time data can provide information on the distribution of pore sizes in a porous material. Typically, for fluids in porous media $T_{1,2} \ll T_{1,2b}$, such that the bulk relaxation term can be ignored and the observed relaxation times, $T_{1,2}$, can be used to obtain pore size distributions. In order to achieve this, relaxation time data first need to converted to relaxation time distributions using inversion algorithms [17]. The relaxation time distributions can then be scaled approximately to pore body size distributions, $d_b$, using [21]:

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2b}} + \rho_{1,2} \frac{S_p}{V_p}, \quad (2.20)$$
\[ \frac{1}{T_{1,2}} \approx \frac{6 \rho_{1,2}}{d_b}. \] (2.21)

Equation 2.21 assumes spherical pores. It is also important to note that Eq. 2.20 is valid if the relaxation is governed by the “fast-diffusion” (or “weak relaxation”) regime [52, 54]. In the fast-diffusion regime, the rate-determining step is relaxation at the pore-grain interfaces, not the transport of magnetisation to the surface. The magnetisation remains uniform in a single pore, and the relaxation is unimodal and depends on the surface-to-volume ratio. In the opposite limit, there is the “slow-diffusion” (or “strong relaxation”) regime [52, 54], in which the decay of magnetisation is controlled by the transport of spins to the surface. In this case, the magnetisation across the pore is non-uniform and relaxation is multimodal. This regime is likely to occur in large pores and materials with strong surface relaxation. However, in most sedimentary rocks, the “fast-diffusion” regime typically dominates [52].

As mentioned earlier in Section 2.2.5.2, \( T_2 \) is also affected by molecular diffusion in the presence of background magnetic field gradients. In porous media, so-called “internal gradients” can significantly alter the observed relaxation time constant \( T_2 \) [21, 35]. Internal gradients are caused by magnetic susceptibility differences between the solid and liquid, and are stronger in smaller pores and materials rich in paramagnetic species [55, 56]. In the context of petrophysics, internal gradients are usually associated with sandstones, which contain significant amount of paramagnetic ions [55]. Furthermore, it has been demonstrated that the strength of internal gradients scales with the field strength, \( B_0 \), as \( B_0^{3/2} \) [35]. Internal gradient effects lead to line broadening in an NMR spectrum, and the expression for the observed relaxation time constant \( T_2^* \) becomes [35]:

\[ \frac{1}{T_2^*} \approx \frac{1}{T_2} + \gamma \Delta \chi B_0 + \gamma \Delta \chi B_0, \] (2.22)

where \( \Delta \chi \) is the magnetic susceptibility difference in a porous medium. Note that \( T_1 \) relaxation measurements are not influenced by the effects of internal gradients [56].

### 2.2.6 Echoes

#### 2.2.6.1 Spin Echo

In 1950, Hahn [49] discovered that the effects of magnetic field inhomogeneity can be refocused by the use of a spin echo (note that the concept of spin echoes was already mentioned earlier in
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Figure 2.7 The spin echo pulse sequence with the corresponding evolution of magnetisation. (a) The $90^\circ_x$ pulse flips the equilibrium magnetisation vector (grey) into the $xy$-plane, after which (b) the spin isochromats start to dephase due to magnetic field inhomogeneities. An interval, $\tau_e$, after the $90^\circ_x$ pulse, the $180^\circ_y$ pulse inverts the spin isochromats, which start to rephase. Full refocusing occurs at time $t_e = 2\tau_e$ (i.e., the echo time) after the $90^\circ_x$ pulse.

Section 2.2.5.2 in the context of $T_2$ measurements. The pulse sequence, which describes the spin echo and its effects on the magnetisation, is illustrated in Fig. 2.7. Immediately following a $90^\circ_x$ pulse applied along the $x$-direction, the magnetisation vector lies in the $xy$-plane, and the spin isochromats (microscopic groups of nuclear spins which resonate at the same frequency) are in-phase and aligned along the $y$-axis. Due to $T_2$ and inhomogeneities in $B_0$, the individual spin isochromats begin to fan out or dephase in the $xy$-plane. At a time $\tau_e$, a $180^\circ_y$ pulse is applied which inverts the phase of each spin isochromat. Because of the inverted positions and the fact that the spin isochromats continue to precess at the same frequency, a perfect refocusing occurs at a time $t_e = 2\tau_e$ after the initial $90^\circ_x$ excitation pulse. The decay of the resulting refocused magnetisation is due to $T_2$ processes. The spin echo is widely exploited in many NMR/MRI experiments.

2.2.6.2 Stimulated Echo

In the stimulated echo pulse sequence (shown in Fig. 2.8), the refocusing $180^\circ$ pulse of the spin echo sequence is replaced by two $90^\circ$ pulses, which are separated by a “storage time”, $t_{store}$. The initial $90^\circ_x$ excitation pulse disturbs the net magnetisation vector in the $xy$-plane, after which the spins undergo $T_2^*$ relaxation. A time $\tau_e$ after the initial $90^\circ_x$ pulse, another $90^\circ_y$ pulse is applied along the $x$-direction, which rotates the $y$-component of magnetisation into the $zx$-plane, where it is stored for time $t_{store}$. In this state, the magnetisation experiences $T_1$ relaxation but
Figure 2.8 The stimulated echo pulse sequence with the corresponding evolution of magnetisation. (a) The $90^\circ_x$ pulse flips the equilibrium magnetisation vector (grey) into the $xy$-plane, after which (b) the spin isochromats start to dephase due to magnetic field inhomogeneities. An interval $\tau_e$ after the initial $90^\circ_x$ pulse, (c) another $90^\circ_x$ pulse is applied which flips the magnetisation in the $zx$-plane, where it is (d) stored for a time period $t_{\text{store}}$, during which the homospoil gradient destroys the residual transverse magnetisation. (e) The third $90^\circ_x$ pulse returns the magnetisation to the transverse plane, where (f) it starts to rephase. (g) The stimulated echo forms a time $\tau_e$ after the last $90^\circ_x$ pulse.

not $T_2$ relaxation. Also, after the second $90^\circ_x$ pulse, any magnetisation in the $xy$-plane, namely the $x$-component of magnetisation, is destroyed by the homospoil gradient, so only 50% of the net magnetisation is utilised this way. The final $90^\circ_x$ pulse flips the magnetisation back into the transverse plane, where the spin isochromats refocus and form a stimulated echo a time $t_e = t_{\text{store}} + 2\tau_e$ after the initial $90^\circ_x$ pulse.

The stimulated echo sequence is particularly useful in cases where the transverse relaxation time, $T_2$, is much shorter than the longitudinal relaxation time, $T_1$, and when studying the translational motion of molecules, because it enables transverse magnetisation to be manipulated over longer time periods.

### 2.2.7 Signal-to-Noise Ratio

NMR has an inherently low sensitivity relative to other spectroscopic techniques due to the small population difference between the lower and upper energy states. NMR signal is also affected by noise originating mainly from random fluctuations in the electronics and the sample; the major contributor is the thermal noise generated in the receiver coil. The noise has a Gaussian distribution about the true sample signal. An important parameter that can be used to quantitatively assess the quality of the true signal is the signal-to-noise ratio or SNR, defined by:
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\[ \text{SNR} = \frac{\mu_s}{\sigma_n}, \]  

(2.23)

where \( \mu_s \) is the mean (true) signal intensity, and \( \sigma_n \) is the standard deviation of noise. In an NMR experiment, the SNR is typically increased by co-adding \( N_s \) successive scans, i.e., by signal averaging. The true NMR signal adds coherently, whereas the random noise adds only as a square root of the number of scans. As a result, the SNR increases as:

\[ \text{SNR} \propto \sqrt{N_s}. \]  

(2.24)

The SNR is also dependent on the recycle delay, \( t_{RD} \). To retain full signal strength between successive scans, a sufficiently long \( t_{RD} \) is required to allow the spins to establish the equilibrium magnetisation, \( M_0 \). This limits the number of scans that can be acquired in a given amount of time. It is possible, however, to saturate the magnetisation by repeating the scans at intervals less than \( t_{RD} \) needed to reach full recovery. It has been found analytically that the optimal SNR per unit time for 90\(^\circ\) pulses is achieved when \( t_{RD} \approx 1.3T_1 \) [57]. This enables NMR data with high SNR to be acquired in a given amount of time. In this case, of course, the acquired NMR signal is no longer directly proportional to the spin density, as was discussed previously in Section 2.2.5.1.

2.2.8 Phase Cycling

Phase cycling is a key procedure in multiple-pulse NMR experiments, where it serves two main purposes [58]. First, it is used to select certain signals of interest, while removing other unwanted “real” signals. Second, it can suppress artefacts, originating from non-ideal pulses or imperfections in the spectrometer hardware (e.g., a direct current offset in the receiver electronics). Phase cycling requires that the experiment is repeated multiple times, which is usually the case anyway for the purpose of improving the SNR, and for each phase cycling increment (scan) the phases of the r.f. pulses are altered in a controlled way. Combining the signals resulting from each scan will lead to addition of the desired signals and cancellation of the unwanted signals.

A commonly used phase cycle is the cyclically ordered phase sequence (CYCLOPS) [59], which is designed to cancel phase and amplitude errors associated with quadrature detection. It consists of four steps, where in each step the phase of the transmitter (pulse) and the receiver is incremented by 90\(^\circ\), so that the relative position of the magnetisation and the receiver remains
the same in each increment. Because the transmitter and receiver phases are incremented systematically, the desired NMR signals from the four increments add, but signal anomalies, which are independent of the transmitter phase, cancel. The CYCLOPS phase cycling scheme is often incorporated within other phase cycles with the aim of removing the aforementioned artefacts.

The design of phase cycling is based on the knowledge of coherence transfer pathways, which evolve from coherence orders present at various points in the pulse sequence [45, 60]. In phase cycling, a path which leads to the desired NMR signals is selected.

### 2.2.9 Chemical Sensitivity

Chemical sensitivity arises from resonance frequency differences of nuclear spins due to different local environments in the molecule, or, alternatively, between different molecules. The electrons in the molecules create small induced magnetic fields associated with them, and these local fields tend to oppose the main magnetic field, $B_0$. This effectively “screens” the nuclei from the full strength of $B_0$. The greater the electron density around the nucleus, the more shielding it experiences, hence nuclei in electron rich environments will experience a lower magnetic field and, as a result, will have a smaller resonance frequency. The resulting chemical shift, $\delta_c$, is defined as the nucleus resonance frequency, $\nu$, relative to a standard reference frequency, $\nu_{\text{ref}}$, as:

$$\delta_c = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6,$$

where $\delta_c$ is expressed in parts per million (ppm). Tetramethylsilane (TMS) is typically used as the reference compound. In an NMR spectrum, the position and number of chemical shifts (peaks) can be used to identify the structure of a molecule. Spectral resolution refers to the overlap between the peaks in an NMR spectrum; the smaller the overlap between the peaks, the higher the spectral resolution. Chemical sensitivity can also be utilised to separate different chemical species based on their chemical shift values, as will be demonstrated in Chapter 8.
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2.3.1 Magnetic Field Gradients

Spatial information can be encoded into the magnetisation using spatially varying magnetic fields (gradients), which are applied in addition to the main magnetic field, $B_0$. The result is a spatially varying frequency, $\omega(r)$, which depends upon the total magnetic field as:

$$\omega(r) = \gamma(B_0 + G \cdot r),$$

(2.26)

where $G$ is the applied magnetic field gradient, and $r$ is a position vector in the sample. Magnetic field gradients can be applied along three orthogonal directions, thus enabling spatial information of an object to be encoded in up to three dimensions. The principle of spatial encoding in one dimension (1D) is simplistically illustrated in Fig. 2.9, where a magnetic field gradient is applied to a tube of water in the $z$-direction. In a uniform magnetic field with no applied field gradient, the NMR signal in the frequency domain is a spectrum with a single peak at the Larmor frequency, $\omega_0$. Upon application of a magnetic field gradient, the Fourier transform of the NMR signal yields a frequency distribution, which is a 1D projection of the tube. The intensity of the resulting frequency distribution is proportional to the spin density at each frequency.

![Figure 2.9](image)

**Figure 2.9** Schematic representation of spatial encoding using magnetic field gradients applied to a tube of water. With no applied field gradient (top), the NMR spectrum will consist of one peak at the Larmor frequency, $\omega_0$. If a magnetic field gradient, $G_z$, is applied in the $z$-direction (bottom), the Larmor frequency of the nucleus becomes dependent on its position in real space along the direction of the applied gradient, yielding a 1D profile of the spin density.
2.3.2 k-Space

In the context of MRI, the spatial frequencies of an image are represented by reciprocal space, commonly referred to as k-space – a formalism introduced by Mansfield [42] that can be used to understand how a particular combination of r.f. pulses and magnetic field gradients can be used to sample reciprocal space. Vector $k$ is defined as:

$$k = \frac{\gamma G t}{2\pi}, \quad (2.27)$$

where $t$ is time for which magnetic field gradient $G$ is applied. The $k$-vector is expressed in units of m$^{-1}$. Equation 2.27 tells us that k-space may be traversed either by varying the time for which the magnetic field gradient is applied or by varying the gradient strength.

Now consider a 3D MRI experiment; neglecting the effects of relaxation, the NMR signal, $dS$, from a volume element, $dV$, at position $r$ is proportional to the local spin density, $\rho_s(r)$, according to:

$$dS(G,t) \propto \rho_s(r) \exp\{i\omega(r)t\} dV. \quad (2.28)$$

Combining Eq. 2.26 and Eq. 2.28 and neglecting the constant of proportionality and the $\gamma B_0$ term (magnetisation is viewed in the rotating frame of reference), followed by integration over all space, the observed signal, $S(t)$, becomes:

$$S(t) = \iiint \rho_s(r) \exp\{i\gamma G \cdot r\} dr. \quad (2.29)$$

This relationship can be simplified by incorporating Eq. 2.27, which gives the acquired NMR signal in k-space, $S(k)$, as:

$$S(k) = \iiint \rho_s(r) \exp\{i2\pi k \cdot r\} dr. \quad (2.30)$$

To obtain an image, $\rho(r)$, an inverse Fourier transform is applied to Eq. 2.30, which yields:

$$\rho(r) = \iiint S(k) \exp\{-i2\pi k \cdot r\} dk. \quad (2.31)$$
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Thus $S(k)$ and $\rho_s(r)$ form a mutually conjugate Fourier transform pair.

### 2.3.3 Field-of-View and Spatial Resolution

The spatial resolution of MRI images is directly linked to the acquired $k$-space data. The defined field-of-view, FOV (in units of m), and pixel width, $\Delta l$, of the image determine the number of $k$-space points that must be acquired to reconstruct an image with the desired resolution. FOV is inversely related to the spacing of points in $k$-space, $\Delta k$, which in turn is related to the applied magnetic field gradient, $G$, and time interval, $\Delta t$; FOV can be expressed (in one direction) as:

$$\text{FOV} = \frac{1}{\Delta k} = \frac{2\pi}{\gamma G \Delta t}.$$  \hspace{1cm} (2.32)

For a given FOV in one direction, the spatial resolution of the real space image is determined by the matrix size, $N$, along that particular direction and is calculated as:

$$\Delta l = \frac{\text{FOV}}{N} = \frac{1}{k_{\text{FOV}}}.$$  \hspace{1cm} (2.33)

Equation 2.33 also shows that the pixel width is inversely proportional to the total extent of $k$-space, which is known as the $k$-space FOV, $k_{\text{FOV}}$; $k_{\text{FOV}} = 2k_{\text{max}}$ (see Fig. 2.11).

In accordance with the Nyquist sampling theory [47], for a fully-resolved image with $M \times N$ pixels, it is necessary to acquire $M \times N$ $k$-space data points. This is referred to as a fully-sampled image.

### 2.3.4 Frequency and Phase Encoding

Frequency encoding causes the resonance frequency to vary as a function of spatial position of the spins. This is accomplished by applying a constant magnetic field gradient, $G_{\text{read}}$, in the “read” direction, which has the effect of moving the magnetisation across $k$-space in a straight line. The frequency-encoding gradient is also called the read or read-out gradient, because it is typically applied during data read-out (sampling). The FOV in the frequency-encoding direction is given by:

$$\text{FOV} = \frac{2\pi}{\gamma G_{\text{read}} \Delta t}.$$  \hspace{1cm} (2.34)
where \( t_d \) is the signal sampling interval, also known as dwell time.

For phase encoding, a magnetic field gradient, known as the phase-encoding gradient, \( G_{\text{phase}} \), is applied for a finite duration of time, \( t_{\text{pe}} \), which results in the phase of the signal to be spatially dependent in the direction of the applied phase-encoding gradient. In MRI experiments with frequency encoding, the phase-encoding gradient is applied in the direction orthogonal to that used for frequency encoding, thus allowing \( k \)-space to be sampled in multiple dimensions. In practice, the phase-encoding time, \( t_{\text{pe}} \), is kept fixed in order to maintain a constant echo time, and the strength of the phase encoding gradient is varied in increments, \( \Delta G_{\text{phase}} \), equally spaced around \( G_{\text{phase}} = 0 \, \text{T m}^{-1} \). The FOV in the phase-encoding direction is given by:

\[
\text{FOV} = \frac{2\pi}{\gamma(\Delta G_{\text{phase}}) t_{\text{pe}}}. \tag{2.35}
\]

### 2.3.5 Soft Pulse Slice Selection

In 2D MRI, slice selection can be achieved by applying a soft r.f. pulse in the presence of a magnetic field gradient, known as the slice gradient, \( G_{\text{slice}} \). Recalling Section 2.2.3, soft r.f. pulses have a narrow excitation bandwidth, i.e., they only excite a small range of frequencies in the NMR spectrum. At the same time, the slice gradient, \( G_{\text{slice}} \), spreads out the spin resonance frequencies along the direction of which this gradient is applied. It follows that the soft r.f. pulse excites only those spins that resonate within its narrow bandwidth, \( \Delta \omega_{\text{bw}} \), which corresponds to selecting a slice image of thickness, \( \Delta z \), that contains these spins (Fig. 2.10). The slice thickness is given by:

![Figure 2.10](image)

**Figure 2.10** Illustration of slice selection in MRI. An r.f. pulse with a narrow excitation bandwidth, \( \Delta \omega_{\text{bw}} \), and a magnetic field gradient, \( G_{\text{slice}} \), are applied simultaneously to select a slice of thickness, \( \Delta z \).
\[ \Delta z = \frac{\Delta \omega_{bw}}{\gamma G_{\text{slice}}} \]  

The slice thickness can be controlled by adjusting the parameters \( \Delta \omega_{bw} \) and \( G_{\text{slice}} \).

Generally, it is desirable to excite slices so that they have well-defined edges. The shape of the excited slice is controlled by the frequency profile of the r.f. pulse; the frequency profile of the pulse is related to its time-domain profile by the Fourier transform. A hard, rectangular pulse has sharp edges in the time domain, which introduces side lobes in its frequency profile. Therefore, the excited slice is not well-defined. The side lobes can be eliminated by the use of so-called shaped pulses, such as Gaussian- or sinc-shaped pulses.

### 2.3.6 Traversing and Sampling k-Space

The way in which k-space is sampled depends on the particular pulse sequence used. In order to illustrate how k-space is traversed and sampled, let us consider a simple example – the 2D spin-warp sequence shown in Fig. 2.11. The pulse sequence starts with a soft 90°

![Figure 2.11](a) Schematic of the 2D spin-warp MRI pulse sequence and (b) a Cartesian k-space raster showing the traversal through k-space during the sequence. A simultaneous application of the 90° soft pulse and the slice-selective gradient \( (G_z) \) flips the magnetisation from within a selected slice into the transverse plane. The dephasing frequency-encoding \( (G_z; \text{red}) \) and phase-encoding \( (G_y; \text{green}) \) gradients move the magnetisation to the bottom right-hand corner of k-space \( (+k_{x,\text{max}}, -k_{y,\text{max}}) \). The 180° pulse (orange) inverts the magnetisation through the centre of k-space; the magnetisation ends up at the top left-hand corner \( (-k_{x,\text{max}}, +k_{y,\text{max}}) \) of the k-space raster. The rephasing frequency-encoding gradient \( (G_x; \text{blue}) \) is applied, traversing a full-line of k-space, during which the NMR signal is sampled. This process is repeated for different increments of \( G_y \) to sample the entire k-space raster; the trajectory for the next phase-encoding increment is represented by the dashed arrows.
r.f. pulse, which rotates the equilibrium magnetisation from within the selected slice into the transverse plane. The magnetisation is at the origin of $\mathbf{k}$-space prior to the application of magnetic field gradients. The (dephasing) frequency-encoding gradient then shifts the magnetisation to the edge ($k_x = +k_{x,max}$) of $\mathbf{k}$-space in the $k_x$-direction, while simultaneously the phase-encoding gradient moves it in the $k_y$-direction along the edge of $\mathbf{k}$-space. Because the frequency-encoding and phase-encoding gradients are applied in the $x$-direction and $y$-direction, here they are denoted by $G_x$ and $G_y$, respectively. The extent to which the magnetisation is traversed in $\mathbf{k}$-space is determined by the particular amplitudes of $G_x$ and $G_y$. For phase encoding, different amplitudes of $G_y$ are chosen to increment $\mathbf{k}$-space in the $k_y$-direction. Next a 180° pulse is applied, which inverts the phases of the spins. In terms of the $\mathbf{k}$-space raster, this has the effect of moving the magnetisation through the origin of $\mathbf{k}$-space to the negative edge ($-k_{x,max}$) of $\mathbf{k}$-space in the $k_x$-direction. Finally, application of the (rephasing) frequency-encoding gradient traverses a line in $\mathbf{k}$-space in the positive $k_x$-direction while data points are sampled from the spin echo signal. Thus, a full line of $\mathbf{k}$-space is sampled in the $k_x$-direction (i.e., the read-out direction). To traverse a full line in $\mathbf{k}$-space, this frequency-encoding gradient has twice the duration but the same amplitude as the first frequency-encoding gradient. This sequence is repeated for other values of $G_y$ to sample the entire $\mathbf{k}$-space raster. If 3D imaging is required, a second phase-encoding gradient is applied to enable data collection in the third dimension. The total experimental time for the spin warp sequence can be calculated by the following equation:

$$t_{\text{exp}} = N_s \times N_{\text{phase}} \times t_{\text{RD}},$$

(2.37)

where $N_{\text{phase}}$ is the number of phase-encoding increments. For example, if we were to acquire a 3D image that contains $128 \times 64 \times 64$ voxels (frequency $\times$ phase $\times$ phase) with $t_{\text{RD}} = 5$ s and $N_s = 2$, then the total acquisition time would be $t_{\text{exp}} \approx 11$ h. The total signal intensity in the images acquired by the spin-warp sequence is weighted by $T_2$. However, because the timing of each $\mathbf{k}$-space acquisition is constant, the relaxation weighting across the images is uniform.

### 2.3.7 Single Point Imaging

Single point imaging (SPI) [61] refers to imaging with pure phase encoding and no frequency encoding. In SPI, each point in $\mathbf{k}$-space is acquired at a fixed phase-encoding time, $t_{\text{pe}}$, in the presence of phase-encoding gradients, following an r.f. excitation pulse. Because the phase-encoding time is typically relatively short (20–300 µs), the acquired images do not contain significant relaxation contrast, hence are generally considered quantitative. However,
SPI is time consuming, because a single point in $k$-space is acquired per r.f. excitation pulse. The acquisition time of a 3D image with the same resolution and experimental parameters as the spin-warp example (Section 2.3.6) would be $t_{\text{exp}} \approx 2$ months. Faster versions of SPI have been developed, such as single point ramped imaging with $T_1$ enhancement (SPRITE) [62]. The SPRITE sequence uses phase-encoding gradients, which are continuously incremented (ramped), and small tip angle r.f. pulses at each step, thus enabling faster acquisition of the entire $k$-space raster compared to the conventional SPI sequence. However, the SPRITE pulse sequence relies on the samples having short $T_1$ relaxation times ($T_1 \sim 10–100$ ms).

### 2.3.8 Rapid Imaging Techniques

This section will introduce rapid imaging techniques that are used to significantly speed up MRI acquisitions relative to the spin-warp and SPI imaging techniques, focusing more on the rapid acquisition with relaxation enhancement (RARE) sequence [33], which was extensively used in this thesis.

#### 2.3.8.1 EPI and FLASH

In echo planar imaging (EPI) proposed by Mansfield [34], multiple lines of $k$-space are sampled following a single r.f. excitation pulse. The acquisition of multiple $k$-space lines is achieved by applying a train of alternating positive and negative frequency-encoding gradients with a “blipped” low-magnitude phase-encoding gradient before each frequency-encoding gradient. The use of gradient reversal to refocus the magnetisation results in the formation of gradient echoes, as opposed to spin echoes which are formed by the application of 180° r.f. refocusing pulses. Because only one r.f. pulse is used in EPI, the echo time is significantly reduced relative to spin echo imaging. However, as gradient echoes are acquired in EPI, the resulting image is weighted by $T_2^*$. This means that EPI is not well-suited for samples with short $T_2^*$ relaxation times, such as water-saturated rock samples. Furthermore, EPI images are susceptible to various types of artefacts [63], such as those arising from local field inhomogeneities.

The fast low angle shot imaging (FLASH) [64] sequence uses a low r.f. flip angle (typically 5–10°) and a single gradient echo to sample a single line of $k$-space in the frequency-encoding direction per signal excitation. The acceleration of this method is achieved by the low flip angles used, which shortens the $t_{\text{RD}}$ needed for signal recovery between successive scans. Although FLASH images suffer less from $T_2^*$ weighting than EPI images, they have an inherently low SNR as the amount of magnetisation flipped into the transverse plane is small.
2.3.8.2 RARE

The RARE [33] imaging sequence uses a train of 180° r.f. refocusing pulses to acquire multiple k-space lines in a single r.f. excitation. It is similar to a CPMG sequence, but a phase-encoding gradient with different amplitudes is applied prior to each echo. A schematic of a 2D RARE sequence along with its trajectory in k-space is shown in Fig. 2.12. The soft 90° r.f. pulse is applied during the slice-selective gradient, \( G_z \), to select a slice of the sample. The dephasing frequency-encoding gradient, \( G_x \), moves the magnetisation along the \( k_x \)-axis to the right-hand side of the k-space raster \((+k_{x,\text{max}}, 0)\). The 180° r.f. refocusing pulse then inverts the magnetisation to \((-k_{x,\text{max}}, 0)\). Application of the first phase-encoding gradient, \( G_y \), shifts the magnetisation in the negative \( k_y \)-direction. Next, the rephasing frequency-encoding gradient is applied during the acquisition of a spin echo to traverse a full line of k-space. Application of the second phase-encoding gradient, which has the same amplitude, but opposite direction to the first phase-encoding gradient, returns the magnetisation to \((+k_{x,\text{max}}, 0)\). By repeatedly applying the 180° r.f. refocusing pulses, wherein in each step the amplitude of \( G_y \) is incremented, multiple lines of k-space are sampled per excitation. The number of 180° r.f.

Figure 2.12 (a) Schematic of the 2D RARE pulse sequence and (b) a Cartesian k-space raster showing the traversal through k-space during the RARE sequence. A simultaneous application of the 90° soft pulse and the slice-selective gradient \( G_z \) flips the magnetisation from within a selected slice into the transverse plane. The dephasing frequency-encoding gradient \( G_x \); red) moves the magnetisation to the right-hand side of k-space to \((+k_{x,\text{max}}, 0)\). The 180° refocusing pulse (orange) inverts the magnetisation to \((-k_{x,\text{max}}, 0)\). The phase-encoding gradient \( G_y \); green) moves the magnetisation in the negative \( k_y \)-direction. The rephasing frequency-encoding gradient \( G_x \); blue) is applied, traversing a full-line of k-space, during which the NMR signal is sampled. The second phase-encoding gradient \( G_y \); purple) returns the magnetisation to \((+k_{x,\text{max}}, 0)\). This loop is repeated \( N_{RF} \) times for different amplitudes of \( G_y \) to sample multiple lines of k-space; the trajectory for the next phase-encoding increment is represented by the dashed arrows.
refocusing pulses and resultant echoes is called the RARE factor \( N_{RF} \). The typical values of RARE factor are \( N_{RF} = 1\text{--}64 \), but they are dependent on \( T_2 \) of the sample. If the whole of \( k \)-space is not acquired after one excitation, then the entire sequence is repeated to sample all \( k \)-space points. During the RARE echo train, the signal intensity will decrease inherently due to \( T_2 \) relaxation, thus the acquired image will be weighted by \( T_2 \). Although RARE is slower than EPI, it is less sensitive to image artefacts since using 180° r.f. refocusing pulses refocus the dephasing caused by magnetic field inhomogeneities. Furthermore, because the RARE imaging method is dominated by \( T_2 \) relaxation, as opposed to \( T_2^* \) relaxation as is the case with EPI and FLASH, it is more suitable for imaging fluids contained in porous media, since for fluids in the pore space \( T_2 > T_2^* \). Compared to SPI and spin-warp imaging sequences, RARE offers significant reduction in acquisition time, the extent of which depends on the chosen \( N_{RF} \). For example, acquiring a 3D image of size \( 128 \times 64 \times 64 \) voxels (frequency \( \times \) phase \( \times \) phase) with \( t_{RD} = 5 \) s, \( N_s = 2 \), and \( N_{RF} = 32 \) would take approximately 21 min (cf. 21 min versus 11 h for spin-warp and 2 months for SPI); in a 3D RARE experiment, a second set of phase-encoding gradients is used instead of slice-selective gradients.

2.3.9 Flow MRI

Flow MRI is an integration of a pulsed field gradient (PFG) NMR experiment, which is used to quantify fluid displacements, with an MRI experiment, which spatially-resolves those displacements. Two different spatially-resolved flow MRI techniques can be distinguished. The first technique is so called velocity mapping where a single, average velocity is spatially-resolved for each of the voxels within an image. The second technique involves the acquisition of a spatially-resolved displacement propagator. A propagator is a probability distribution of molecular displacements over a given observation time (typically in the range between a few milliseconds up to \( T_1 \) of the fluid under study).

This section will briefly review the basic principles of the acquisition of velocity maps and spatially-resolved propagators. It will also introduce the PFG techniques that were used in this thesis to encode fluid displacements.

2.3.9.1 Velocity Mapping

Velocity mapping, also referred to as phase-shift velocimetry, relies on making the phase of the NMR signal sensitive to translational motion. This can be understood by considering the effects of the applied pulsed field gradient, \( g \), during a time, \( \delta \), on the phase of the moving spins, \( \phi(t) \). Using Eq. 2.26 and applying the concept of the rotating frame of reference, the phase shift experienced by a spin along a path \( r(t) \) then can be written as:
\[ \phi(t) = \gamma \int_0^t g(t) r(t) dt. \] (2.38)

Thus, application of a single magnetic gradient pulse will impart a phase shift \( \gamma \delta g \cdot r \) to a spin located at position \( r \) (this assumes that gradient pulses are sufficiently short that motion over their duration can be neglected, i.e., the narrow gradient pulse approximation \[44\]). After some time (an observation time, \( \Delta \), is used in MR experiments), the phase shift can be inverted by a second magnetic gradient pulse. If during this time no molecular motion occurs, the phase of spins will fully refocus. If, however, the molecular motion occurs during this observation time, and the spins have moved to \( r' \) (corresponding to a phase shift \( \phi' \)) at the time of the second gradient pulse, then the residual phase shift, \( \phi_{\text{res}} \), is:

\[ \phi_{\text{res}} = \gamma \delta g \cdot (r' - r). \] (2.39)

Similar to the relationship between the real image space and \( k \)-space, the reciprocal space of the space of dynamic displacements, \( (r' - r) \), is known as \( q \)-space, defined by \( q = \frac{\gamma \delta g}{2\pi} \) in reciprocal space units (m\(^{-1}\)). Because the absolute value of the measured phase is arbitrary, two images need to be acquired at different \( q \) values to calculate the net difference in the phase shift, \( \phi_{\text{net}} \). The measured velocity, \( v \), of the moving spins in the direction of the applied gradient over an observation time, \( \Delta \), can then be calculated by rearranging Eq. 2.39 and using \( \phi_{\text{net}} \) as:

\[ v = \frac{\phi_{\text{net}}}{\gamma g_i \delta \Delta}, \] (2.40)

where \( g_i \) is the difference in applied pulsed-field gradient strength between the two \( q \)-images. Since the pulsed magnetic field gradient, \( g \), can be applied in any of the three (\( z, x, y \)) orthogonal directions, the velocities \( v \) can be measured as 3D vectors, which show the local velocity and direction of the flow. Note that the flow-encoding parameters must be carefully set such that the measurements lie within a \( 2\pi \) window to avoid phase-wrapping artefacts.

### 2.3.9.2 Propagator Measurements

Displacement propagators are probability distributions of molecular displacements, denoted by \( \hat{P}(\mathbf{R}, \Delta) \), where \( \hat{P} \) is the probability that spins will move a distance \( \mathbf{R} = r' - r \) in the time \( \Delta \). To acquire a propagator, the signal intensity, \( S \), is measured as a function of \( q \), typically by varying the strength of the applied gradient, \( g \), as:
\( S(q) = \int \bar{P}(R,\Delta) \exp[i2\pi q \cdot R] dR. \) 
(2.41)

The propagator is related to the acquired NMR signal via Fourier transformation as:

\( \bar{P}(R,\Delta) = \int S(q) \exp[-i2\pi q \cdot R] dq. \) 
(2.42)

A spatially-unresolved propagator (i.e., q-space) measurement can be combined with a k-space measurement to enable acquisition of spatially-resolved propagators. In the case of a 3D spatially-resolved propagator, a 4D k,q data space is acquired.

Propagator measurements capture both coherent (bulk flow) and incoherent (diffusion and dispersion) motion of spin-bearing molecules. This is in contrast to velocity mapping, which is only sensitive to coherent motion, but not – to the effects of incoherent motion.

2.3.9.3 PFG Techniques

One of the most widely used PFG techniques is the pulsed gradient spin echo (PGSE) sequence (see Fig. 2.13), which was first demonstrated by Stejskal and Tanner in 1965 [65]. It consists of a pair of unipolar magnetic field gradient pulses of strength \( g \) and duration \( \delta \) either side of a 180° r.f. refocusing pulse, which are separated by an observation time, \( \Delta \). If a spin migrates over the observation time between the two gradient pulses, it will acquire a residual phase shift. During the observation time, the signal attenuates due to molecular self-diffusion. The signal attenuation is described by the well-known Stejskal-Tanner equation [65], written as:

**Figure 2.13** Pulsed gradient spin echo (PGSE) sequence. Two pulsed field gradient pulses of amplitude \( g \) and duration \( \delta \) are applied on either side of a 180° r.f. pulse. The gradient pulses are separated by an observation time, \( \Delta \). The echo is acquired at time \( t_e = 2\tau_e \).
\[ S(g) \frac{S(0)}{S(0)} = \exp(-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)), \]  

(2.43)

where \( D \) is the self-diffusion coefficient. By measuring the signal for a range of different \( g \) values, the self-diffusion coefficient of fluids can be determined.

When performing PFG MR measurements in porous media, magnetic susceptibility induced internal gradient effects can lead to significant signal attenuation. These effects can be minimised by using the alternating pulsed gradient stimulated echo (APGSTE) sequence developed by Cotts et al. [66] (Fig. 2.14). This sequence is based on a stimulated echo and spin-echo dephasing and rephasing segments, each of which comprises a pair of bipolar gradients of equal magnitude separated by a 180° r.f. pulse. The first gradient pair encodes the spin phase during the first part of the sequence. The nuclear spins are then stored on the \( z \)-axis for time \( t_{\text{store}} \) during which the spins undergo \( T_1 \) relaxation. The displacement that occurs during \( t_{\text{store}} \) is encoded by the second set of bipolar gradients. The second set of bipolar gradients also effectively refocuses the spin dephasing caused by internal gradients during the first part of the sequence; as can be seen from the net effective gradients in Fig. 2.14, the overall effect of background gradients is cancelled, and the spins effectively only experience the applied pulsed

![Figure 2.14](image_url)

**Figure 2.14** Alternating pulsed gradient stimulated echo (APGSTE) sequence, designed to minimise the effect of background (internal) gradients. A pair of bipolar gradients of amplitude \( g \) and duration \( \delta/2 \) are applied on either side of each of the two 180° r.f. pulses. The \( z \)-storage interval and observation time are given by \( t_{\text{store}} \) and \( \Delta \), respectively. The echo is acquired at time \( 4\tau_e + t_{\text{store}} \). \( G_0 \) represents a steady internal gradient. \( g^* + G_0^* \) is the net effective gradient.
field gradients, $g$. Although the APGSTE sequence suffers from the inherent 50% signal loss of the stimulated echo, it generally has advantages when using long observation times (e.g., in propagator measurements) and when studying systems where $T_2 \ll T_1$ (e.g., porous materials with strong internal gradient effects).

These PFG techniques can be incorporated into MRI pulse sequences (e.g., RARE) to enable acquisition of spatially-resolved flow and diffusion information of fluids.
Chapter 3

Digital Image Processing

3.1 Introduction

In order to be able to extract accurate petrophysical information from high-resolution MRI and µCT images, significant processing first needs to be performed on the acquired data. This is because images are often corrupted by noise and various types of artefacts that can affect the quantitative and qualitative analysis of the acquired images. The main image processing steps include image reconstruction, artefact removal, image denoising, and image segmentation. In the image processing workflow, the image segmentation step is particularly important, as improper partitioning of the image can lead to misidentification of the pore space and rock matrix phases, and hence yield inaccurate rock properties (e.g., porosity) and DR simulation results [4, 5, 67].

In this chapter, image processing techniques that are relevant to this thesis for processing MRI and µCT images are discussed. A description of image co-registration is also given.

3.2 Image Reconstruction

The fully-sampled MRI data reconstruction methods have already been discussed in some detail in Chapter 2 (Section 2.3.2). Fully-sampled k-space data are reconstructed using the Fourier reconstruction method – a fast Fourier transform algorithm is used to convert k-space into the real space image by computing the (inverse) discrete Fourier transform of the data. The reconstructions of under-sampled k-space data, which will be discussed in detail in Chapter 4 (Section 4.4.2.2), are based on non-linear reconstruction techniques, i.e., the compressed sensing approach.
A 3D X-ray µCT image is obtained by reconstructing a set of projection images of an object acquired over a range of different projection angles [68]. This is achieved by rotating the object through 180° or 360° in steps and acquiring a 2D projection image at each of these steps. Next, the projection images are converted into a series of sinograms, which are a series of 2D data arrays each containing a set of projections acquired at different rotation angles. Sinogram data are then reconstructed using mathematical reconstruction algorithms to yield a 3D µCT intensity image; the most widely used reconstruction technique is the filtered backprojection algorithm [69], which is computationally fast, simple to implement, and accurate. In the reconstructed µCT images, the intensity (CT number) in each voxel is proportional to the X-ray attenuation, representing X-rays that are either scattered or absorbed in that volume element. X-ray attenuation strongly depends on the X-ray energy and the density and atomic number of the attenuating material. It is worth noting that projection acquisition and reconstruction techniques can also be used to acquire and reconstruct MRI data, however these techniques are less widely used compared to the Fourier imaging.

### 3.3 Artefacts and Their Removal

MRI and X-ray µCT are both susceptible to artefacts that can impair the quality of the acquired images and render the subsequent image analysis more challenging. Good knowledge of the potential artefacts can help the experimentalist to avoid them or use suitable post-processing techniques that can compensate for them. In this section, some of the most common artefacts in MRI and µCT are briefly described, along with the methods for artefact suppression.

MRI is prone to several types of artefacts, some of which can severely affect the quality of MRI images [70]. MRI artefacts can be categorised as hardware-related, pulse sequence/data acquisition-related, and sample-related. Hardware-related artefacts can be difficult to eliminate, because they are inherent to the equipment used to acquire the images. Some of the hardware-related artefacts include the zipper artefact, which is caused by leaking r.f. signals, and k-space spikes, which may result from faulty components in the r.f. circuit. Another common artefact is a data-clipping artefact, which typically occurs if the receiver (amplifier) gain is set too high. If this is the case, this artefact can be eliminated by properly setting the receiver gain. Artefacts can also be caused by $B_0$ and $B_1$ field inhomogeneity and gradient non-linearity. Pulse sequence/data acquisition-related artefacts typically result from improper selection of pulse sequences and/or data acquisition parameters. Some commonly encountered artefacts, such as wrap-around artefacts, truncation (Gibbs) artefacts, and partial volume effects, all belong to this category of MRI artefacts. The wrap-around artefact occurs when the object size in the phase-encoding direction is larger than the imaging FOV; an easy way to overcome
this problem is to increase the FOV. The truncation artefact, also known as the Gibbs or ringing artefact, results from abrupt signal truncation at the edges of $k$-space, manifesting in periodic undershoot and overshoot oscillations around the image feature causing it. Although truncation artefacts cannot be entirely eliminated, they can be minimised by increasing the spatial resolution or by multiplying the $k$-space data by a filter or window-function such that the data smoothly decay. Partial volume effects arise when more than one phase (object) occur in a voxel. Partial volume effects can be reduced by increasing the spatial resolution or using zero-filling interpolation methods [71, 72]. Another type of artefact, which belongs to this class of artefacts, is partial volume artefacts. These artefacts, if $k$-space is incoherently sampled, can be removed using CS algorithms, as will be discussed in Section 4.4.2. Two common sample-related artefacts are motion artefacts and magnetic susceptibility artefacts. Motion artefacts typically appear as ghosting or blurring in the images. These artefacts are common in medical MRI due to patient movement during the scans. They can, however, be avoided if the sample is kept in place during an imaging experiment, for example, by keeping the sample in a holder. Magnetic susceptibility artefacts occur due to local magnetic field inhomogeneities, induced by magnetic field susceptibility differences at interfaces between materials in a sample, for example between a porous rock matrix and a pore fluid in a saturated rock plug. The presence of these local magnetic field heterogeneities leads to the formation of spatially varying field gradients known as internal gradients, which were already briefly introduced in Chapter 2. The two main effects of internal gradients are geometric distortions of the image (i.e., shifting of voxels due to the distortion of the main magnetic field) and additional signal loss in the voxels affected by this artefact due to stronger dephasing of spins (faster $T_2^*$ decay). These artefacts appear as bright and dark areas in the image; the bright areas are voxels where signal is spatially moved on top of other signal. In the case of MRI velocity imaging, in any voxel affected by the internal gradient effects, the internal gradient could be adding to or subtracting from the applied velocity-encoding gradient, thus giving an error in the velocity measurement for that voxel. For a given magnetic field strength, magnetic susceptibility artefacts can be minimised by using (fast) spin-echo-based pulse sequences and by keeping the echo time as short as possible. Increasing the spatial resolution and spectral bandwidth can also reduce the effects of magnetic susceptibility artefacts [70, 73]. In MRI flow velocity measurements, the effects of internal gradients can additionally be minimised by using an APGSTE-based flow imaging pulse sequence. More information on MRI artefacts can be found elsewhere [70, 73].

X-ray µCT is also prone to different types of artefacts. As with MRI, the artefacts seen in µCT images can originate from hardware-, software- or sample-related problems and factors. Three common artefacts in X-ray µCT are a beam hardening artefact, ring artefact, and partial volume effects. The most commonly encountered artefact in µCT imaging is beam
hardening [68]. The beam hardening artefact results from the increase in mean X-ray energy (“hardening”) as a polychromatic beam passes through an object. This is because the lower-energy X-rays are attenuated more than the high-energy X-rays. This artefact generally manifests itself as darkening at the central region of an object, and brightening at the edges of an object. Two possible approaches to prevent beam hardening include: (1) pre-hardening – X-ray beam is passed through an attenuating filter (e.g., aluminium) fitted to the X-ray source, and (2) beam hardening correction during image reconstruction. Ring artefacts are another common problem in X-ray µCT [68]. The ring artefact is generally caused by a miscalibrated or defective X-ray detector. Because miscalibration or a shift in the detector response can be caused by change in temperature or beam strength, the effect of this artefact can be minimised by frequent recalibrations and careful control of experimental conditions. Another source for ring artefact formation can be beam hardening, which is why methods to reduce beam hardening artefacts, such as the attenuating filter, can be used for the suppression of ring artefacts [68]. Ring artefacts can also be reduced during image reconstruction. As with MRI, partial volume effects can make the quantitative analysis of the acquired µCT images more problematic. However, for the same object (e.g., a rock type), the partial volume effects are expected to be less pronounced in µCT data compared to MRI data, since µCT images are generally acquired at a higher spatial resolution.

3.4 Denoising Procedures

Experimentally acquired images are not only susceptible to imaging artefacts, but also to random noise. Compared to imaging artefacts, which typically appear as false structures in the image, noise normally is distributed homogeneously through images and is random in nature. High noise level (poor SNR) in the acquired images can make image segmentation and hence quantitative analysis more difficult, therefore it is often necessary to reduce the level of noise in the acquired images. Image noise is typically reduced using so-called denoising algorithms, which are typically based on image filters that modify the intensity value of each voxel depending on its neighbourhood in the original image.

One way to reduce noise in images is to use simple, linear denoising algorithms. In linear filtering, each value of the output voxel is a linear combination of the values of the voxels in the neighborhood of the original voxel. One such filter is the Gaussian filter, which replaces the value of the original voxel by a Gaussian weighted mean of the voxels in the local neighborhood. Another example is the mean filter, which simply replaces the value of the centre voxel in a given window around this voxel with the mean value of the window. Although these algorithms may be effective at reducing noise in some cases, they generally tend to blur edges, textures, and
interfaces between different phases (like a low-pass filter) [74, 75], which may alter important features in the images.

More sophisticated image filters which both reduce image noise and preserve sharp features are called edge-preserving filters. The simplest method within this category of filters is the median filter [76], in which the gray-level value of each voxel is replaced by the median value of the voxels in the local neighborhood. However, using this algorithm, the amount of denoising that can be applied to images, while maintaining the sharpness of the images, is small compared to other edge-preserving algorithms [75].

Another popular edge-preserving technique is the anisotropic diffusion filter [77]. This filter encourages diffusion (smoothing) of the image regions with low magnitudes of intensity gradient, but inhibits diffusion of areas with high magnitudes of intensity gradient. In this way, noise from images can be removed while preserving image features.

A very powerful edge-preserving denoising method is the non-local means filter [74, 78]. To obtain the new value of a target voxel, this algorithm computes the weighted average of voxels in a given search window. The weight with which each voxel in the search window will affect the target voxel is determined by the similarity between the neighborhoods of all voxels within the search window and the neighborhood of the target voxel; voxels that have a neighborhood similar to the one of the target voxel have larger weights. Although this algorithm is very effective for denoising, while preserving edges and textures, it can also be computationally costly and time consuming to run [79]. Because of this reason, the non-local means filter is typically used in 2D mode. In this thesis, the acquired µCT images were denoised using the non-local means filter, as it gives high SNR and has good edge and interface preserving properties [75], relative to other denoising filters.

It is worth noting that another way to denoise images is to use the CS approach, because the CS reconstruction is inherently a denoising procedure [36]. Non-linear denoising algorithms based on total variation (TV) regularisation (see Section 4.4.2.2 in Chapter 4) have been demonstrated to be effective at preserving edges [80]. Hence, in this work, MRI images reconstructed from under-sampled MRI data using CS were not additionally denoised using spatial domain filtering.

3.5 Image Segmentation

The next step in the image processing workflow is image segmentation. Image segmentation is the procedure of partitioning a digital image into multiple parts, which, in the context of DR physics, are the pore space and the grain matrix of rocks. It is the fundamental step in digital image processing as improper segmentation can lead to incorrect extraction of rock properties.
In this section, some of the main segmentation methods, mainly those relevant to this thesis, are described. A more comprehensive review of image segmentation algorithms applied to porous media can be found in the following papers [81, 82].

The simplest image segmentation method is global thresholding, where a single intensity value (threshold) is chosen to partition the entire image into two phases – voxels with intensities below this threshold value are assigned to one phase, but voxels with intensities above this threshold to the other phase. The resulting image is called a binary image, where each of the voxels has a value of 0 or 1. One of the most popular approaches within this category of segmentation methods is the Otsu’s method [83], which is also widely used for the segmentation of porous media images [6]. The Otsu’s method is an automatic, histogram-based method that works by finding the threshold that minimises the intra-class variance, defined as a weighted sum of variances of the two classes (peaks in the histogram) [83]. However, it relies on the image to have a bimodal distribution of gray-level values and a deep valley between the two intensity peaks, otherwise this approach may determine the threshold incorrectly and lead to misidentification of voxels. Image segmentation can also be performed by manually selecting the threshold value, however manual segmentation is operator-biased and may lead to inconsistencies in the way images are segmented [81]. A common problem for the global thresholding methods is the fact that they may misidentify certain voxels and introduce artefacts in phase transition regions (i.e., on the interfaces between different phases), which are blurred by noise and partial volume effects [79]. The watershed-based segmentation can provide a solution to these problems in many instances.

The watershed algorithm [84] is a powerful, versatile method in image processing, in which a digital image is treated as a topographic landscape with watersheds and catchment basins; the term watershed refers to the ridge that separates adjacent catchment basins. In digital image processing, the watershed algorithm is widely used for two applications – image segmentation and pore classification (i.e., separation of binary pore space image into individual pores). Both of these techniques were extensively used in this thesis, the details of which are discussed below. The generic principle of the watershed algorithm is illustrated in Fig. 3.1. The first step in the algorithm involves detecting the local minima points in the intensity image. These points in Fig. 3.1 are represented by markers a, b, and c. The flooding then starts from these labelled regions, which expands the regions by assigning progressively more voxels to different catchment basins (this process can be viewed as a progressive immersion of a landscape). To avoid over-segmentation due to spurious local minima (b in Fig. 3.1), which can be created by noise or small variations in image intensity, certain thresholds can be set to merge the basins associated with these local minima with the catchment basins that have larger local minima; such threshold is represented by the contrast factor, $h_c$, in Fig. 3.1. These catchment basins keep
Figure 3.1 Principle of the watershed algorithm. The black curved line represents the intensity profile of an image. Markers a, b, and c represent the local minima of the intensity profile, i.e., points at the bottom of the catchment basins where the flooding starts. Points 1 and 2 represent the local maxima, i.e., points for potential watershed lines. Although three local minima are present in the profile, only two segments are formed, separated by the watershed line (the dashed vertical line). This is because regions b and c have been merged, as determined by the contrast factor, $h_c$.

expanding until the watershed lines (local maxima) are reached. At these locations (marked as 1 in Fig. 3.1), the neighbouring basins come into contact, and the flooding process stops. The voxels in the image can now be classified into different segments, as determined by the watershed lines.

The watershed algorithm can be used for image segmentation by applying the watershed transform on the gradient of a grayscale image [75, 79]. First, the gradient magnitude of the image is computed. Markers are then set in the low gradient areas of the image. This is achieved by defining a gradient mask, that can be imposed in the regions of the image where markers cannot be set, and then using global thresholding to select intensity range for each set of markers (different phases). Each region with the marker then grows to areas with progressively higher grayscale gradient magnitudes. When, during this process, two catchment basins of the same phase grow to the point that they touch each other, they merge and form a larger connected cluster. However, when two catchment basins of different phases touch each other, a phase boundary is formed. This process continues until all regions of the image are assigned to each of the phases.

To illustrate the effectiveness of the watershed algorithm, μCT images of two rocks, namely Ketton and Estailledes limestones, were segmented using the marker-based watershed segmentation approach and Otsu’s method; image segmentation was performed in the Avizo image
Figure 3.2 Comparison between the watershed segmentation algorithm and Otsu’s method for (a) Ketton and (b) Estaillades rocks. The blue pixels represent the rock matrix phase.

analysis package (FEI Visualisation Sciences Group, USA). The segmented images are shown in Fig. 3.2, along with the corresponding grayscale images and image histograms of both rocks. As can be seen in Fig. 3.2, both segmentation methods yield similar results for the Ketton rock.
3.5 Image Segmentation

Figure 3.3 Main steps in the analysis of high-resolution images of rocks using the watershed algorithm: (a) μCT intensity image of the Ketton limestone rock; (b) binary grain space image obtained using the watershed segmentation algorithm; (c) binary pore space image, generated by calculating the complement image of the corresponding grain space image; (d) distance map of the binary pore space image; (e) labelled distance map; (f) labelled inverted distance map, where colours represent different local minima; (g) the computed watershed lines that are used to separate the connected pores; (h) labelled, separated pores, where each colour denotes a distinct pore. The field-of-view of the images is 2.75 mm × 2.75 mm.

The Otsu method performs well in this case because the background noise and foreground signal intensities are well separated. In the case of Estaillades rock, Otsu’s method does not yield satisfactory results as many of the pixels that belong to the rock matrix have been assigned to the pore space in the binarized image. This is because the Estaillades rock exhibits a broad distribution of grayscale intensities, and the background noise and foreground signal intensities are not well separated. In addition, the foreground signal of the rock is represented by two merged peaks (lower intensities represent microporosity, but higher intensities – dense rock grains), which may complicate the segmentation process. On the contrary, the watershed segmentation algorithm overcomes the problem of voxel misidentification and gives well-separated pore space and rock matrix phases in the image.

The watershed algorithm can also be used to separate connected objects, such as connected pores in a rock, when conducted on a distance map. This form of the watershed algorithm is used when performing quantitative image analysis (e.g., to obtain a pore size distribution), as simple segmentation of an image into the rock matrix and the pore space yields many connected objects, which does not provide accurate information about the pore-scale statistics. The process of using the watershed algorithm for pore separation is illustrated in Fig. 3.3. For
this illustration, a region extracted from the 2D image of the Ketton rock is used. The first step involves generating a binary image from the corresponding intensity image using image segmentation. Because the goal is to separate connected pores, the pore space binary image of the rock needs to be generated. Next, a distance map (e.g., Chamfer distance map) is computed from this binary pore space image. The distance map represents, for each pixel in the object (or the background) of the original binary image, the minimal distance to the nearest pixel in the background (or the object). Markers are then set in the regional maxima of the distance map, some of which are merged, as determined by the contrast factor parameter, $h_c$. Each marker is also given a unique label to distinguish different catchment basins. In the next step, the distance map needs to be inverted, as the markers will be expanded towards increasing values of the distance map, where the dark areas represent low values of the distance map, but bright areas – high values of the distance map. The inverted distance map can now be viewed as the intensity profile shown in Fig. 3.1 with the markers set in the regional minima. Lastly, the watershed algorithm is applied to the inverted distance map, which expands the markers and creates separated watershed basins on the basis of watershed lines, where each basin represents an individual, separated pore. The watershed lines split the pores in the most constricted areas of the pore space, i.e., pore throats. In this thesis, the “Separate Objects” module (one-step implementation in Avizo), which is a combination of the distance map, contrast factor (also known as H-maxima), and watershed algorithm, was used to separate the connected binarized pore spaces of rocks.

### 3.6 Image Co-Registration

Image registration is defined as the process of aligning two or more images of the same scene into a single coordinate system [85]. These images can be taken at different times, from different viewpoints, or can be obtained using different imaging modalities, such as MRI or X-ray µCT. Image registration is required to be able to extract more complete information about the object or processes occurring in the object. In the context of DR physics, a good example is co-registration of flow MRI data with high-resolution µCT images of the same rock sample, where MRI provides information about the fluid flow, but µCT provides information about the structure of the rock. Such combined datasets can then be used to study structure-flow correlations in rocks, which will be demonstrated later in Chapter 6.

From a practical perspective, the process of image co-registration can be divided into three main steps: (1) pre-alignment, (2) automatic refined image registration, and (3) image re-sampling and visualisation. These steps are visualised in Fig. 3.4. In the first step, the model image (image to be transformed), also known as the source image, and the reference image
Figure 3.4 Basic steps of the image registration procedure showing the orientation of MRI and µCT images of the same Ketton limestone rock core plug: (a) orientation of images as acquired and loaded in Avizo; (b) orientation after manual pre-alignment of µCT data; (c) alignment of images after refined co-registration; (d) orientation of images after re-sampling µCT image on the MRI coordinate system; (e) 3D section of the co-registered MRI and µCT data of the rock.

should be positioned as close as possible to their optimal alignment so that more efficient refined image registration can be performed afterwards. This step can be performed by either manually aligning images or by using automatic approximate registration. In automatic approximate
image registration, images can be automatically aligned based on, for example, their principal axes \[79\]. However, as was tested in practice with MRI and µCT data, better results can generally be obtained by manually aligning images using basic image transformations, such as translation and rotation. This is because images acquired using different imaging modalities can be in very different orientations (e.g., rotated by 180° relative to each other) which often results in non-optimal starting alignment for the image registration step. Of course, in order to be able to manually align images, samples need to contain easily identifiable physical features (e.g., one side of the rock is skewed) or markers which can be added to the samples prior to imaging; in this work, all samples studied contained distinct physical features which helped to identify the approximate relative orientation of images.

In the second step, refined co-registration of images is performed. This is an automated, iterative optimisation of the image alignment, which itself contains three coupled components: (1) image alignment (similarity) measure that quantifies the quality of alignment, (2) geometric transformations that are applied to the model image to modify its position, and (3) an optimiser that seeks the transformations that maximise the similarity between the images as determined by the chosen similarity metric. These three components will now be briefly discussed. A variety of image quality metrics have been proposed for image registration purposes, which can be broadly categorised into two groups – feature-based and intensity-based metrics. Feature-based metrics are based on so-called control points, which represent the centres of gravity, line endings, distinctive points, and other features in images. The aim of the feature-based methods is to find the correspondence between these control points in the reference and model images. The drawbacks of the feature-based methods are that they often require user input and the features can sometimes be difficult to extract, which can lead to unreliable results. Intensity-based metrics, also referred to as area-based metrics, use the intensity patterns in the two images. The advantage of these methods is that they use greater information content of the images (i.e., all or a large proportion of the data) and do not require extraction of features. However, the intensity-based metrics are computationally more expensive to calculate due to the fact that greater information content needs to be processed. A summary of the feature-based and intensity-based methods can be found in the following review \[85\]. In this thesis, the similarity of images during image registration was measured using normalised mutual information, which belongs to the category of intensity-based metrics. The normalised mutual information is a robust metric and has become a standard technique for multi-modal image registration. Technically speaking, mutual information is based on the measure of information (often termed information entropy) and is defined as the difference between joint entropy and the sum of the marginal entropies (i.e., information in each image) of the two images \[86\]. In image registration, the goal is to align images in such way that they contain maximum
information about each other, which corresponds to maximising mutual information. The normalised version of the mutual information similarity metric is simply the ratio of the sum of the marginal entropies and the joint entropy, which provides a more robust measure with respect to changes in image overlap, compared to the standard mutual information metric [86]. The mathematical formulation of mutual information is beyond the scope of this thesis, but can be found elsewhere [86, 87]. The second component of the refined image registration involves using certain geometric transformations that are applied to the model image in order to align its position relative to that of the reference image. Different transformations with varying degree of complexity (i.e, the number of degrees of freedom) can be used to modify the model image. Common geometric transforms include a rigid transform, which allows translations and rotations, an affine transform, which also admits scaling and shearing, and local mapping transforms, which are more complex transforms that enable different transformations to be applied in different regions across the image, thus accounting for any local deformations.

The last component of the refined image registration process is the choice of the optimisation strategy. Image registration essentially is an optimisation problem that seeks an optimal image alignment, depending on the chosen transformations and similarity measure. There are many different optimisation strategies available that can be used for the purpose of image registration. A few examples include Quasi-Newton methods, conjugate-gradient methods, and Powell’s direction set method [88]. In the Avizo image analysis software package, which was the tool used for image registration in this work, the optimisation procedure is typically conducted in incremental steps at different spatial resolutions. In this workflow, images are first down-sampled and their position optimised using the selected optimiser. This process is then repeated in steps at increasing spatial resolutions; at the finest spatial resolution, a Quasi-Newton optimiser is used [79].

After images have been co-registered, the final step is to re-sample the aligned image onto the reference image coordinate system in order to generate a new aligned image suitable for further processing and visualisation. This can be achieved using data interpolation methods. Nearest neighbor, linear, and Lanczos [89] methods are some of the commonly used interpolation methods, and are also the choices available in the Avizo image analysis package. The Lanczos method [89], which approximates a low-pass filter, is generally a reliable choice and yields the most accurate results. It is, however, slower than the other two approaches. In this thesis, the Lanczos method was used for re-sampling the co-aligned images. After re-sampling, the co-registered and reference images can be simultaneously visualised using special data fusion methods that are available in Avizo [79]; this will be demonstrated in Chapters 6–8.
Chapter 4

High-Resolution MRI

4.1 Introduction

The first MRI image was published in 1973 by Lauterbur [41], who acquired 2D images of two tubes of water using projection imaging [43], or as he referred to it as – zeugmatography. Since the early reports on MRI, the quality and resolution of the MRI images have improved significantly, driven by advances in the hardware, software, and image processing techniques used for MRI applications. Using commercially-available imaging systems in combination with conventional imaging techniques, spatial resolution on the order of a few hundred microns is now typically achieved in routine MRI acquisitions. For medical applications, the spatial resolution of images is typically on the order of $\approx 1\, \text{mm}$.

Although “high resolution” is a relative term and is dependent on the size of the features that we want to resolve, it is useful to define what “high resolution” means in the context of MRI. For this purpose, the definition of magnetic resonance microscopy (MRM) could be used. MRM is generally referred to as the application of MRI that enables acquisition of images with spatial resolution better than 100 $\mu$m [90]. Hence, in this thesis, the term “high-resolution MRI” will be used for images with spatial resolution higher than 100 $\mu$m.

High-resolution MRI images with spatial resolution of up to 1 $\mu$m have been reported [90, 91]. Obtaining MRI images at $\mu$m-scale spatial resolutions typically relies on using specially-constructed MRI equipment (e.g., sensitive r.f. coils) in combination with high magnetic field strength and high magnetic field gradient strength [90]. The use of sensitive r.f. coils and high magnetic field strengths are aimed at increasing the sensitivity or SNR of MRI acquisitions. Meanwhile, higher magnetic field gradient strengths enable acquisition of images with higher voxel resolution, i.e., smaller voxel size. However, hardware requirements are not the only factor influencing the limits of MRI resolution. Other, more intrinsic NMR processes, such as relaxation, self-diffusion, or internal gradient effects, are often the key factors that limit
the spatial resolution that can be achieved in MRI. Overall, it is the SNR that determines the fundamental limits of spatial resolution in MRI since the SNR improves only as square root of the number of scans and the signal available per volume element decreases with increasing spatial resolution. For example, doubling the resolution in three dimensions would decrease the voxel SNR by a factor of 8, thus 64 times more scans would be required to restore the original SNR. These factors will be discussed in more detail in Section 4.3.

To this date, the highest spatial resolution of an MRI image has been reported by Lee et al [91], who obtained a 2D image of bulk hydrocarbon oil at 1 µm (in-plane) spatial resolution. This was achieved using a specially-built microscopy probe at high magnetic field strength (14.1 T; 600 MHz for $^1$H). The microscopy probe comprised a micro-coil of diameter 500 µm and gradient coils capable of delivering high gradient strengths ($10$ T m$^{-1}$). In addition, the diffusion coefficient of the hydrocarbon oil used was two orders of magnitude smaller than that of water, thus significantly reducing signal attenuation due to diffusion. Several groups have reported MRI images with an impressive spatial resolution of $\approx 3$ µm acquired on polymer beads [92], glass beads [93], and glass fibres [94] in fluids. All of these high-resolution experiments were performed at high magnetic field strengths ($B_0 = 9$–18.8 T) using sub-mm sized micro-coils and strong magnetic field gradients ($G = 6$–65 T m$^{-1}$). Additional improvements in the sensitivity (SNR) of the MR methods can be achieved at low temperatures [93], where the spin system has greater spin polarisation at thermal equilibrium and reduced thermal noise, and using dynamic nuclear polarisation (DNP) at low temperatures [95], where the sensitivity is additionally enhanced by transferring the large polarisation of electrons to nuclei. Compared to experiments at room temperature, imaging at low temperatures (i.e., 30 K or $-243$ °C) can enhance the SNR by a factor of 30, but using DNP at low temperatures – by a factor of 100 [93].

This chapter describes the aspects of high-resolution MRI that were considered as part of the planning process for high-resolution MRI experiments that were performed on porous rocks in this thesis. This includes the evaluation of commercially-available imaging systems, which was performed as part of this project and resulted in procurement of a new MRI system, and assessment of realistic rock types for high-resolution MRI. The strategy for high-resolution imaging also involved an integration of MRI pulse sequences that are suitable for pore-scale imaging, $k$-space under-sampling, and compressed sensing data reconstruction techniques; the basics of these concepts are also discussed in this chapter.
4.2 MRI Hardware: the Importance of Gradient Strength

The acquisition of spatially-resolved MRI data relies on the application of magnetic field gradients. It is not only the spatial resolution that is dependent on the gradient technology, but also the imaging speed. The two main quality factors of magnetic field gradients are their maximum gradient strength, \( G_{\text{max}} \), and slew rate. The maximum gradient strength is important for high resolution imaging because it does limit the achievable resolution in MRI. By combining Eq. 2.32 and Eq. 2.33, the following relationship between the pixel width, \( \Delta l \), and the gradient strength, \( G \), can be obtained:

\[
\Delta l = \frac{2\pi}{N\Delta t \gamma G}.
\] (4.1)

From Eq. 4.1 it is clear that higher spatial resolution can be achieved using stronger gradients. Another way of interpreting Eq. 4.1 is that at a fixed resolution stronger gradients enable \( k \)-space to be sampled more quickly since larger \( G \) means smaller \( \Delta t \). This analysis, of course, is purely based on the effects of the gradient strength alone and does not include other factors, such as relaxation, diffusion, and magnetic susceptibility, which often limit the maximum achievable resolution in MRM. As mentioned, the performance of gradients is also determined by the slew rate. The slew rate is the rate of change of the magnetic field gradient strength. It is calculated by dividing the maximum gradient strength by rise time, which is the time required to increase the gradient amplitude from zero to its maximum value. The higher the slew rate, the faster the gradients can be switched, thus reducing the minimum achievable \( t_e \) and \( t_{RD} \) and minimising NMR signal losses during imaging experiments.

During the early phases of the DR project, an evaluation of MRI systems was carried out with an aim to find a system that would be capable of delivering pore-scale (sub-50 µm) spatial resolutions in porous rocks. An overview of the commercially-available MRI systems that were considered for this purpose is compiled in Table 4.1. Although the initial plan was to build an

<table>
<thead>
<tr>
<th>( B_0 ) (T)</th>
<th>Bruker B-GA-6S-100</th>
<th>Bruker Micro5</th>
<th>Bruker Micro2.5</th>
<th>Bruker Mini0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>r.f. coil diam. (mm)</td>
<td>15–35</td>
<td>5–10</td>
<td>20–30</td>
<td>38</td>
</tr>
<tr>
<td>( G_{\text{max}} ) (T m(^{-1}))</td>
<td>1.0</td>
<td>2.9</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>rise time (µs)</td>
<td>111</td>
<td>11</td>
<td>60</td>
<td>56</td>
</tr>
<tr>
<td>slew rate (kT m(^{-1}) s(^{-1}))</td>
<td>9</td>
<td>267</td>
<td>25</td>
<td>9</td>
</tr>
</tbody>
</table>
High-Resolution MRI imaging system from separate components, based on the assessment of commercially-available MRI systems, it was determined that the latest specification, commercially-available Bruker spectrometer with the Micro5 gradient system satisfies the project requirements. This imaging system is capable of delivering MRI images at pore-scale spatial resolutions (see Section 4.3), has an excellent imaging speed (high slew rate), and is highly compatible with the sample sizes that were intended to be used. The maximum gradient strength, $G_{\text{max}}$, and the slew rate of this system are $2.9 \text{ T m}^{-1}$ and $267 \text{ kT m}^{-1} \text{s}^{-1}$, respectively, which are significantly higher than those of other commercially-available imaging technologies listed in Table 4.1. As a result of this assessment, the Bruker Micro5 tri-axial gradient system, with a maximum gradient strength of $2.9 \text{ T m}^{-1}$ in the three orthogonal $x$-, $y$-, and $z$-directions, and a 7.0 T vertical-bore magnet controlled by a Bruker BioSpin Avance III HD spectrometer were procured and commissioned. This imaging system is also compatible with the smallest diameter coils among the four imaging systems considered, which perfectly fit the 4-mm-diameter core plugs that were used in this work, and hence provide the greatest sensitivity (i.e., the highest SNR) [90]. The vast majority of MR data in this thesis were acquired on this imaging system.

4.3 Assessment of Realistic Rocks for High-Resolution MRI

For bulk liquids, it is the diffusion of nuclear spins that limits the achievable spatial resolution of MRI [90]. The distance scale of diffusion is defined as the root-mean-square (r.m.s.) distance diffused in a time, $t$, by a molecule with a self-diffusion coefficient, $D$, that is undergoing Brownian motion. In 1D, this diffusion distance is expressed as $\sqrt{2Dt}$ [43]. In the case of bulk water, with $D = 2 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ (at room temperature) and an encoding time of $t = 5 \text{ ms}$, the r.m.s. diffusion distance would be $\approx 3 \mu\text{m}$. This means that obtaining a spatial resolution greater than $3 \mu\text{m}$ would not be possible under these conditions. Note that diffusion can also cause signal attenuation in spin echo imaging sequences [43], and hence lead to lower image SNR. However, for liquids confined in porous media, molecular diffusion through the internal magnetic field gradients, induced by magnetic susceptibility differences at solid-liquid interfaces, contributes to the loss in NMR signal and causes additional line broadening leading to even lower resolution limits.

In the early stages of the DR project, an assessment of commonly-used rock samples was conducted to determine the most suitable rock types for high-resolution imaging experiments. This assessment was based on the $T_2^*$ values of water-saturated rock samples. To determine the characteristic $T_2^*$ value of each rock, an NMR spectrum for each rock was acquired using a basic 1D pulse-acquire NMR experiment. $T_2^*$ can then be calculated from the FWHM of the spectral line using Eq. 2.19; note that in many rocks $T_2^*$ is multi-exponential, and calculating $T_2^*$ from
Table 4.2 FWHM, $T_2^*$, and the corresponding resolution limit estimates, $\Delta l_{\text{relax}}$, of different rock samples. NMR spectra, on the basis of which the FWHM was determined, were recorded at 300 MHz ($^1$H).

<table>
<thead>
<tr>
<th>Rock</th>
<th>Lithology</th>
<th>FWHM (Hz)</th>
<th>$T_2^*$ (ms)</th>
<th>$\Delta l_{\text{relax}}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentheimer Sandstone</td>
<td>Sandstone</td>
<td>1150</td>
<td>0.28</td>
<td>9</td>
</tr>
<tr>
<td>Berea Sandstone</td>
<td>Sandstone</td>
<td>2909</td>
<td>0.11</td>
<td>24</td>
</tr>
<tr>
<td>Fontainebleau Sandstone</td>
<td>Sandstone</td>
<td>718</td>
<td>0.44</td>
<td>6</td>
</tr>
<tr>
<td>Estaillades Carbonate</td>
<td>Carbonate</td>
<td>508</td>
<td>0.63</td>
<td>4</td>
</tr>
<tr>
<td>Indiana Carbonate</td>
<td>Carbonate</td>
<td>990</td>
<td>0.32</td>
<td>8</td>
</tr>
<tr>
<td>Kettton Carbonate</td>
<td>Carbonate</td>
<td>994</td>
<td>0.32</td>
<td>8</td>
</tr>
<tr>
<td>Portland Carbonate</td>
<td>Carbonate</td>
<td>596</td>
<td>0.53</td>
<td>5</td>
</tr>
</tbody>
</table>

FWHM gives an estimate of the mean $T_2^*$. Recall from Section 2.2.5.3 that the measured $T_2^*$ decay is influenced by spin-spin interactions ($T_2$), static magnetic field inhomogeneity ($\Delta B_0$), and magnetic susceptibility induced internal gradient ($\Delta \chi B_0$) effects. In liquid-saturated porous rocks, the internal gradient-related effects can dominate the relaxation mechanism, especially at higher magnetic field strengths [35]. In the cases where the spatial resolution is limited by $T_2^*$, the achievable pixel size, $\Delta l_{\text{relax}}$, is given by [43]:

$$\Delta l_{\text{relax}} = \frac{1}{\pi T_2^*} \frac{2\pi}{\gamma G}.$$  \hspace{1cm} (4.2)

Based on the measured $T_2^*$ values, Eq. 4.2, and the (maximum) gradient strength of $G = 2.9$ T m$^{-1}$ of the imaging system that will be used for the MRI experiments, the $T_2^*$-based resolution limits were calculated for a range of sandstone and carbonate rock samples; the results of this analysis are summarised in Table 4.2. The data in Table 4.2 show that, overall, higher spatial resolution can be achieved in carbonates than in sandstones. These observations are consistent with the fact that the internal gradient effects tend to be stronger in sandstones than in carbonates [21]. This is because sandstones generally contain a greater concentration of paramagnetic ions (e.g., Fe$^{3+}$, Mn$^{2+}$) which are associated with stronger internal gradients [17, 55]. From all the rocks studied, the Berea sandstone has the lowest resolution limit of 24 µm, but the Estaillades carbonate has the highest spatial resolution limit of 4 µm. It is interesting to note that the Fontainebleau sandstone formation has a higher resolution limit than some carbonate rocks, indicating that the internal gradients in this rock are relatively weak.

The above assessment of rock types was based on the intrinsic $T_2^*$ resolution limits of rocks, which allows us to select the most “NMR-friendly” rock types for high-resolution MRI experiments. Another important aspect that needs to be considered when selecting the types
of rocks to be studied is the size of the pores within the rocks. This aspect of rock properties needs to be addressed because, in order to be able to resolve the pore space, the size of the voxels in the acquired images need to be comparable to or smaller than the pore sizes in rocks. Imaging rocks at spatial resolutions at which the pore space can be readily discerned can not only ease the quantification of the accuracy of the acquired structural images [96] and velocity maps [97], but can also increase the accuracy of the computed, image-based rock properties [67]. Note that in the context of pore-scale imaging of rocks in this thesis, the term “pore size” is generally used to refer to intergranular porosity (i.e., pores between the grains). This applies to both MRI and µCT imaging modalities, which, for the rock sizes used, are largely unable to resolve microporosity in rocks. Microporosity can constitute about 50% of the total porosity in carbonate rocks [21, 98] and, by definition, have pore body diameters \( (d_b) \) of less than \( d_b < 2 \mu m \).

To highlight the differences in pore sizes between different rock types, the pore throat size distributions of three rocks, namely the Bentheimer sandstone, Estaillades carbonate, and Ketton carbonate, were determined using mercury intrusion porosimetry (MIP); the measurements were performed on a Micromeritics AutoPore IV 9500 V1.06 porosimeter. The results from this analysis are shown in Fig. 4.1. The Bentheimer sandstone exhibits a unimodal pore size distribution with a characteristic pore throat diameter \( (d_t) \) of \( d_t \sim 30 \mu m \). The pore throat size distribution of the Estaillades carbonate is bimodal with two distinct peaks, of which the one at larger pore diameters corresponds to macroporosity (intergranular pores), but the one at smaller pore diameters – to microporosity (intragranular pores). The typical pore throat

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**Figure 4.1** Pore throat size distributions of Bentheimer sandstone (---), Estaillades carbonate (—), and Ketton carbonate (—) rocks, as determined from mercury intrusion porosimetry (MIP) measurements. Similarly to Estaillades carbonate, the Ketton rock also exhibits bimodal pore size distribution, but, due to an incomplete MIP measurement, only the macropore throat size data were available.
4.3 Assessment of Realistic Rocks for High-Resolution MRI

Figure 4.2 µCT images of (a) Ketton and (b) Estaillades carbonate rocks. The black regions denote pore space, whereas the light regions indicate dense rock grains. The grey color represents intragranular porosity (i.e., porosity within the rock grains).

sizes in Estaillades are 0.2–1 µm and 5–30 µm for the microporous and macroporous regions, respectively. Note that the pore size distribution of Estaillades is much broader than that of Bentheimer, indicating a greater degree of heterogeneity in the rock structure. The Ketton limestone rock also exhibits a bimodal pore size distribution [98, 99], but, due to an incomplete MIP measurement, the data corresponding to the micropore peak in Ketton were not recorded. In Ketton rock, the micropores have pore throats with diameters ranging from 0.02 µm to 0.2 µm [98, 99]. The macropores in Ketton (Fig. 4.1) are larger than those in Estaillades and Bentheimer, with the majority of macropore throat diameters lying in the range from 30 to 100 µm. Note that MIP determines the size of pore “throats”, so that the pore bodies behind the throats are assigned the same radius as the throats themselves, which leads to an underestimation of pore body sizes; in the case of intergranular porosity, pore throats are defined as narrow spaces between grains. In sandstone rocks, the pore bodies have similar size to the pore throats, and the body-to-throat ratio (BTR) is ∼1. However, carbonate rocks, including the Estaillades and Ketton limestone formations, typically exhibit a BTR > 1 [21, 98] and can have BTR values as high as 70 [100]. Hence, the expected fraction of pore space that can be captured by high-resolution MRI at sub-50 µm resolution in Ketton and Estaillades rock formations is greater than depicted in Fig. 4.1.

In this thesis, high-resolution MRI experiments were predominately performed on Ketton and Estaillades limestone rock samples. Ketton limestone has a relatively high $T_2^*$-based
resolution limit (8 µm) and large pores with the vast majority of macropore throat diameters $d_t > 8$ µm. These characteristics make this rock an ideal candidate for high-resolution MRI since the majority of macropores can be captured at the intended MRI resolutions, allowing direct comparison with the µCT data (see Chapter 5). Ketton limestone is an oolitic grainstone (see Fig. 4.2) made up mostly of ooids (spherical or elliptical grains composed primarily ($\sim 99\%$) of calcite, CaCO$_3$) and grain fragments. It was deposited $\sim 180$ million years ago (the Jurassic period) and is named after the village of Ketton in England. It has been widely used as a building stone; for example, the Wren library at Trinity College (Cambridge) is built of Ketton stone. Estaillades limestone is the most “NMR-friendly” rock sample (i.e., the highest $T^*_2$-based resolution limit – 4 µm) from the rocks studied and is structurally more heterogeneous than Ketton (Fig. 4.2) with a wide range of pore sizes (Fig. 4.1), which makes it an interesting sample to study, e.g., in terms of single- and multi-phase fluid flow (see Chapters 7 and 8, respectively). Estaillades limestone is a bioclastic grainstone (see Fig. 4.2); it is composed of shell debris and fossils, cemented together by calcite ($\sim 97\%$). The rock is quarried in Oppede, France, and was deposited 22 million years ago (in the Miocene epoch, the Neogene period).

### 4.4 Rapid MRI Acquisitions – Combining MRI with Compressed Sensing

In previous sections, MRI hardware and rock types suitable for high-resolution MRI were discussed. The next step is to determine MRI methods that can be used to acquire high-resolution, high-quality images in a reasonable experimental time. In this work, a combination of rapid pulse sequences, data under-sampling and CS reconstruction techniques were used to achieve pore-scale spatial resolution in rocks; these techniques are now described.

#### 4.4.1 Rapid Pulse Sequences – 3D RARE

The main imaging technique that was used to acquire pore-scale 3D images in this project was 3D RARE. More specifically, a variant of the 3D RARE sequence (see Fig. 4.3) was extensively used, either as a stand-alone sequence for structural imaging, or in combination with other pulse sequences that utilise MR contrast mechanisms, such as flow and chemical sensitivity. Compared to the classical approach, which utilises soft, typically Gaussian-shaped, pulses for signal excitation and refocusing, this variant of 3D RARE uses hard pulses. Because the duration of hard pulses typically is two orders of magnitude shorter than that of soft pulses, using hard pulses significantly shortens the echo spacing, $t_e$, and thus also minimises any signal losses due to relaxation.
4.4 Rapid MRI Acquisitions – Combining MRI with Compressed Sensing

The main advantages of choosing to use RARE over other MRI techniques were described in Section 2.3.8; in short, the main advantages are: (1) it is much faster than SPI-based sequences (see Section 2.3.7), and (2) its robustness with respect to image artefacts and the fact that RARE images are weighted by $T_2$, as opposed to $T_2^*$ (cf. EPI and FLASH; see Section 2.3.8). Another advantage of RARE is that it is particularly well-suited to compressed sensing applications as the magnetisation is returned to the same position in $k$-space after acquisition of each echo, thus allowing a great degree of freedom in designing $k$-space sampling schemes [29, 96, 101].

4.4.2 Under-Sampling and Compressed Sensing

In order to speed up MRI acquisitions even further, RARE can be combined with CS techniques; this combined approach will be referred to as CS-RARE, or, more generally, as CS-MRI. In CS-MRI, additional scan acceleration is achieved by acquiring only a subset of the $k$-space data that would be acquired in conventional MRI. For example, if the acquisition time of a conventional, fully-sampled MRI experiment is 20 h, then the acquisition time of a CS-MRI experiment with a $k$-space sampling fraction of 0.25 would be 5 h. The images are then reconstructed from the acquired under-sampled $k$-space data using a non-linear optimisation scheme, in which prior knowledge about the images is used to obtain an optimal reconstruction.

Three main requirements have to be fulfilled in order to be able to successfully apply CS in MRI [36]. Firstly, the aliasing artefacts that arise in the images due to under-sampling of $k$-space must be incoherent, i.e., noise-like – a condition which can be achieved by sampling $k$-space randomly. Secondly, the images need to have a sparse representation in some mathematical
**Figure 4.4** Diagram illustrating the process of k-space under-sampling and CS reconstructions. FT and IFT denote the Fourier transform and inverse Fourier transform, respectively. ZF stands for zero-filled.
transform domain. Thirdly, images need to be reconstructed using a non-linear reconstruction algorithm, which enforces both the sparsity and consistency with the acquired k-space data. A diagram, which illustrates k-space data under-sampling and image reconstruction, is shown in Fig. 4.4. Further details of under-sampling and CS pertinent to this thesis are given below.

4.4.2.1 k-Space Under-Sampling Strategies

Prior to performing CS-MRI acquisitions, one first needs to generate under-sampling schemes on the basis of which k-space points can be selectively sampled. Various strategies have been developed for the generation of k-space sampling schemes, which can be roughly divided into two categories – Cartesian and non-Cartesian (i.e., the k-space trajectory does not fall on a Cartesian grid) sampling strategies [102]. Cartesian sampling strategies are more widely used, because they are relatively easy to implement in practice, and image reconstruction from Cartesian-based sampling schemes can be done more easily compared to non-Cartesian methods. On the other hand, using non-Cartesian sampling has the advantage of increased flexibility in terms of k-space sampling trajectories [102]. Two well-known non-Cartesian methods are radial [103] and spiral [104] sampling trajectories.

The most popular class of under-sampling schemes, amongst those designed on a Cartesian grid, is based on variable density k-space sampling [36, 96, 105]. Using this approach, k-space under-sampling schemes are designed such that the sampled point density is decreasing from the centre to the periphery of k-space [36]. An important requirement in the design of sampling schemes is that the sampling point selection needs to be as random as possible in order to ensure high degree of incoherence and, because of this, better reconstruction quality. In practice, the generation of variable density sampling schemes is not a fully random process, but is based on pseudo-random k-space point selection with (typically) denser sampling at the centre of k-space. Sampling the central regions of k-space more densely than the outer portions of k-space captures most of the highest intensity Fourier coefficients, which are found close to the centre of k-space [36] and are responsible for the SNR and contrast information of the real space image; the periphery of k-space, which contains little energy, provides information about fine spatial details of the image. Sampling the central regions of k-space more densely than the edges of k-space results in less severe aliasing artefacts in the real image space, because the high-frequency k-space components (outer portions of k-space) contain little energy, so they alias less [36]. In such situations, where the k-space data are sampled more densely in the centre of k-space using variable density sampling, the aliasing artefacts appear as white noise in the real image space, which then can be efficiently removed using CS. Further details on variable density k-space sampling strategies, including a novel variable density sampling approach developed in this project, are discussed in Chapter 5.
A $k$-space sampling scheme shows which points in $k$-space need to be sampled, however, it does not indicate how those points can be sampled experimentally. More specifically, the order in which the selected $k$-space points are acquired is important, especially, in the RARE sequence, where a long train of echoes, which decays with $T_2$, is collected. In this project, the experimental implementation of $k$-space data sampling for most 3D CS-RARE experiments is based on the previous work by Ramskill et al. [101]. In short, using this strategy, all sampled points in the two phase-encoding dimensions, $k_x$ and $k_y$, (the frequency-encoding direction, $k_z$, is fully sampled) are first sorted according to their proximity to the centre of $k$-space and divided into a number of subsets, each of size $N_{RF}$. Each subset is then sorted individually such that the points in closest proximity to the centre of $k$-space are acquired in the middle of the echo train, which ensures uniform relaxation weighting across $k$-space [101]. Note that this strategy is different from the one used in conventional 3D RARE acquisition, wherein $N_{RF}$ points are acquired at different positions in one phase-encoding dimension ($k_x$) for a single position in the other phase-encoding dimension ($k_y$). Three representative trajectories for $k_x$ and $k_y$ during the RARE echo train with $N_{RF} = 16$ are shown in Fig. 4.5, along with the corresponding $k$-space sampling scheme from which these trajectories were obtained. It can be seen in Fig. 4.5b that the centre of $k$-space is approached around the middle of the echo train. An advantage of this approach is that the point at which the centre of $k$-space is approached within the echo train can be shifted and optimised depending on the nature of the
4.4 Rapid MRI Acquisitions – Combining MRI with Compressed Sensing

MRI experiment. For example, if an MRI image with increased overall SNR is required, the trajectory can be easily modified to ensure that the centre of k-space is acquired earlier in the echo train. This added flexibility to shift the point at which the centre of k-space is acquired in the echo train was utilised in Chapter 5 to acquire high-resolution MRI images of a rock sample. A different strategy to generate k-space trajectories was used for the acquisition of quantitative, chemically-selective MRI data; this strategy will be demonstrated in Chapter 8.

4.4.2.2 Compressed Sensing Reconstructions

The next step in the CS workflow is to reconstruct the acquired under-sampled k-space data. All CS reconstructions in this thesis were carried out using an in-house Matlab toolbox, Object Oriented Mathematics for Inverse Problems (OOMFIP), for which the implementation is presented in [106]. This methodology has been shown to yield good quality reconstructions for both magnitude and phase (i.e., velocity data) MRI data.

In CS-MRI, the goal is to recover a complex image, \( m \), from an acquired under-sampled k-space dataset, \( y \), which are related by the following equation as:

\[
\mathcal{F}_u m + \varepsilon = y, \tag{4.3}
\]

where \( \mathcal{F}_u \) is the under-sampled Fourier transform operator on the basis of some under-sampling pattern, and \( \varepsilon \) is the normally-distributed noise with standard deviation \( \sigma_n \). A naive approach to recover an image \( m \) would be to fill the missing k-space points with zeros and apply an inverse Fourier transform on the k-space data – this is referred to as the zero-filled Fourier transform solution. However, this solution is sub-optimal and typically results in an image dominated by artefacts due to violation of the Nyquist sampling rate [36]. CS enables us to find a better solution to \( m \) using a variational regularisation approach which incorporates prior knowledge about \( m \) into the reconstruction problem. In the case of the CS reconstruction, the prior knowledge is that the image can be sparsely represented in an appropriate sparsifying transform domain. The type of regularisation functional, \( J \), that is used to map the image into the transform domain depends on the nature of the image to be recovered. In this thesis, total variation (TV) regularisation, which is based on the finite-difference transform of \( m \), was used for CS reconstructions, unless stated otherwise. It has been demonstrated that TV yields a good reconstruction quality for structural images [96, 101], velocity images [28, 106], and spatially-resolved propagators [29, 107] acquired on rocks and other porous systems similar to rocks. The TV regularisation promotes sparsity of the gradient of an image and has edge-preserving properties. TV can be expressed as:
\[ J(m) = TV(m) = \|\nabla m\|_{2,1}, \quad (4.4) \]

where \( \| \nabla m \|_{2,1} \) is 1-norm of the 2-norm of the finite difference approximation of the gradient of the image with zero Neumann boundary conditions.

Next, a non-linear reconstruction algorithm is used to compute a solution for \( m, m_{CS} \), on the basis of this prior knowledge (i.e., the optimal sparsifying transform). In this thesis, an optimisation algorithm based on a Bregman iteration scheme was used to reconstruct the under-sampled \( k \)-space data; it is expressed as:

\[
\begin{align}
\mathbf{m}_{CS}^k & \in \arg\min_{\mathbf{m}} \left\{ \frac{1}{2}\|\mathbf{y}^{k-1} - \mathcal{F}_u \mathbf{m}\|_2^2 + \alpha J(m) \right\}, \\
\mathbf{y}^k & = \mathbf{y}^{k-1} + \mathbf{y} - \mathcal{F}_u \mathbf{m}_{CS}^k,
\end{align}
\]

where \( \alpha \) is a regularisation parameter that balances the weight between the fidelity term, \( \frac{1}{2}\|\mathbf{y} - \mathcal{F}_u \mathbf{m}\|_2^2 \), and the regularisation term, \( \alpha J(m) \). Using this method, a series of \( k \) problems is solved, where in each Bregman iteration, the loss of contrast present in the previous iteration is added back into the \( k \)-space data, which has been demonstrated to enhance the signal contrast in the reconstructed images [106]. Although the Bregman iteration scheme might slightly improve the quality of the reconstruction, it comes at a cost of longer reconstruction time. Because of this, in the cases where large data sets or a large number of 3D images had to be reconstructed, only one Bregman iteration (equivalent to no Bregman iterations) was used. In these cases, the solution is computed as:

\[
\mathbf{m}_{CS} \in \arg\min_{\mathbf{m}} \left\{ \frac{1}{2}\|\mathbf{y} - \mathcal{F}_u \mathbf{m}\|_2^2 + \alpha J(m) \right\}. 
\]

Equation 4.6 is generally known as the Tikhonov regularisation scheme.

The last step in the image reconstruction process is to optimise the regularisation parameter, \( \alpha \). One way to choose the value of the parameter \( \alpha \) is to use the Morozov’s discrepancy principle [108], which states that the error between the measurement and the reconstruction should not be larger than the noise level in the image, otherwise the solution would be fitted to noise. Morozov’s discrepancy principle is written as:
\[ \| y - \mathcal{F}_u m \|_2 \leq \sigma_n \sqrt{n}, \]  
(4.7)

where \( n \) is the number of k-space samples. In practice, the optimal value of \( \alpha \) is determined by running several image reconstructions for different \( \alpha \) values, and then choosing the maximum value of \( \alpha \) that satisfies the condition in Eq. 4.7.

### 4.5 Conclusions

This chapter has laid the foundation for the following chapters by introducing important aspects of high-resolution MRI. First, as part of the DR project, commercially-available MR imaging and gradient technologies were assessed, as they impose a practical restriction on achievable resolution. Factors, such as the maximum achievable gradient strength and slew rate, were considered. Based on this analysis, Bruker BioSpin Avance III HD spectrometer (7.0 T) with Micro5 tri-axial gradient system capable of delivering a maximum gradient strength of 2.9 T m\(^{-1}\) was procured and commissioned. All high-resolution MRI experiments presented in this thesis were conducted on this imaging system. Another important consideration of high-resolution MRI experiments was the choice of rock samples. More specifically, \( T_2^* \) resolution limits, as determined by the internal gradient effects, and pore sizes in a range of sandstone and carbonate rocks were assessed and compared. This analysis revealed that Ketton and Estaillades carbonate rocks are attractive candidates for high-resolution MRI experiments. In the case of sandstones, the Fontainebleau rock seems to be a promising candidate for high-resolution MRI due to its high \( T_2^* \)-limited resolution of 6 µm. Last, rapid MRI data acquisition methods were discussed. In this thesis, the 3D RARE pulse sequence is combined with CS to reduce the total image acquisition time and to enable acquisition of MRI images at higher spatial resolutions, for which the acquisition times would otherwise be prohibitively long.
Chapter 5

Identification of Optimal Sampling Patterns for CS-MRI in Porous Media

5.1 Introduction

Optimal $k$-space sampling pattern design is a critical aspect of CS-MRI. The routine approach to selecting a $k$-space under-sampling pattern involves using model functions which contain one or more adjustable parameters. These parameters are either arbitrarily chosen, which may give a sub-optimal sampling pattern, and hence reconstruction quality, or are optimised using a fully-sampled MRI image. Another approach to identifying an under-sampling pattern is to use a fully-sampled 3D MRI dataset directly to “learn” the most effective $k$-space sampling scheme. However, high-resolution 3D fully-sampled MRI acquisitions are associated with prohibitively long acquisition times (on the order of weeks). Thus, this chapter introduces a novel, data-driven, parameter-free approach that uses input from high-resolution 3D X-ray µCT images that are typically acquired at resolutions of a few microns to derive optimal $k$-space sampling schemes for acquiring high spatial resolution 3D MRI images of rocks.

The structure of this chapter is as follows. First, existing methods for obtaining MRI sampling patterns are discussed (Section 5.1.1). Then, in Section 5.2, the new method proposed is described. The experimental details of µCT and under-sampled MRI data acquisitions, and benchmarking of the sampling strategies are given in Section 5.3. The results of this work are discussed in Section 5.4. First, the performance of the proposed approach is benchmarked against other under-sampling strategies using data for a sample of Ketton rock, for a $k$-space sampling fraction of 0.25. The benchmarking was then extended to consider a range of additional sampling fractions (0.125, 0.1875, 0.3125, and 0.375) and two further rock types (Estaillades limestone and Fontainebleau sandstone) to confirm that the new method is robust.
This new method was then implemented experimentally to acquire under-sampled MRI data of a water-saturated Ketton limestone plug of 4 mm diameter at both 35 µm and 17.6 µm spatial resolutions; 17.6 µm is the highest spatial resolution reported for a magnetic resonance image of rock samples. The resulting 3D reconstructions are then analysed in terms of their pore space characteristics, benchmarked against the pore space characterisation obtained from the high-resolution µCT dataset.

### 5.1.1 Existing Approaches to Identification of Sampling Patterns

The most popular class of under-sampling strategies is based on variable density sampling on a Cartesian grid [36, 105, 109–112]. Within this category, pseudo-random variable density sampling following the Monte Carlo approach of Lustig et al. [36] has been used most extensively. Lustig’s sampling method [36] is based on a probability density function (pdf) which is calculated using a polynomial function as:

\[
pdf = (1 - r_N)^p,
\]

where \( r_N \) is the normalised distance from the origin to the corner of \( k \)-space, and \( p \) is the value used to modify the shape of the pdf. According to the constructed pdf, sampling points are then randomly selected, yielding a sampling pattern with diminishing density towards the periphery of \( k \)-space. In addition, this strategy contains an adjustable normalised radius \( r_A \), which forces all the phase-encoding points within the region \( r_N < r_A \) to be fully sampled. Sampling the central regions of \( k \)-space more densely than the edges of \( k \)-space results in less aliasing, hence better reconstruction quality [36]. Although this method allows the user to generate widely different shapes for the pdf by varying \( p \) and \( r_A \) values, this is also its limitation – a suboptimal choice of the parameters can significantly degrade the quality of the reconstructed image. Further, even if a conventional fully-sampled image can be acquired from which to optimise these parameters, the optimisation process is a time-consuming process, and a new optimisation would be required for any change in image resolution.

Another class of under-sampling strategies is data-driven sampling which involves learning \( k \)-space sampling from the acquired MRI datasets. The rationale behind these methods is that the underlying \( k \)-space energy distribution contains information about the morphological structure of the image which can guide the selection of \( k \)-space sampling points. Two sub-classes can be identified for the data-driven methods, one of which is based on systematic iterative optimisation of \( k \)-space sampling based on objective criteria related to image features [113–115], and the other which uses fully-sampled \( k \)-space magnitude data as input.
for a pdf [105, 111, 112, 116, 117] from which sampling points are drawn in a way similar to the variable density sampling approach; in this work, the focus will be on the latter. Several methods have been proposed for using fully-sampled k-space data as a pdf for sampling scheme generation. Vellagoundar & Machireddy [112] have reported a method where the sampling density is controlled by the integral of segments into which the fully-sampled k-space magnitude data are divided. However, this approach requires optimisation of the segment width which complicates the use of this method. Zhang et al. [111] have proposed a way to modify the pdf obtained from fully-sampled MRI images by applying a Hamming window function to the initial pdf to enforce sampling of the high frequency k-space points, but this again requires tuning of one parameter to adjust the distribution of the pdf. In this case, sampling is controlled by changing the threshold of the pdf above which all the sampling points are selected. Parasoglou et al. [116] used k-space magnitude data calculated from binary-gated fully-sampled MRI images to generate sampling schemes that maximise the SNR of the acquired MRI datasets. The sampling schemes were generated by selecting a certain fraction of the highest intensity k-space points, as determined by the selected sampling fraction. Possibly the best known method from this category is an adapted variable density sampling (AVDS) strategy developed by Knoll et al. [105]. This strategy uses the magnitude of a fully-sampled k-space dataset at a certain resolution as a pdf. Based on this pdf, which is first normalised to unity, the corresponding cumulative distribution function (cdf) is calculated. Sampling pattern indices are then randomly drawn from this cdf to give a sampling scheme with the desired sampling fraction. This method also contains a user-adjustable parameter which determines the maximum number of unsampled k-space points that can exist between the sampled points by sampling a point if this number is exceeded, thus covering k-space more uniformly. Knoll et al. showed that their method produces similar quality images to the ones obtained by Lustig’s approach with an optimised value of p; for a k-space sampling fraction of 0.25, p = 7.

The aim of this chapter is to present a new, robust, optimisation-free CS-MRI sampling method which uses high-resolution µCT data as an input for generating optimal k-space sampling patterns. The motivation for this approach arises from two practical considerations. First, acquisition of acceptable-quality fully-sampled high spatial resolution MRI images as a basis for sampling pattern design can be prohibitively time-consuming. Second, for some applications, including DR physics, µCT images are acquired and analysed as a matter of course and hence are already available as input for the optimisation of the CS sampling pattern. Because of its connection to µCT, this method will be referred to as µCT-based variable density sampling (µCT-VDS).
5.2 Proposed Method: Data-Driven Learning from Higher Spatial Resolution Data

Data-driven \( k \)-space sampling strategies rely on the observation that structurally similar images have a similar distribution of the magnitude of \( k \)-space energy values. Hence, it is proposed to use \( \mu \)CT images as input for generating sampling schemes for MRI images. The different steps to generate a \( k \)-space sampling scheme from the \( \mu \)CT data are summarised below and in Fig. 5.1:

1. *Generating simulated MRI images from \( \mu \)CT data.* A 3D \( \mu \)CT dataset is segmented to obtain voxels containing rock grains (i.e., grain space) and then inverted to obtain a complement image, which represents the pore space and is referred to as the simulated MRI image. This image is then multiplied by a cylindrical binary mask to isolate the region of the rock matrix and down-sampled to obtain a noise-free MRI image at the desired spatial resolution.

2. *Obtaining a pdf.* The second step involves using the Fourier transform to calculate the probability distribution function of the \( k \)-space magnitude data associated with the simulated MRI image at the selected resolution. Because of the experimental MRI method used in this work, a 2D pdf is required. Taking the central \( k \)-space slice in the frequency-encoding direction would be equivalent of the entire structure in that direction and so microstructural features would be largely averaged out. To incorporate low and high spatial frequency 3D \( k \)-space information in a 2D dataset, the 3D simulated \( k \)-space magnitude data are therefore summed along the frequency-encoding dimension. To avoid dependence of the sampling scheme on the specific rotation of the rock in the \( xy \)-plane of the rock during the MRI acquisition relative to the \( \mu \)CT acquisition, the \( k \)-space is then azimuthally averaged to obtain a 1D pdf. A 2D matrix of the same size as the original \( k \)-space data is then populated with probabilities from the 1D pdf to generate a 2D pdf reflecting intensity distribution in \( k \)-space for a specific rock type for any azimuthal orientation.

3. *Scaling the pdf.* The pdf is then scaled, setting all values greater than 1 to be equal to 1, such that the integral of the 2D pdf is equal to the number of points to be sampled. This is done so that the correct number of points can be selected in the next step. Setting larger values in the pdf to a maximum of 1 results in a fully-sampled central region, the extent of which depends on the degree of sampling. Sampled points outside of the fully-sampled central region will be selected according to the shape of the pdf.
5.2 Proposed Method: Data-Driven Learning from Higher Spatial Resolution Data

Figure 5.1 Diagram illustrating the steps of the µCT-based variable density sampling (µCT-VDS) approach. Step 1 involves generating a simulated MRI image from a high-resolution µCT image. Step 2 takes the Fourier transform of the simulated MRI image to obtain \( k \)-space magnitude data (\( pdf \)). Step 3 scales the \( pdf \) based on the desired sampling fraction. Step 4 generates a \( k \)-space sampling scheme. \( k_x \) and \( k_y \) correspond to \( k \)-space points in the phase-encoding directions \( x \) and \( y \). The line plots shown represent the \( k \)-space values along \( k_y \) through the central point of \( k_x \). The white pixels in the sampling scheme correspond to the points sampled in both phase-encoding directions. For a 3D RARE experiment, a line in the frequency-encoding direction, orthogonal to \( k_x \) and \( k_y \), is fully sampled for each of these points.

4. **Sampling point selection.** Uniformly distributed random numbers in the interval \([0,1]\) are generated on a Cartesian grid of the same size as the (2D) \( pdf \). A point on this grid will be sampled if the value of the scaled \( pdf \) is greater than the randomly generated number; this process will be repeated until there is a match between the desired sampling fraction and the result of the random sampling point selection. This procedure is repeated again (typically 1000–10000 times) from which the sampling pattern with the greatest incoherence is chosen; the incoherence in the sampling pattern is measured from the density-compensated point spread function of the pattern as detailed in Lustig et al. [36].

The output of steps 1–4 is a 2D variable density sampling scheme with a pre-determined fraction of under-sampling. For the 3D RARE experiment used in the present work, the 2D sampling scheme is used in the phase-encoding directions (i.e., only the phase-encoding dimensions are under-sampled), whereas the frequency-encoding direction is fully sampled. In principle, this method can be extended for generating sampling patterns for MRI acquisitions.
with one and three phase-encoding directions. In the context of DR technology, this approach can also be used to accelerate other CS-MRI techniques, such as flow and relaxation time mapping. However, in such cases, in which other contrast mechanisms are built in into the experiment (flow, diffusivity, relaxation), the optimised sampling patterns may differ from that identified for the structural image.

Compared to Lustig’s sampling approach, the new μCT-based method offers a parameter-free approach to obtain k-space sampling schemes, circumventing the need for any optimisation. The fundamental difference between the AVDS and μCT-VDS strategies is the type of the distribution function used for sampling point selection. The AVDS method does not use the pdf of the k-space data for drawing sampling pattern indices, but instead it uses the cdf of the pdf, which may not accurately represent the k-space energy distribution. In contrast, the μCT-VDS strategy uses a more intuitive way to modify the pdf of k-space data by scaling it; first, this produces a sampling pattern with a relatively large fully-sampled central region, thereby minimising aliasing artefacts, and also gives good SNR; second, it ensures that the higher-frequency regions of k-space, responsible for the detail of the image, are sampled according to the actual pdf of k-space.

An additional strength of μCT-VDS lies in the fact that it enables the use of high-resolution μCT images, which are typically acquired at resolutions of a few microns, to generate optimal k-space sampling patterns for MRI acquisitions at any resolution up to that of the μCT dataset. This means that acquiring fully-sampled k-space MRI data is no longer needed, since a simulated fully-sampled MRI image can now be obtained from the corresponding μCT data.

5.3 Materials and Methods

This section is structured as follows. After a description of the sample preparation steps, the experimental data acquisition methods of X-ray μCT and MRI are described. A description of the way 2D simulated MRI images were generated and used in CS reconstructions is then given. Finally, details are given of the sampling scheme generation and implementation, and also image quality assessment methods, namely image quality metrics and 3D pore space characterisation, that were used to compare the performance of the sampling schemes.

5.3.1 Materials

Two carbonate rocks (Ketton and Estaillades) and one sandstone rock (Fontainebleau) were used in this study. The cylindrical rock core plugs had the following dimensions (diameter × length): Ketton (3.84 ± 0.01 mm × 11.11 ± 0.37 mm), Estaillades (3.87 ± 0.01 mm × 9.19 ±
0.01 mm), and Fontainebleau (4.00 ± 0.01 mm × 9.29 ± 0.01 mm). All rock samples were dried in an oven at 70 °C overnight before μCT acquisitions.

The pore space of the Ketton sample, which was used for MR experiments, was vacuum-saturated with distilled water using a saturation rig (~ 24 h).

### 5.3.2 X-ray Micro-Computed Tomography

X-ray micro-computed tomography images of the dry rock samples were obtained using a Bruker micro-CT SkyScan 1172 scanner (Bruker Micro-CT, Belgium) at an isotropic resolution of 5.00 µm for Ketton and 3.98 µm for Estaillades and Fontainebleau rocks. For all rock samples, 802 projections were acquired with a source voltage of 60 kV, a source current of 165 µA, and an Al (0.5 mm) filter. 10 images were acquired for each position resulting in a total acquisition time of approximately 11.5 h. Projection images were reconstructed using the NRecon software (Bruker, v1.6.8.0) to give 2666 cross-sectional images for the Ketton, Estaillades, and Fontainebleau rock samples. 3D μCT images of rocks were generated by successively stacking all 2D cross-sectional slices in Avizo 9.5.0 (FEI Visualisation Sciences Group, USA).

### 5.3.3 Magnetic Resonance Imaging

#### 5.3.3.1 MRI Acquisitions at 35 µm Resolution

At 35 µm resolution, both fully-sampled and CS-MRI images of the water-saturated Ketton rock were acquired on a 7.0 T vertical-bore magnet controlled by a Bruker BioSpin Avance III HD spectrometer. A Bruker Micro5 tri-axial gradient system with a maximum gradient strength of 2.9 T m$^{-1}$ was used to achieve spatial resolution. A 10 mm r.f. saddle coil tuned to a resonance frequency of 299.84 MHz ($^1$H) was used for spin excitation and signal detection. The images were acquired using a 3D RARE pulse sequence [33] (see Fig. 4.3 in Chapter 4) with $N_{RF} = 16$. Hard 90° excitation and 180° refocusing r.f. pulses of duration 8.4 µs and 16.8 µs, respectively, were used. The spectral width (SW) was set to 200 kHz. For both the fully-sampled and CS acquisitions, the echo spacing in the 180° pulse train was 3.1 ms, and 64 scans were acquired with a recycle delay of $t_{RD} = 1.1$ s. Using bi-exponential fits, the longitudinal ($T_1$) and transverse ($T_2$) relaxation times of the water-saturated Ketton sample were determined to be 0.13 s and 0.86 s, and 0.01 s and 0.15 s, respectively. The short and long relaxation times are associated with intra- and inter-grain liquid, respectively. The phase encoding start value (PESV) for the fully-sampled experiment was −0.5, corresponding to a shift of 4 echoes. Although this shift improves the overall SNR of the image, because it reduces
Identification of Optimal Sampling Patterns for CS-MRI in Porous Media

Figure 5.2 Representative trajectories for $k_x$ and $k_y$ with the echo train length of $N_{RF} = 16$ and an echo shift of $-4$ echoes. The black (—), red (—–), and blue (——) lines represent the 1st, 64th, and 256th (last) echo train (i.e., excitation), respectively.

The effects of $T_2$ attenuation, it comes at the cost of a lower SNR of the echoes acquired from points further out in $k$-space, which represent finer details in the images. A PESV of $-0.5$ was found to give a good balance between the SNR and the sharpness of the image. The SNR of the fully-sampled acquisition in the image domain was $\sim 40$. The experimental time for the fully-sampled MRI acquisition was $\sim 20$ h. The images were acquired with a FOV of 13.5 mm $\times$ 4.5 mm $\times$ 4.5 mm and 384 voxels $\times$ 128 voxels $\times$ 128 voxels in the frequency- ($z$) and both phase-encoding directions ($x$ and $y$), respectively, yielding 3D images with an isotropic resolution of 35.2 µm. This resolution was chosen because the fully-sampled MRI image at this resolution can still be acquired in a reasonable experimental time.

The experimental implementation and strategy of the $k$-space data sub-sampling for the 3D CS-RARE experiment is based on the previous work by Ramskill et al. [101] and was already described in Section 4.4.2.1. A similar strategy was used in this study, but, instead of approaching the centre of $k$-space in the middle of the train of echoes (see Fig. 4.5), each subset was shifted such that the centre of $k$-space was approached four echoes earlier in the echo train (Fig. 5.2), at which point less $T_2$ attenuation has occurred. This corresponds to a PESV of $-0.5$ in the fully-sampled acquisition. As already mentioned, for the fully-sampled acquisition, a shift of 4 echoes was found to give a good balance between the SNR and the sharpness of the image. A sampling fraction of 0.25 was chosen as it gives significant reduction in the acquisition time compared to the fully-sampled acquisition, which in this case is from 20 h to 5 h, and still provides high quality images [26, 101].
5.3 Materials and Methods

5.3.3.2 MRI Acquisitions at 17.6 µm Resolution

The same water-saturated Ketton sample was also imaged at 17.6 µm resolution using the CS-RARE method based on µCT-VDS with a k-space sampling fraction of 0.25. The CS-MRI image of Ketton was acquired on the same Bruker spectrometer and gradient system using a 5 mm r.f. saddle coil tuned to a resonance frequency of 299.84 MHz (1H). The duration of the hard 90° excitation and 180° refocusing pulses was 4.5 µs and 9.0 µs, respectively. 128 scans were acquired with N_{RF} = 8, an echo shift of 2 (PESV = −0.5), SW = 400 kHz, t_e = 3.5 ms, t_{RD} = 1.1 s, and an experimental time of ~ 3.3 days. The image was acquired with a FOV of 10.125 mm × 4.5 mm × 4.5 mm and 576 voxels × 256 voxels × 256 voxels (frequency (z) × phase (x) × phase (y)) corresponding to an isotropic spatial resolution of 17.6 µm.

It is important to note at this point that the calculated spatial resolution of MRI images (voxel size = FOV/voxels) is, in fact, not the true spatial resolution of the images and there may be blurring caused by T_2 relaxation in the phase-encoding directions and T_2^* in the frequency-encoding direction. The blurring effect due to T_2 relaxation is more important for long echo trains (large N_{RF}) and short T_2 materials [118–120]. In general, the echo train duration should be \( \lesssim T_2 \), and so for shorter T_2 materials a reduced echo train duration may be required. In this work, the T_2 of the inter-grain liquid is longer than the duration of the echo train thus the spatial resolution in the phase-encoding directions is not significantly affected. A more detailed analysis of the effect of T_2 and k-space acquisition ordering during the RARE imaging sequence can be found elsewhere [118, 119]. The effect of T_2^* values on the spatial resolution limits in the frequency-encoding direction in porous rocks was already discussed in Section 4.3. The spatial resolution limits [43] in the frequency-encoding direction at the maximum gradient strength of the hardware used here are estimated to be 8, 4, and 6 µm respectively for the Ketton (T_2^* = 0.32 ms), Estaillades (T_2^* = 0.63 ms), and Fontainebleau (T_2^* = 0.44 ms) rocks (see Table 4.2 in Chapter 4). These resolution limits are smaller than the voxel size in the images and therefore it is considered that the blurring effects associated with T_2 and T_2^* relaxation are minimal. However, for a Berea sandstone, with a typical T_2^* of 0.11 ms, the spatial resolution limit would be \( \approx 24 \) µm, and therefore would influence the quality of the images obtained.

Note that due to magnetic susceptibility induced internal gradient effects present in saturated rock samples spatial distortions or signal misregistration can occur in some regions of the image and hence can lead to image artefacts that can be larger than the aforementioned resolution limits; magnetic susceptibility artefacts can be seen in the acquired MRI images of Ketton rock in Fig. 5.11 as bright voxels, which were estimated to constitute approximately 0.3 % of voxels within the rock (for this calculation, the bright voxels were considered as voxels with intensities two times higher than the mean intensity in the macropores).
5.3.4 Generation of Fully-Sampled 2D Simulated MRI Images and CS Reconstructions

To assess the performance of the µCT-VDS strategy relative to existing methods, a 2D simulated MRI image of Ketton rock at 35 µm spatial resolution was obtained from the high resolution µCT data. The reason for using 2D µCT images is twofold. First, under-sampling in the MRI measurements is only done in two dimensions since the frequency-encoding direction is fully sampled. Second, 2D CS reconstructions are much faster to perform than the 3D ones, which gives significant time savings when performing a large number of reconstructions, which is the case in this work; 135 sampling patterns of all the sampling strategies considered were tested for each sampling fraction.

To generate the 2D MRI image of Ketton rock used in this analysis, seven 5 µm resolution µCT cross-sectional (xy) images of Ketton were binarized (Otsu’s algorithm [83]), inverted, and summed, such that the total thickness of the resulting slice was 35 µm. This image was then multiplied by a circular mask to identify pixels associated with rock grains and down-sampled to obtain the noise-free fully-sampled 2D MRI image shown in Fig. 5.3. Next, k-space was calculated by applying a Fourier transform to the noise-free simulated MRI image. To mimic noisy MRI data, white noise was added to the calculated k-space such that the SNR of the central k-space point was \( \sim 300 \), which represents the SNR of a typical MRI image; the SNR in the image domain was determined to be \( \sim 34 \). The noisy k-space data were then under-sampled using the µCT-VDS, AVDS, and Lustig’s variable density strategies, and reconstructed using CS. For all the sampling methods, sampling patterns with the following sampling fractions were generated: 0.125, 0.1875, 0.25, 0.3125, and 0.375. Five Bregman iterations were used for reconstructions with \( \alpha = 0.05 \) for sampling fractions \( \leq 0.25 \) and \( \alpha = 0.1 \) for sampling fractions \( > 0.25 \).

![Figure 5.3](image_url) (a) The simulated fully-sampled MRI image of Ketton rock at 35 µm spatial resolution. The white box represents (b) the region of interest for which the image quality metrics were calculated.
2D simulated MRI data of Estaillades and Fontainebleau rocks were also generated from high-resolution µCT images of these rocks. The same strategy as for the Ketton rock was used to obtain 2D images at 35 µm resolution, but nine individual µCT cross-sectional (xy) images were summed to obtain 2D simulated MRI images, and the images of Estaillades rock were binarized using a watershed algorithm [84] due to its more complex rock structure. For both Estaillades and Fontainebleau, white noise was added to k-space data giving an SNR of $\sim 170$ (lower than for Ketton due to lower total signal intensity because of the lower porosity of these samples). This SNR in k-space corresponds to an SNR of $\sim 32$ in the image domain for both rocks. The noisy k-space data were then under-sampled (0.25) and CS-reconstructed using five Bregman iterations and $\alpha = 0.05$.

All CS reconstructions were carried out using an in-house Matlab toolbox, OOMFIP [106]. For more details, see Section 4.4.2.2.

### 5.3.5 Benchmarking Performance of Under-Sampling Methodologies

#### 5.3.5.1 Image Quality Metrics

In order to quantitatively assess the performance of the different sampling strategies, the quality of the CS reconstructions ($m_{\text{CS}}$) with respect to the fully-sampled reference image ($m_{\text{FS}}$) needs to be measured. For this purpose, two standard image quality metrics, namely peak signal-to-noise ratio (PSNR) and structural similarity index (SSIM), were used. The PSNR is a simple metric which measures the error between the reconstructed and the reference images and is written as:

$$\text{PSNR}(m_{\text{CS}}, m_{\text{FS}}) = 10 \log_{10} \left( \frac{(\max |m_{\text{FS}}|)^2}{\|m_{\text{CS}} - m_{\text{FS}}\|_2^2 / N_{\text{vox}}} \right),$$  \hspace{1cm} (5.2)

where $N_{\text{vox}}$ is the number of voxels in the image. Higher values of PSNR correspond to better quality reconstructions. The SSIM is a more advanced metric which correlates well with the human perception of image quality [121]. The local SSIM (LSSIM) is given by:

$$\text{LSSIM}(m_{\text{CS}}, m_{\text{FS}}) = \frac{(2 \mu_{m_{\text{CS}}} \mu_{m_{\text{FS}}} + C_1)(2 \sigma_{m_{\text{CS}}} \sigma_{m_{\text{FS}}} + C_2)}{\left( \mu_{m_{\text{CS}}}^2 + \mu_{m_{\text{FS}}}^2 + C_1 \right) \left( \sigma_{m_{\text{CS}}}^2 + \sigma_{m_{\text{FS}}}^2 + C_2 \right)},$$  \hspace{1cm} (5.3)

where $\mu_m$ and $\sigma_m$ are the mean and standard deviation of the image intensity in a local Gaussian window, and constants $C$ ($C_1 = (0.01 \max |m_{\text{FS}}|)^2$ and $C_2 = (0.03 \max |m_{\text{FS}}|)^2$) are included to avoid instabilities in the image regions where local mean or standard deviation is close to zero.
The global SSIM of the entire image is obtained by averaging the LSSIM values. SSIM = 1 indicates an ideal reconstruction.

### 5.3.5.2 Implementation of Lustig and AVDS approaches

When generating sampling schemes for all the strategies, including µCT-VDS, the scheme with the highest incoherence, as measured from the point spread function, was selected out of 1000 schemes. In total, five sampling schemes for each strategy were compared, and the average PSNR and SSIM values were calculated. Further details of Lustig and AVDS strategies, with respect to their implementation in this work, are briefly summarised below.

**Lustig approach**

To find the optimal $p$ and $r_A$ values for the polynomial distributions, sampling schemes were generated with $p$ values incrementing from $p = 2.5$ to $p = 10.5$ in increments of 2, and $r_A$ values of $r_A = 0$, $r_A = 0.1$, $r_A = 0.15$, $r_A = 0.2$, and $r_A = 0.25$ for each $p$ increment, giving 25 different polynomial sampling strategies to test for each sampling fraction; a range of $p$ and $r_A$ values similar to those used in literature were chosen. Based on the image quality metrics, $p$ and $r_A$ values for the optimised (highest PSNR and SSIM) and non-optimised (lowest PSNR and SSIM) sampling schemes were determined. Non-optimised sampling schemes were considered to study the effects of non-optimal $k$-space sampling on reconstruction quality.

**AVDS**

For AVDS, the averaged $k$-space data of the 3D simulated MRI was used as an input to design the sampling schemes. The user-adjustable parameter for $k$-space sampling was set to 6, except for the sampling fraction of 0.125, where a larger value of 8 was used due to the smaller number of sampled points.

### 5.3.5.3 Comparison of Pore Space Characteristics

Image analysis software was used to characterise the pore size distribution (PSD) and pore coordination number distribution (CND) for the 3D MRI images acquired on Ketton rock. These statistics were then benchmarked against the statistics derived from the high-resolution X-ray micro-computed tomography datasets of Ketton. Image processing was carried out using Avizto. The raw 5 µm µCT images of Ketton rock were denoised using a non-local mean filter [78] and binarized using Otsu’s algorithm [83]. The 17.6 µm and 35 µm µCT images were generated by down-sampling the 5 µm image to give a direct comparison with the acquired MRI data. The nominal resolution of the lower resolution µCT and MRI images...
was increased to 5 µm by a zero-filling interpolation method [71, 72] in the Fourier space of the image to reduce partial volume effects and to ensure that these datasets are treated in the same way as the 5 µm µCT image. The 35 µm fully-sampled MRI image was denoised using a non-local means filter; no additional denoising was applied to the 35 µm and 17.6 µm CS-MRI images since CS is intrinsically denoising. The 17.6 µm and 35 µm µCT images and all MRI datasets were binarized using the watershed-based segmentation algorithm [84] to deal with the partial volume effects. For all images, the touching (i.e., connected) pores in the pore network were separated into individual pores using the “Separate Objects” module based on watershed, distance transform (Chamfer distance) and numerical reconstruction algorithms with a contrast factor of 3. The connected pore space was obtained using the “Axis Connectivity” module. Equivalent effective pore body radii (i.e., a radius of the sphere with the same volume as a pore) and coordination numbers of the segmented pore space of all images were obtained using the “Generate Pore Network Model” module [13].

5.4 Results and Discussion

This section is presented as follows. First, the µCT-VDS approach is benchmarked against the Lustig and AVDS methods using 2D simulated MRI images of Ketton rock. Next, the benchmarking is extended to study the performance of the new approach for a range different sampling fractions and rock types. Last, the new method is implemented experimentally to acquire high-resolution MRI images of a water-saturated Ketton limestone rock at 35 µm and 17.6 µm spatial resolutions. The pore space analysis of the acquired images is also performed, and the results are benchmarked against the statistics obtained from the high-resolution µCT dataset.

5.4.1 Assessment of CS Reconstruction Quality Using the µCT-VDS Approach Based on 2D Simulated MRI Images

5.4.1.1 CS Reconstructions of Ketton Images with a k-Space Sampling Fraction of 0.25

To investigate the reconstruction quality using the µCT-VDS approach and to benchmark it against the AVDS and Lustig sampling strategies, Ketton images were first reconstructed from a fraction of k-space data points of 0.25. Figure 5.4 shows the pdfs used for µCT-VDS, optimised and non-optimised Lustig pattern generation, and the sampling patterns for the µCT-VDS, optimised Lustig, AVDS, and non-optimised Lustig strategies. The $p$ and $r_A$ values of the polynomial functions for the optimised Lustig scheme were $p = 2.5$ and $r_A = 0.2$. To illustrate the effect of the optimisation procedure, $p = 10.5$ and $r_A = 0$ were used to represent
Figure 5.4 (a) Probability density functions (pdfs) for µCT-VDS (---), optimised Lustig sampling ($p = 2.5$, $r_A = 0.2$; ----), and non-optimised Lustig sampling ($p = 10.5$, $r_A = 0$; ..., and (b) the generated sampling schemes for µCT-VDS, optimised Lustig sampling, AVDS, and non-optimised Lustig sampling for Ketton rock. The sampling patterns were generated with a k-space sampling fraction of 0.25.

Figure 5.5 (a) Compressed sensing and (b) zero-filled Fourier transform reconstructions of the simulated MRI images of Ketton rock obtained using µCT-VDS, optimised Lustig sampling, AVDS, and non-optimised Lustig sampling with a k-space sampling fraction of 0.25. The spherical grains in the Ketton rock are shown as regions of low signal intensity (black). The pore space is identified as regions of high signal intensity associated with the water within the void space between the grains.

the non-optimised Lustig scheme. It is interesting to note (Fig. 5.4a) that the shape of the pdf of the optimised Lustig scheme ($p = 2.5$ and $r_A = 0.2$) approximates well the shape of the pdf generated using the µCT-VDS approach, which suggests that µCT-VDS generates optimised or near-optimised pdfs. Figure 5.5 shows the CS reconstructions obtained using the µCT-
Table 5.1: PSNR and SSIM values of the CS images of Ketton rock reconstructed using the µCT-VDS, optimised Lustig sampling, AVDS, and non-optimised Lustig sampling strategies with a k-space sampling fraction of 0.25. The values given in the table are the average values with standard deviations from five different sampling schemes using the same pdf. The p and r_A values of the optimised and non-optimised polynomial Lustig sampling schemes were p = 2.5 and r_A = 0.2, and p = 10.5 and r_A = 0, respectively.

<table>
<thead>
<tr>
<th>Sampling scheme</th>
<th>PSNR</th>
<th>SSIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>µCT-VDS</td>
<td>24.5 ± 0.4</td>
<td>0.882 ± 0.002</td>
</tr>
<tr>
<td>Optimised Lustig</td>
<td>24.3 ± 0.6</td>
<td>0.883 ± 0.004</td>
</tr>
<tr>
<td>AVDS</td>
<td>23.8 ± 0.5</td>
<td>0.871 ± 0.005</td>
</tr>
<tr>
<td>Non-optimised Lustig</td>
<td>21.9 ± 0.5</td>
<td>0.686 ± 0.019</td>
</tr>
</tbody>
</table>

VDS, AVDS, and the Lustig approach with the optimised and non-optimised parameters and compares them to the zero-filled Fourier transform reconstructions. As can be seen in Fig. 5.5, all zero-filled Fourier transform reconstructions contain noise-like aliasing artefacts, but they are more pronounced for the images obtained using the AVDS and non-optimised sampling trajectories, likely due to less dense sampling of the central regions of k-space compared to the µCT-VDS and the optimised polynomial sampling methods. For the sampling scheme with non-optimised parameters, the intensity of the artefacts is comparable to the actual pore-space signal intensities so that it can potentially mask important pore-space information. Similar trends in image quality can be seen for the CS images, as the reconstructions obtained using the AVDS and non-optimised polynomial sampling schemes have a lower contrast than the images recovered using other two sampling schemes. These observations are also reflected by the values of the image quality metrics shown in Table 5.1. Using the new µCT-VDS method, CS images can be obtained with the same quality as the optimised Lustig sampling, since PSNR_{µCT-VDS} = 24.5 ± 0.4 and PSNR_{opt.Lustig} = 24.3 ± 0.6, and SSIM_{µCT-VDS} = 0.882 ± 0.002 and SSIM_{opt.Lustig} = 0.883 ± 0.004. Further, they perform significantly better than the AVDS and non-optimised sampling strategies. The latter gives the lowest PSNR (21.9 ± 0.5) and SSIM (0.686 ± 0.019) values highlighting the importance of choosing a suitable k-space sampling scheme to generate good quality images.

5.4.1.2 Robustness of µCT-VDS to the Sampling Fraction for Ketton Rock

To further investigate the performance of the new sampling method and to benchmark it against the AVDS and the polynomial approaches, CS reconstructions were performed at different sampling fractions. For each sampling fraction, all possible combinations of p and r_A values were tested to find the optimised and non-optimised parameter configuration; note that the
optimised parameter combination may be different for different sampling fractions. The resulting sampling schemes generated for different sampling fractions are shown in Fig. 5.6.

The average PSNR and SSIM values of the CS reconstructions obtained for the selected range of sampling fractions are shown in Fig. 5.7. As expected, it is seen that the quality of reconstructions deteriorates with decreasing sampling fraction, but, among the four datasets, the non-optimised sampling shows the largest drop in image quality, followed by AVDS which also generally gives poorer quality images compared to the μCT-VDS and optimised Lustig approaches. So, for example, the difference in image quality metrics, namely ΔPSNR and ΔSSIM, between the highest and lowest sampling fraction for μCT-VDS and non-optimised Lustig sampling was ΔPSNR = 5.1 and ΔSSIM = 0.198, and ΔPSNR = 9.5 and ΔSSIM = 0.423, respectively. It can also be seen that at larger sampling fractions, the image quality is affected less by the selection of k-space sampling points, but, when moving to smaller sampling fractions, the image quality becomes increasingly more dependent on the selection of k-space
5.4 Results and Discussion

Figure 5.7 Average (a) PSNR and (b) SSIM values of the CS reconstructions of the simulated MRI data of Ketton rock for a range of different sampling fractions using the µCT-VDS (○), optimised Lustig sampling (△), AVDS (×), and non-optimised Lustig sampling (■) strategies. Lines are shown to guide the eye.

Most importantly, Fig. 5.7 shows that across the different sampling fractions, µCT-VDS gives similar performance to the optimised Lustig sampling. This similarity in image quality may be expected given that there is close resemblance between the sampling schemes of the µCT-VDS and the optimised polynomial sampling, as is evident from Fig. 5.6. The biggest discrepancy between µCT-VDS and the optimised sampling are observed for the sampling fraction of 0.125, where, for the optimised sampling scheme as predicted by the polynomial Lustig approach, the vast majority of sampling points are located in the central region of $k$-space (see Fig. 5.6), as opposed to a more gradual decrease in sampling density in the case of µCT-VDS. However, the difference in image quality between the optimised polynomial sampling and µCT-VDS is relatively small when compared to the non-optimised polynomial sampling. Overall, these results indicate that optimal $k$-space sampling schemes can be derived from high-resolution µCT data for a range of sampling levels without need for parameter optimisation.

5.4.1.3 Bespoke Sampling for Different Rock Types

Sampling schemes for data acquisition from Estaillades limestone and Fontainebleau sandstone rocks were then generated using the new approach. The sampling schemes with a sampling fraction of 0.25, and the corresponding pdfs of the two rocks are given in Fig. 5.8 and Fig. 5.9, respectively. The Ketton data are also included for comparison. It is clearly seen that the µCT-VDS approach produces a bespoke sampling scheme for each rock type as the $k$-space energy distribution in each rock is different. For Estaillades and Fontainebleau rocks, there is
Figure 5.8 Images of Ketton limestone, Estaillades limestone, and Fontainebleau sandstone and the corresponding sampling schemes of these rocks as generated by µCT-VDS for a $k$-space sampling fraction of 0.25. The white boxes represent the region of interest for which the image quality metrics were calculated.

Figure 5.9 Comparison of the pdfs of Ketton (---), Estaillades (-- - -), and Fontainebleau (-----) rocks for a $k$-space sampling fraction of 0.25. For Estaillades and Fontainebleau, more points are sampled towards the outer regions of $k$-space compared to Ketton.

more dense sampling in the periphery of $k$-space compared to Ketton. This is consistent with Estaillades and Fontainebleau containing smaller pores than Ketton, hence more high frequency information is needed to retain the detail of the pore structure of these two rocks.
5.4 Results and Discussion

Figure 5.10 Regions of the CS-reconstructed images of (a) Estaillades and (b) Fontainebleau rocks obtained using the µCT-VDS and non-optimised Lustig strategies with a $k$-space sampling fraction of 0.25. The CS reconstructions obtained using the optimised Lustig and AVDS approaches are not shown, but they appear visually very similar to the µCT-VDS case. The fully-sampled image is also shown for comparison.

The $k$-space data of Estaillades and Fontainebleau rocks were also under-sampled and CS-reconstructed using the AVDS, optimised and non-optimised Lustig sampling strategies. For Estaillades, the $p$ and $r_A$ values of the optimised and non-optimised polynomial Lustig sampling schemes were $p = 2.5$ and $r_A = 0.1$, and $p = 10.5$ and $r_A = 0$, respectively, and for Fontainebleau, these values were $p = 2.5$ and $r_A = 0$, and $p = 10.5$ and $r_A = 0$, respectively. It is noted that $r_A$ for the optimised Lustig scheme varies from $r_A = 0$ (Fontainebleau) to $r_A = 0.2$ (Ketton) depending on the rock type used. The CS reconstructions of Estaillades and Fontainebleau using the µCT-VDS and non-optimised Lustig sampling approaches, along with the fully-sampled reconstructions of these rocks, are shown in Fig. 5.10; the images reconstructed using the optimised Lustig sampling and AVDS strategies are not shown, but are visually similar to the µCT-VDS case. It is seen that the CS reconstructions suffer from some loss of information due to under-sampling, especially in the smaller pores. In the case of Ketton rock, this was less obvious since it contains relatively large pores compared to Estaillades and Fontainebleau rocks. Higher sampling fractions (typically $> 0.3$) are required to retain
Identification of Optimal Sampling Patterns for CS-MRI in Porous Media

Table 5.2 PSNR and SSIM values of the CS images of Estaillades and Fontainebleau rocks reconstructed using the µCT-VDS, optimised Lustig sampling, AVDS, and non-optimised Lustig sampling strategies with a k-space sampling fraction of 0.25. The values given in the table are the average values with standard deviations from five different sampling schemes using the same pdf. For Estaillades, the p and r_A values of the optimised and non-optimised polynomial Lustig sampling schemes were p = 2.5 and r_A = 0.1, and p = 10.5 and r_A = 0, respectively, but for Fontainebleau, these values were p = 2.5 and r_A = 0, and p = 10.5 and r_A = 0, respectively.

<table>
<thead>
<tr>
<th>Sampling scheme</th>
<th>Estaillades</th>
<th>Fontainebleau</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSNR</td>
<td>SSIM</td>
</tr>
<tr>
<td>µCT-VDS</td>
<td>23.5 ± 0.3</td>
<td>0.732 ± 0.002</td>
</tr>
<tr>
<td>Optimised Lustig</td>
<td>23.5 ± 0.3</td>
<td>0.747 ± 0.003</td>
</tr>
<tr>
<td>AVDS</td>
<td>23.2 ± 0.2</td>
<td>0.707 ± 0.010</td>
</tr>
<tr>
<td>Non-optimised Lustig</td>
<td>22.3 ± 0.1</td>
<td>0.624 ± 0.015</td>
</tr>
</tbody>
</table>

Table 5.3 PSNR and SSIM values of the CS images of Ketton limestone, Estaillades limestone, and Fontainebleau sandstone reconstructed using µCT-VDS of the three rock types with a k-space sampling fraction of 0.25. The values given in the table are the average values with standard deviations from five different sampling schemes using the same pdf. The PSNR and SSIM values identifying the optimum sampling schemes for each rock type are highlighted in bold.

<table>
<thead>
<tr>
<th>Sampling scheme</th>
<th>Ketton</th>
<th>Estaillades</th>
<th>Fontainebleau</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSNR</td>
<td>SSIM</td>
<td>PSNR</td>
</tr>
<tr>
<td>µCT-VDS Ketton</td>
<td>24.5 ± 0.4</td>
<td>0.882 ± 0.002</td>
<td>22.9 ± 0.5</td>
</tr>
<tr>
<td>µCT-VDS Estaillades</td>
<td>23.6 ± 0.3</td>
<td>0.873 ± 0.005</td>
<td>23.5 ± 0.3</td>
</tr>
<tr>
<td>µCT-VDS Fontainebleau</td>
<td>23.6 ± 0.3</td>
<td>0.875 ± 0.006</td>
<td>22.9 ± 0.3</td>
</tr>
</tbody>
</table>

image quality for rocks which contain small pores (of diameter similar to the spatial resolution of MRI) or are highly heterogeneous. Further, it is seen that the images reconstructed using µCT-VDS seem to have better visual quality than in the case of the non-optimised polynomial sampling, where the pore space appears smoothed. The image quality metrics in Table 5.2 support these observations, as the PSNR and SSIM values of the images reconstructed using the non-optimised Lustig sampling are significantly smaller than those for other three methods. As with Ketton, µCT-VDS again produces sampling patterns which yield similar quality images to the optimised Lustig approach, as is evident from the image quality metrics. In order to further test the specificity of the µCT-VDS approach, the µCT-VDS patterns of each rock were used to reconstruct the images of the other two rock types. The results from these
reconstructions are summarised in Table 5.3, where the PSNR and SSIM values of optimal sampling schemes for each rock type are highlighted in bold. It can be seen that, overall, the quality of reconstructions is higher if the $k$-space data of a rock is under-sampled using the µCT-VDS pattern of that particular rock type, although in some cases the difference in the quality of an image reconstructed using the µCT-VDS of different rock types is relatively small. These results confirm that the µCT-VDS approach provides a bespoke sampling scheme for each rock type, which does not require parameter optimisation for its successful implementation.

5.4.2 Experimental Implementation of the µCT-VDS Approach and 3D Pore Space Analysis

5.4.2.1 MRI Acquisitions and Pore Space Characterisation of Ketton Rock at 35 µm Spatial Resolution

Typically, to assess the quality of reconstructions or images in general, objective image quality metrics, such as PSNR or SSIM, are used. However, such metrics do not reflect physically relevant characteristics of the 3D image, as has been noted previously [105]. In this case, such physically relevant characteristics are, for example, the pore space statistics of the rocks. Hence, in this work the performance of different sampling approaches was compared using physical metrics derived from digital image analysis, namely pore size distributions and coordination number distributions. As a demonstration, high-resolution MRI images of Ketton rock at 35 µm spatial resolution were acquired using the µCT-VDS approach with a $k$-space sampling fraction of 0.25. Residual bulk water surrounding the submerged plug is seen around the plug.

![Figure 5.11](image_url) 2D (a) axial (xy) slices and regions of the (b) longitudinal (zx) slices taken from the experimentally acquired fully-sampled and CS images of Ketton rock at 35 µm spatial resolution. The CS image was acquired using the µCT-VDS approach with a $k$-space sampling fraction of 0.25. Residual bulk water surrounding the submerged plug is seen around the plug.
Figure 5.12 Comparison between (a) the pdfs obtained using the simulated (—) and real (---) fully-sampled MRI data of Ketton rock and (b) the corresponding sampling schemes for a k-space sampling fraction of 0.25. A good agreement is seen between the two datasets.

rock have been acquired at 35 µm spatial resolution and processed in Avizo. For the CS-MRI acquisitions, the µCT-VDS sampling scheme was experimentally implemented and compared to the optimised \((p = 2.5; r_A = 0.2)\) and non-optimised \((p = 10.5; r_A = 0)\) Lustig sampling implementations. To benchmark the results obtained from MRI data, pore scale statistics were also derived from the much higher-resolution µCT data acquired for the Ketton rock.

2D xy- and zx-slices taken from the acquired 3D fully-sampled and CS-MRI (µCT-VDS) images of Ketton rock are shown in Fig. 5.11; it is seen that CS in combination with µCT-VDS is able to efficiently recover the pore-scale information of the Ketton rock, as the CS-MRI image slices are visually very similar to the fully-sampled image slices even though only a fraction of 0.25 of k-space data points has been sampled. In addition, because now a real fully-sampled MRI dataset is available, a pdf and the corresponding k-space sampling scheme can be generated from this dataset in a similar way to the proposed approach. The pdfs and the corresponding sampling schemes (k-space sampling fraction of 0.25) obtained from the real and µCT-derived simulated MRI data are shown in Fig. 5.12. As can be seen in Fig. 5.12, the pdfs and k-space sampling schemes are very similar, indicating that the simulated MRI data represent real MRI data well despite potential phase errors and NMR relaxation effects. This agreement might depend on \(T_2\) and \(T_2^*\) values of the rock under study. To further assess the quality of reconstructions, the pore space statistics of the MRI images will be considered next, along with those calculated from the higher-resolution µCT images of Ketton rock.

For the pore space analysis, a 3D volume of the connected pore space of approximately 8.9 mm \(\times\) 2.6 mm \(\times\) 2.6 mm was first extracted from each image and then segmented, separated into individual pores, and analysed. Three of these images, namely the 5 µm µCT image, the 35 µm fully-sampled MRI image, and the 35 µm CS-MRI image acquired using the µCT-
5.4 Results and Discussion

Figure 5.13 Segmented and labelled connected pore networks of Ketton rock representing the (a) 5 µm spatial resolution μCT image, (b) 35 µm fully-sampled MRI image, and (c) 35 µm CS-MRI image acquired using μCT-VDS. Different colours identify individual pores of the pore space.

Figure 5.14 PSDs of the μCT and MRI images of Ketton rock. (a) The 35 µm μCT data are compared to the 5 µm μCT data; (b) the μCT-VDS CS-MRI data are compared to the 35 µm fully-sampled (FS) MRI and 5 µm μCT data; (c) a comparison between the PSDs obtained from the three sampling schemes is shown, i.e., μCT-VDS, optimised Lustig sampling, and non-optimised Lustig sampling. All CS-MRI images were acquired with a k-space sampling fraction of 0.25.

VDS approach, are shown in Fig. 5.13. The PSDs of the connected pore space of MRI and μCT images are shown in Fig. 5.14. When comparing the PSDs of the 5 µm and 35 µm
Table 5.4 Apparent porosity of the connected pore networks extracted from the µCT and MRI images of Ketton rock.

<table>
<thead>
<tr>
<th>Image</th>
<th>Apparent porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>µCT 5 µm</td>
<td>14.1</td>
</tr>
<tr>
<td>µCT 35 µm</td>
<td>12.4</td>
</tr>
<tr>
<td>MRI fully-sampled</td>
<td>12.9</td>
</tr>
<tr>
<td>MRI µCT-VDS</td>
<td>12.7</td>
</tr>
<tr>
<td>MRI optimised Lustig</td>
<td>12.8</td>
</tr>
<tr>
<td>MRI non-optimised Lustig</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Figure 5.15 CNDs of the µCT and MRI images of Ketton rock. (a) The 35 µm µCT data are compared to the 5 µm µCT data; (b) the µCT-VDS CS-MRI data are compared to the 35 µm fully-sampled (FS) MRI and 5 µm µCT data; (c) a comparison between the CNDs obtained from the three sampling schemes is shown, i.e., µCT-VDS, optimised Lustig sampling, and non-optimised Lustig sampling. All CS-MRI images were acquired with a k-space sampling fraction of 0.25.

µCT data in Fig. 5.14a, it can be seen that the structural information of the pore network of Ketton rock is accurately captured at 35 µm resolution. Figure 5.14b shows that µCT-VDS produces very similar results to the fully-sampled MRI and the 5 µm µCT images, thus again demonstrating that the new sampling strategy in combination with CS yields accurate pore space reconstructions. Regarding the performance of the Lustig sampling strategies, it is seen in Fig. 5.14c that the PSD of the non-optimised Lustig sampling shows significant deviation from the PSDs of the optimised Lustig sampling and µCT-VDS strategies for pore radii < 160 µm. The apparent porosity of the images obtained using the non-optimised sampling is also approximately two percentage points lower than in the case of the optimised sampling methods (see Table 5.4), indicating that non-optimised sampling does not efficiently capture pore space information compared to optimised k-space sampling strategies.
Figure 5.15 shows the results of the CND analysis for the Ketton sample. In Fig. 5.15a, it is seen that that the pore space identified in the 35 µm µCT image is less coordinated than that of the 5 µm µCT image. Similar to the 35 µm µCT case, Fig. 5.15b shows that the pore space of the fully-sampled MRI image is less skewed to high coordination numbers than that of the 5 µm µCT image. Given the much better agreement between the PSDs obtained from the same datasets, the reduction in the population of highly connected pores in the 35 µm MRI data is most likely associated with the existence of pore necks below the resolution of the data. In addition, the enhanced decay of transverse magnetisation in the narrowest parts of the rock (i.e., pore necks) can also contribute to the observed reduction of pore connectivity in the 35 µm MRI data. As with the PSDs, the CNDs of the images acquired using µCT-VDS and the optimised Lustig sampling are very similar (Fig. 5.15c), but the CND of the image obtained using the non-optimal Lustig sampling exhibits a shift to lower coordination numbers than the CNDs of optimally-sampled CS images, and hence has poorer agreement with the 5 µm µCT dataset.

5.4.2.2 MRI Acquisition and Pore Space Characterisation of Ketton Rock at 17.6 µm Spatial Resolution

One advantage of the µCT-VDS approach is that it can produce sampling schemes for MRI acquisitions at resolutions for which the fully-sampled MRI data would have taken prohibitively long to acquire. In this section, the pore space analysis is presented for a CS-MRI image of Ketton rock acquired at 17.6 µm resolution. The acquisition time of this image was \( \sim 3.3 \) days, meaning the acquisition time of a fully-sampled MRI image at the same resolution and SNR would take more than 13 days, which is not practical and is susceptible to various sources of experimental instability.

Figure 5.16 shows the extracted PSD and CND of the 17.6 µm CS-MRI image of Ketton rock; the PSDs and CNDs of the 5 µm and 17.6 µm µCT, and 35 µm fully-sampled MRI and CS-MRI (µCT-VDS) images are also included for comparison. As can be seen in Fig. 5.16a, there is a good agreement between the PSDs of the 17.6 µm µCT and MRI images and the PSD of the 5 µm µCT dataset. No significant improvement in the PSD relative to the 5 µm µCT data is seen when comparing the PSDs of the 35 µm MRI and 17.6 µm MRI datasets (Fig. 5.16b), as the 35 µm MRI images already give PSDs that are very similar to the 5 µm µCT PSD. Figure 5.16c indicates that the pore network of the 17.6 µm MRI image is somewhat more poorly connected than those of the 5 µm and 17.6 µm µCT images; however, it is better connected than the pore space of the 35 µm MRI images (Fig. 5.16d) and is tending towards the results of the analysis of the µCT images. This observation is also supported by the mean coordination numbers \( \mu_{CN} \) of the pore spaces as the \( \mu_{CN} \) of the 17.6 µm CS-MRI image
Figure 5.16 Pore space characteristics of the 17.6 µm CS-MRI (µCT-VDS) image of Ketton rock. (a, c) PSD and CND of the 17.6 µm CS-MRI image compared to the 17.6 µm µCT and 5 µm µCT data. (b, d) PSD and CND of the 17.6 µm CS-MRI image compared to the 35 µm CS-MRI (µCT-VDS), 35 µm fully-sampled MRI (FS-MRI), and 5 µm µCT data. All CS-MRI images were acquired with a \( k \)-space sampling fraction of 0.25.

\( \mu_{CN} = 3.8 \) is greater than the \( \mu_{CN} \) of the 35 µm fully-sampled MRI (\( \mu_{CN} = 3.4 \)) and 35 µm CS-MRI (\( \mu_{CN} = 3.0 \)) datasets; the \( \mu_{CN} \) of the 5 µm µCT reference image is \( \mu_{CN} = 5.5 \).

5.5 Conclusions

In this chapter, a novel \( k \)-space sampling method for high-resolution MRI acquisitions of rocks, referred to as µCT-based variable density sampling (µCT-VDS), has been demonstrated. This method exploits the \( k \)-space energy distribution derived from high-resolution µCT images.
of rocks to produce optimal $k$-space sampling patterns without the need for any parameter optimisation.

To test the performance of the µCT-VDS methodology, it was benchmarked against other Cartesian sampling strategies using µCT-derived simulated MRI images, and image quality assessment using PSNR and SSIM metrics. It was shown that for Ketton rock at 35 µm spatial resolution, µCT-VDS gives better quality reconstructions than AVDS and comparable results to the optimised Lustig sampling for a range of different sampling fractions. Given that the Lustig polynomial approach contains two adjustable parameters, $p$ and $r_A$, and requires a ground-truth fully-sampled reference image, the new method offers substantial advantages in generating optimal $k$-space sampling schemes. µCT-VDS was also applied to Estaillades limestone and Fontainebleau sandstone rocks. For each rock type, the new method produced a bespoke sampling scheme according to the morphology of the rock, e.g., in the case of Fontainebleau, which contains small pores, the high-frequency regions of $k$-space are sampled more than in the case of Ketton.

The µCT-VDS method was implemented to acquire MRI images of Ketton rock at both 35 µm and 17.6 µm isotropic resolution. The 35 µm image was analysed to obtain both the PSD and CND characterising the pore space, with the aim of learning how sampling strategy influences the accuracy of pore space statistics. This analysis confirmed that the images acquired using µCT-VDS and the optimised Lustig sampling give statistically more similar results to the 5 µm µCT image than the non-optimised sampling, consistent with the analysis using numerical image quality metrics. The acquisition and analysis of the 17.6 µm CS-MRI image highlighted that the µCT-VDS approach produces sampling patterns that yield accurate pore space reconstructions at resolutions which would be difficult, if not impossible, to achieve using fully-sampled MRI acquisitions.

At the high spatial resolutions that have become accessible using CS-MRI using the novel µCT-VDS approach, it has been shown that the pore scale statistics approach those derived from high-resolution µCT images. In the following chapters, the µCT-VDS approach will be used to speed up other multi-dimensional MRI acquisitions relevant to DR applications, such as spatially-resolved propagators and fluid velocity maps. Whilst the method has been demonstrated in application to MRI microscopy of porous rocks, the approach is entirely generic and can be used to achieve isotropic spatial resolution (10–20 µm) 3D magnetic resonance images of any system amenable to study by conventional MRI methods.
Chapter 6

Characterising Pore-Scale Structure-Flow Correlations in Rocks Using MRI

6.1 Introduction

Imaging techniques that can be used to visualise fluid transport phenomena in the pore space of porous materials are of significant interest in many industries, including the oil and gas industry. In the context of oil and gas industry, understanding the physics of fluid flow and transport phenomena in the pore space of porous sedimentary rocks plays a key role in tuning and deployment of technologies such as EOR and carbon capture and storage (CCS). As mentioned earlier in Chapter 1, DR technology aims to augment conventional characterisation of sedimentary rocks, which relies on measurements of macroscopic petrophysical properties (e.g., porosity, permeability) of a whole core plug sample. Although these bulk properties are critical to any petrophysical analysis, they provide little insight into the degree of spatial variation of these properties. However, heterogeneity in petrophysical properties is a key factor underlying the efficiency of hydrocarbon recovery and CCS processes. X-ray µCT is currently the primary tool for obtaining structural images of the rock matrix, and such images are routinely acquired on the micrometre scale. It remains necessary, however, to initialize, validate, and calibrate DR simulations on the basis of laboratory measurements that also capture the spatial variation in petrophysical properties within the rock.

In this chapter it is demonstrated how a toolbox of MRI flow methods are developed and utilised to obtain quantitative, 3D spatially-resolved flow information about fluids in rocks at a pore-scale resolution. Chapter 5 showed that using a combination of sensitive MRI equipment, rapid and under-sampled MRI pulse sequences, and CS techniques, it is possible to acquire 3D MRI images of the Ketton carbonate rock at a spatial resolution of 17.6 µm, which is at least
an order of magnitude higher than the resolution of conventional MRI, and is a resolution at which pore-scale features can be clearly discerned. In this work, it is demonstrated how this approach has been extended to include quantitative image contrast and hence the ability to extract structure-flow correlations at the pore scale. More specifically, fluid displacements were encoded into the images under single-phase flow conditions in a Ketton limestone rock core plug with a diameter of 4 mm. Two types of displacement experiments were performed, namely velocity mapping and spatially-resolved propagators. Recall that velocity mapping gives a single, average velocity for each of the voxels within an image, and are generally much quicker to measure and can therefore be performed at higher spatial resolution more easily compared to spatially-resolved propagator measurements. On the other hand, spatially-resolved propagators give a distribution of fluid displacements over a given observation time for each voxel within the image and provide information about molecular self-diffusion and local, time-dependent flow dispersion within the pores.

This chapter is organised as follows. First, in Section 6.1.1, some background of single-phase flow in porous media is presented, focusing on the hydrodynamics in experimental model systems (bead packs) and rocks. This is followed by a description of the pulse sequences and under-sampling strategies used for pore-scale flow MRI (Section 6.2). The experimental details of the under-sampled 3D velocity mapping and 3D spatially-resolved propagator measurements are then given in Section 6.3. In the results section (Section 6.4), the acquired 3D velocity and spatially-resolved propagator data of Ketton rock are presented. First, the high-resolution 3D velocity maps are analysed to extract transport-structure relationships in the rock. These velocity maps were acquired at 35 µm spatial resolution, which, to the best of my knowledge, is the highest spatial resolution reported for MRI velocity data in porous materials. Second, 3D spatially-resolved propagators that were acquired at 94 µm isotropic spatial resolution are used to examine flow dispersion within the rock by analysing each of the 331,776 local propagators as a function of observation time. Furthermore, it is demonstrated how through co-registration of the resulting velocity and spatially-resolved propagator data with µCT images, which have an order-of-magnitude higher spatial resolution, the details of the flow distribution can be correlated with the microstructural features of the rock.

6.1.1 Single-Phase Flow in Porous Media

6.1.1.1 Background

Fluid flow in porous media is a complex phenomenon that involves many physical processes and has many different variables. Broadly speaking, flow fields in porous media can be categorised into three types [44] – laminar flow, turbulent flow, and dispersive flow (see Fig. 6.1). A laminar
Figure 6.1 Flow field types in porous media: (a) steady state laminar flow, (b) turbulent flow, and (c) dispersive flow, in which the particles start together on the same streamline but with time follow different paths.

Flow refers to a well-ordered flow where the fluid particles move in smooth layers (laminae) and no mixing occurs between adjacent layers. In laminar flow, the flow field is intrinsically at steady state (i.e., fluid flow properties do not change over time). By contrast, a turbulent flow is a type of flow in which fluid flow field exhibits irregular, chaotic fluctuations, thus enhancing fluid mixing. In dispersive flow, even though the fluid flow may be at steady state, the initially adjacent particles that belong to the same streamline or occupy the same location become separated during flow, as the particles follow very different trajectories. This type of flow is especially characteristic for fluid particles moving through porous media, and fluid spreading and mixing that results from dispersion has immense practical significance in many industrial processes, including hydrocarbon recovery. Dispersion is a complex phenomenon which is intrinsically driven by a combination of stochastic processes including advective velocity gradients, molecular diffusion, and boundary layer effects [44]. Note that dispersion is similar to self-diffusion in the sense that they both are governed by stochastic processes. From the NMR perspective, dispersive flow is a complex but interesting process to investigate because it enables many of the length and time scales that are imparted by dynamical flow processes and structural features of porous media to be studied. The fluid mixing processes during a single-phase flow through a rock, studied using spatially-resolved propagator measurements, will be discussed in more detail in Section 6.4.2 of this chapter.

The underlying mathematics that is used to describe flow in porous media is now briefly discussed, along with some important concepts pertinent to this chapter. The governing equations of flow phenomena of a viscous fluid are based on fundamental classical principles,
namely conservation of momentum and mass. For an incompressible Newtonian fluid of a fixed (dynamic) viscosity, $\mu_f$, the momentum equations are given by the Navier-Stokes equations as [122]:

$$\mu_f \nabla^2 \mathbf{v} = \rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) + \nabla p_f - \rho g, \quad (6.1)$$

where $\mathbf{v}$ is the vector of velocity field, $\rho$ is the (fluid) mass density, $p_f$ is the fluid pressure, and $g$ is the acceleration due to gravity. In the Navier-Stokes equation, the fluid flow is driven by the pressure gradient and gravity. The term involving viscosity represents the viscous force that resists flow. For a complete description, the conservation of mass is given as: $\nabla \cdot \mathbf{v} = 0$. Combining Eq. 6.1, conservation of mass, surface energy conservation, and boundary conditions enables fluid configuration and fluid movement in a porous medium to be described [122].

Another fundamental relationship that is used to describe fluid motion in porous media is Darcy’s law. The law was formulated by Henry Darcy in 1856 as:

$$q_d = -\frac{K_p}{\mu_f} (\nabla p_f - \rho g), \quad (6.2)$$

where $q_d$ is the Darcy velocity, i.e., the volume of fluid flowing per unit time through a unit area of the porous medium, and $K_p$ is permeability. Permeability is defined as the porous material’s ability to transmit fluids and is an intrinsic property of the pore structure of the material. Note, however, that Darcy’s law is only valid for laminar flow in a porous medium.

It is useful to introduce some other important concepts related to porous media in the context of this chapter, and those include representative elementary volume (REV), Reynolds number ($Re$), and Péclet number ($Pe$). Representative elementary volume or REV is an important characteristic of porous materials and is defined as the smallest volume element from which the material’s macroscopic properties can be determined [44]. REV can be calculated for many material properties, such as porosity, pore size distribution, or certain flow properties. The REV analysis is typically carried out by measuring a specific property for increasingly larger volume elements extracted from the sample. Then a volume element beyond which the fluctuations of the property being measured are damped for further increase in the volume is chosen as the REV [44]. The Reynolds number ($Re$) is a dimensionless quantity that measures the ratio of advective inertial forces to viscous forces. For flow in porous media, it can be defined as [122]:
where $l_c$ is the characteristic length scale of the system, $v$ is the typical flow velocity, and $v_f$ is the kinematic viscosity of fluid (i.e., $v_f = \frac{\mu_f}{\rho}$). Note that there is no single way to define the length scale $l_c$ since most rocks have very complex void structures. Traditionally, for a granular porous material, such as sandstones, Ketton limestone rock, and bead packs, the mean grain diameter can be used as $l_c$, however, for more complex rock geometries, such as Estaillades limestone, the pore diameter of the rock is a more representative descriptor of $l_c$. The Reynolds number is used to predict different flow regimes. In the cases where $Re \ll 1$, i.e., inertial effects are small compared to viscous forces, the fluid will exhibit so called Stokes flow (also known as creeping flow), which is a type of laminar flow. If the Reynolds number is increased, for example, by increasing the fluid flow rate (advective inertial forces increased), such that $Re \gg 1$, the fluid can transition from laminar to turbulent flow. The Péclet number is another dimensionless number that can be used to describe the flow dynamics. It is defined as a ratio of advection to diffusion. It is related to $Re$ via:

$$Pe = Re \frac{v_f}{D}.$$  

When $Pe \gg 1$ the flow processes are dominated by advection, but when $Pe \ll 1$ diffusion dominates. $Pe$ is also useful in understanding dispersion processes. According to Koch and Brady [123], who carried out theoretical analysis for flow in a packed bed of spheres, three different physical dispersion processes can be distinguished that scale differently with $Pe$. The three dispersion processes are: (1) mechanical dispersion, which results from the stochastic variations of the flow velocity field due to the geometry of the pore space and scales with $Pe$; (2) Taylor dispersion [124], which arises from molecular diffusion of fluid molecules across streamlines and scales with $Pe^2$; and (3) holdup dispersion, which is caused by boundary layer effects and the presence of dead-end pores and stagnant regions and scales with $Pe \log(Re)$. The Péclet number will be used in the discussion of spatially-resolved propagator measurements.

### 6.1.1.2 Single-Phase Flow in Bead Packs

Bead packs are not only an interesting system to study from the chemical engineering perspective, to better understand chemical reaction processes in packed bed reactors, but are also widely used as model systems to represent porous media, such as rocks. The advantage of
packed beds is that the pore size of the system can be tuned so that it matches the resolution of the imaging technique that is used to probe the system. This then enables hydrodynamics and flow-structure correlations in porous media to be investigated at the pore scale.

A variety of experimental techniques have been used to study bead packs [125–130]. Among these, several optical techniques for measuring transport information in porous media have been reported [126, 127, 129], such as particle image displacement velocimetry. The main disadvantage of optical techniques is that they can only be used to study transparent systems, thus limiting the types of porous media and fluids that can be studied.

In contrast to the optical measurement techniques, MRI can detect signal from optically opaque systems, thus allowing direct flow and transport measurements to be made in these systems. The idea of using MR for flow measurements was probably first reported in 1950 by Suryan [131], who observed that for fluid flowing through an r.f. coil the NMR signal intensity increases, as partially saturated spins are replaced by unsaturated flowing spins. A decade later, the same effect was utilised by Singer [132] and Bowman and Kudracev [133] who developed quantitative MR techniques for measuring blood flow. These and other ideas and techniques [134–136] have laid the foundation for flow MRI as we know it today, namely a technique that is capable of measuring fluid flow rates from microns per second up to meters per second in a time scale starting from a few milliseconds [18]. One of the early reviews on MR in flow is written by Singer [137]. More recent reviews on flow MR in porous media can be found elsewhere [18, 30, 138].

Bead packs have been extensively studied using non-spatially resolved [128, 139–141] and spatially-resolved [29, 140–145] flow MR techniques; here the focus will be on the latter. One of the early, relatively high-resolution MR flow studies in bead packs was carried out by Rajanayagam et al. [142] who used a 2D spin echo imaging sequence to obtain quantitative flow and diffusion maps in bead packs of various sizes (down to 1 mm in diameter) at 114 µm spatial resolution. They demonstrated that the flow rates determined from the acquired images are in good quantitative agreement with the flow rates measured using direct methods (< 10 % difference), and that the main source of error in spatially-resolved velocity data is partial volume effects. Kutsovsky et al. [140] acquired 2D velocity images (at 170 µm spatial resolution) in a packing of 6-mm-diameter glass beads at various Re (Re ~ 15–45). They showed that the axial velocity profiles in the pores of the 6 mm bead pack are roughly parabolic at all Re and observed flow in a direction opposite to that of the superficial flow velocity – a phenomenon known as backflow, which will be discussed in greater detail later in the chapter. Sederman et al. [143, 144] published two related papers in which they studied structure-flow correlations in packed beds composed of 5-mm-diameter spherical beads using velocity mapping. The flow in the bead pack was imaged using a 2D spin echo velocity imaging sequence at 195 µm spatial
resolution. In order to obtain structural information, a 3D structural image of the bead pack was also acquired using a spin-warp imaging sequence, and its pore space was partitioned into individual pores using a variant of the morphological thinning algorithm [146]. They observed that the flow in the bead pack is highly heterogeneous with 40% of the flow being carried by approximately 10% of the pores and that the majority of pores locally approximate laminar flow conditions (flow rate = 2 ml s$^{-1}$; diameter of the bead pack = 4 cm). Structure-flow correlations were found between the flow velocity within a pore and the local Reynolds number ($Re_l$) and coordination number associated with that pore [144]; it was shown that the flow velocity within pores with $Re_l = 3–7$ decreases with increasing coordination number of these pores (this range of $Re_l$ lay in the upper portion of the pore $Re_l$ in the bead pack studied). The local $Re$ analysis was introduced to better understand pore-scale flow regimes within the bead pack. This work was further extended by Johns et al. [145] who used velocity mapping to study structure-flow relationships in the same packed bed comprised of 5-mm-diameter spherical beads for two Newtonian fluids of different viscosities (water and glucose solution) over a range of $Re$ ($Re = 0.84–14.52$). The main conclusions from this work were that the flow through an individual pore scales linearly with the global volumetric flow rate through the bead pack, except for pores that contain near-stagnant fluid, and that locally a transition from creeping to inertial-forces-dominated flow regime occurs at a local $Re$ of $\sim 30$.

Displacement propagator measurements have been widely used to study self-diffusion and dispersion processes in bead packs [29, 128, 139–141, 147], however most of them are spatially-unresolved. Some of the works relevant to this thesis are now briefly discussed. Lebon et al. [139] used PFG spin echo and PFG stimulated echo techniques to acquire spatially-unresolved displacement propagators to study the effects of diffusion and dispersion in a packing of 0.8-mm-diameter glass spheres. They observed that at displacements on the order of the pore size the overall shape of the displacement distributions becomes strongly distorted and a secondary peak that represents the fastest flowing particles is formed. The distortion of the displacement distributions was explained by the fact that at larger length scales (i.e., displacement distances) the displacement of the fluid molecules is not negligible relative to the pore and grain sizes, in which case the classical (mechanical) dispersion process can take place as the fluid particles can now explore a sufficiently large number of pores. Manz et al. [141] studied flow and dispersion in random packings of glass spheres (with sphere diameters $\leq 1$ mm) using LBM simulations, velocity mapping, and spatially-unresolved propagator measurements. It was demonstrated using the experimental and simulated displacement propagators that mechanical dispersion dominates the dispersion of the flow over the range of the normalised length scales ($\frac{\Delta l}{\epsilon}$) studied. However, at length scales much smaller than the individual pore (i.e., displacements smaller than the pore), Taylor dispersion governs the dispersion in the pores,
but, at the largest length scales (i.e., at displacements much greater than the individual pore), holdup dispersion can be significant. In addition, they observed that at large displacements the experimentally acquired propagators tend towards a Gaussian shape. Regarding spatially-resolved propagator measurements, de Kort et al. [29] developed an under-sampled APGSTE-RARE sequence to acquire 2D spatially-resolved displacement propagators at 320 µm spatial resolution. The approach was demonstrated for a single-phase flow through a packed bed of hollow cylinders. Via optimisation of under-sampling schemes and CS reconstruction parameters, good quality spatially-resolved propagators were obtained by sampling only 6.25% of all q,k-space data points. Different local propagators were identified, and their shapes were correlated with the structural features of the packed bed. This work was later extended to develop a CS-RARE approach for the acquisition of 3D spatially-resolved propagators [107].

6.1.1.3 Single-Phase Flow in Rocks

Although packed beds are often used as simple model systems for rocks to study the fundamentals of flow processes or to validate new MRI experiments, the ultimate goal is to use these techniques and the knowledge gained on real, more complex porous systems. Both spatially-unresolved [148–150] and spatially-resolved [29, 107, 148, 151, 152] MR flow measurements in rocks have been reported. Shukla et al. [152] studied water flow through a Bentheimer sandstone using spatially-resolved PFG techniques (APGSTE-RARE) at 1 mm spatial resolution and demonstrated that the accuracy of phase-shift velocity measurements (i.e., velocity mapping) in the rock can be affected by the symmetry of displacement distribution within each voxel. It was shown that if the propagator in a given voxel is asymmetric, which could arise from coupling between flowing molecules and molecules located in stagnant zones, the accuracy of the resulting average velocity measurement can be compromised, as the phase shift induced by the velocity-encoding gradient is no longer proportional to the flow velocity. They concluded that by keeping the phase shift small and ensuring high SNR of the images, more accurate velocity measurements can be achieved. Similar observations for the accuracy of velocity maps to increase with the symmetry of the propagator were also made elsewhere [148], where flow in a Bentheimer sandstone sample was studied using velocity mapping (at 1 mm spatial resolution) and spatially-unresolved propagator measurements. In another study, Romanenko et al. [151] used APGSTE in combination with the SPRITE pulse sequence to acquire 3D quantitative velocity maps at 1 mm spatial resolution for single-phase flow in three different rock types (two sandstones and one carbonate). Although the voxel size was larger than the pore size of the rocks studied, macroscopic variations in porosity and flow fields were observed. In all three rock samples, regions of stagnant or near-stagnant fluid were identified. A correlation between local porosity and flow velocity was also noted; it was shown that water tends to
flow through regions of higher porosity and across zones of lower porosity. In more recent works, de Kort et al. used under-sampled APGSTE-RARE experiments to acquire quantitative 2D [29] and 3D [107] spatially-resolved displacement propagators in heterogeneous carbonate rock core plugs at 352 µm and 1 mm spatial resolutions, respectively. In the case of the 3D measurements [107], 3D spatially-resolved propagators with 134,000 voxels, each containing a local propagator, were acquired and reconstructed using only 12.5 % of $q_k$-space data points, thus reducing the acquisition time by almost an order of magnitude relative to the fully-sampled acquisition. Local, per voxel propagators with different flow behaviours, such as near-stagnant fluid and significant flow, were identified. The technical aspects of this work, namely the design of pulse sequences, under-sampling schemes, and details of CS reconstructions, formed the basis for the development of spatially-resolved propagator techniques in this chapter.

6.2 Pore-Scale Flow MRI

It was shown in Chapter 5 that by combining rapid MRI pulse sequences with $k$-space under-sampling and subsequent compressed sensing reconstructions, 3D images with isotropic resolutions up to 17.6 µm can be acquired. This was accomplished by using the novel µCT-based (µCT-VDS) under-sampling strategy, which is informed by high-resolution µCT images of the rocks, implemented on a high-field (300 MHz) magnet with strong gradients of a maximum strength of 2.9 T m$^{-1}$. Using this under-sampling strategy, the technique was extended to acquire 3D velocity maps and spatially-resolved propagators to study flow-structure correlations in a Ketton limestone rock at a pore-scale resolution.

6.2.1 Pulse Sequences for Flow MRI

As previously mentioned, flow MRI is an integration of a pulsed field gradient nuclear magnetic resonance (PFG NMR) experiment, which is used to quantify fluid displacements, with an MRI experiment, which spatially-resolves those displacements. Two different spatially-resolved flow MRI measurement techniques were used in this work, namely velocity mapping and spatially-resolved propagators. In velocity mapping, a single, average velocity is spatially-resolved for each of the voxels within an image. In spatially-resolved propagator measurements, local displacement propagators are spatially-resolved for each voxel within an image. It is helpful to recall at this point that displacement propagators are probability distributions of molecular displacements, $\bar{P}(R, \Delta)$, where $\bar{P}$ is the probability that a spin moves over a dynamic displacement, $R = r' - r$, in an observation time, $\Delta$ (typically in the range between a few milliseconds up to a few seconds). By spatially-resolving the propagator, information about
local, time-dependent flow dispersion, which arises due to molecular self-diffusion of fluid molecules across streamlines, can be obtained, as well as measurements of flow velocity. The average velocity (i.e., a velocity map) can also be extracted from the spatially-resolved propagators by calculating the mean of each of the local propagators and dividing it by $\Delta$ [29]. It has been shown that this method can provide a more accurate estimate of local velocity than the velocity mapping measurements in case the shape of the underlying propagator is not symmetric [152, 153]. However, because propagator measurements are slower than velocity mapping experiments, the propagator-based approach for measuring per-voxel velocities is mainly beneficial at lower spatial resolutions and longer observation times, $\Delta$. Under these conditions, more per-voxel velocity dispersion is expected, leading to strong asymmetry in the propagator (see Fig. 6.10).

X-ray µCT has also been used to study displacement processes in rocks [6, 8, 15]. Measurements are achieved by tracking the movement of a fluid interface between two different fluid phases. In contrast, flow MRI offers a direct and robust measurement of a flow velocity within a fluid phase and is a well-established tool for studying flow phenomena in porous media. In this chapter, only single-phase flow MRI experiments will be shown, but two-phase (oil-water) sensitivity is straightforward to implement, without a need for doping of the fluids to enhance image contrast, as will be demonstrated in Chapter 8.

From the experimental perspective, velocity mapping and acquisition of a spatially-resolved propagator are based on similar NMR experiments – data are acquired by combination of a displacement-encoding PFG experiment to encode $q$-space (i.e., displacements), and an imaging experiment to acquire $k$-space (i.e., an image), though there are likely to be different requirements for the sequence chosen. For example, velocity imaging experiments usually require a short observation time, $\Delta$, such that there is no acceleration of the fluid over $\Delta$ and therefore an accurate instantaneous velocity can be calculated. In contrast, spatially-resolved propagator measurements may use a range of larger $\Delta$ to investigate the effects of self-diffusion and fluid mixing over a longer time scale.

A schematic of the velocity-encoded MRI pulse sequence used to acquire velocity maps is shown in Fig. 6.2 – it combines a pulsed gradient spin echo (PGSE) sequence that is used to encode for velocities, with a RARE imaging sequence that is used to spatially-encode the measured velocities. The RARE sequence was selected, as it is well-suited for CS applications and imaging fluid-saturated porous rocks, as was described in Chapter 4. Velocity-encoded MRI experiments are typically based on either a spin echo or a stimulated echo velocity-encoded preparation sequence. The reason for selecting the spin-echo-based PFG sequence for the acquisition of high-resolution velocity maps in this work is twofold. Firstly, the stimulated-echo-based approaches inherently suffer from a 50 % signal loss compared to the spin-echo-based
Figure 6.2 Schematic of the pulse sequence used to acquire high-resolution velocity maps. It combines a pulsed gradient spin echo (PGSE) sequence with a rapid acquisition with relaxation enhancement (RARE) imaging sequence used for velocity and spatial encoding, respectively. The velocity encoding is achieved by a pair of unipolar gradients of strength $g$ and duration $\delta$, separated by an observation time, $\Delta$. The spatial encoding is achieved using the frequency-encoding gradient, $G_z$, and the phase-encoding gradients, $G_x$ and $G_y$.

 approaches [44]. A high SNR is a prerequisite for accurate velocity maps since the error in measured velocities is inversely proportional to the SNR of the images [148] and sufficient SNR needs be retained on a per voxel basis to make an accurate measurement. Second, in the current application of velocity imaging, short echo train lengths ($< T_2$ of the sample) and observations times (a few milliseconds) were used, hence the signal loss due to magnetic susceptibility induced internal gradients effects that are present in porous media are minimised. In addition, carbonate rocks generally exhibit relatively weak internal gradients compared to, for example, sandstone rocks [21]. The stimulated-echo-based approaches are preferred in the measurements with longer observation times (a few hundred milliseconds), relative to $T_2$ of the sample. This is generally the case when using spatially-resolved propagator measurements in rocks. Spin-echo-based PFG imaging sequences have successfully been used in the past to acquire accurate velocity maps in porous media [28, 154, 155]. Holland et al. [28] used a spin echo velocity imaging sequence, wherein each echo was acquired per signal excitation, in combination with compressed sensing, to acquire quantitative 2D velocity maps of liquid and gas flow through a packed bed of spherical glass beads at spatial resolutions of 178 µm and 230 µm, respectively. To speed up the acquisition of velocity maps, Huang et al. [154] combined a spin-echo-based velocity encoding module with a (fully-sampled) RARE sequence to image water flow through porous deep bed filters at an isotropic spatial resolution of 160 µm. In this work, both the RARE sequence and a compressed sensing approach are exploited to speed up acquisition and enable 3D velocity mapping at 35 µm spatial resolution.
Figure 6.3 Schematic of the APGSTE-RARE pulse sequence used to acquire 3D spatially-resolved propagators. It consists of a 13-interval APGSTE sequence and a RARE imaging sequence. The displacement encoding was achieved by gradients $g$ which can be applied in any of the three orthogonal directions ($z$, $x$, or $y$). In this work, the displacement-encoding gradient was applied parallel to the superficial flow direction ($z$). The spatial encoding was achieved by the frequency-encoding gradient, $G_z$, and phase-encoding gradients, $G_{x,y}$.

A schematic of the pulse sequence used to acquire 3D spatially-resolved propagators is shown in Fig. 6.3. This sequence has been described in detail in [107], where the acquisition of 3D spatially-resolved propagators of flow in rocks was demonstrated at a much coarser spatial resolution than is shown in this work. This sequence combines an APGSTE [66] sequence that is used to encode for displacements, with the RARE imaging sequence used in the velocity imaging sequence. A stimulated echo sequence is needed for the longer observation times used for the propagator measurements. The APGSTE, or Cotts 13-interval, sequence has been selected as it has been shown to minimise the signal loss due to motion in background field gradients and is well suited to measurement of flow in porous media.

6.2.2 k-Space Data Under-Sampling in Flow MRI

In order to further speed up the acquisition of MRI flow data, the PGSE-RARE and APGSTE-RARE pulse sequences were combined with k-space data under-sampling approaches.

Sampling patterns for the acquisition of velocity maps were generated using the µCT-VDS strategy described in the previous chapter. This strategy relies on the observation that structurally similar images have a similar distribution of the magnitude of k-space energy values. Since in an under-sampled velocity map it is important to accurately preserve the spatial distribution of the encoded velocities, the use of this approach is justified. Furthermore, it was verified that the magnitude data of k-space energy distribution, on the basis of which
6.3 Materials and Methods

6.3.1 Materials

A Ketton limestone rock core plug, $3.84 \pm 0.01$ mm in diameter and $11.10 \pm 0.37$ mm in length, was used in this study. After drying the sample in an oven at 70 °C for 12 h and acquiring µCT images, the rock sample was vacuum-saturated with deionised water; based on the gravimetric analysis, the porosity ($\phi_g$) of the rock sample was estimated to be $\phi_g = 21 \pm 4\%$. For the flow MRI experiments, the sample was placed in Adtech fluorinated ethylene propylene (FEP) heat shrink tubing which was used to connect the sample to inlet and outlet FEP tubing and to provide confinement. A constant flow rate of water was imposed using a Vindum VP-6 metering pump. Imposed flow rates were accurate to within 0.1 % of the set point.
6.3.2 X-Ray Micro-Computed Tomography

The (dry) Ketton rock core plug was imaged using a Bruker SkyScan 1172 micro-CT scanner (Bruker Micro-CT, Belgium) at an isotropic resolution of 5.00 µm. Imaging was performed using a source voltage of 60 kV, a source current of 165 µA, and an Al (0.5 mm) filter. 802 projection images (10 scans per position) were acquired by rotating the sample through 200.5° with a 0.25° rotation step resulting in a total acquisition time of ≈ 11.5 h. Projection images were reconstructed using the NRecon software (Bruker, v1.6.8.0) to give 2666 cross-sectional slices. A 3D µCT image of the rock sample was generated by successively stacking all 2D cross-sectional slices.

6.3.3 Magnetic Resonance Imaging Experiments

Three pore scale MRI datasets were acquired on the Ketton plug: a velocity map and two spatially-resolved propagators, with different observation times (Δ), as detailed below. The experiments were carried out on a 7.0 T vertical-bore magnet controlled by a Bruker BioSpin Avance III HD spectrometer. A Bruker Micro5 tri-axial gradient system with a maximum gradient strength of 2.9 T m$^{-1}$ in the three orthogonal x-, y-, and z-directions was used to achieve spatial resolution. An 8 mm r.f. saddle coil tuned to a resonance frequency of 299.84 MHz ($^1$H) was used for spin excitation and signal detection.

A velocity map was also acquired for water flow through a packed bed comprised of spherical 4-mm-diameter glass beads, with velocities encoded in the superficial flow direction (z); the internal diameter and the length of the bead pack were 38 mm and 69 mm, respectively. The experiment was conducted on a Bruker vertical super-wide bore superconducting magnet with a static magnetic field strength of 7.1 T (300.87 MHz $^1$H resonance frequency) in combination with a Bruker Avance III spectrometer. An r.f. coil of diameter 66 mm was used, and the maximum magnetic gradient strength available was 0.78 T m$^{-1}$.

6.3.3.1 3D Velocity Mapping

An under-sampled PGSE-RARE experiment (Fig. 6.2) was used to acquire velocity maps in Ketton rock. Under-sampling patterns for the acquisition of velocity maps were generated using the µCT-VDS approach with a k-space sampling fraction of 0.25. The duration of the hard 90° excitation and 180° refocusing r.f. pulses were 6 µs and 12 µs, respectively. Velocity encoding was achieved by a pair of unipolar gradients $g$ of amplitude $g = 2.0$ T m$^{-1}$ ($g_1 = 4.0$ T m$^{-1}$) and duration of $\delta = 0.132$ ms either side of the first 180° pulse, separated by an observation time $\Delta = 4$ ms. Spatial encoding was attained by using a 3D RARE experiment, where the z-dimension ($k_z$) is frequency encoded and the x- ($k_x$) and y-dimensions ($k_y$) are phase encoded.
The RARE factor was $N_{RF} = 8$ with an echo spacing of $t_e = 2.2$ ms. The spectral width was set to $SW = 400$ kHz. 32 scans were acquired for signal averaging with a recycle delay of $t_{RD} = 1.1$ s and a $k$-space sampling fraction of 0.25, giving a total acquisition time of 20 h for a single velocity component (i.e., for a velocity map with velocities encoded in one direction). To correct for the velocity offsets caused by gradient imperfections, no-flow images (images acquired with the pump switched off) were also acquired for each image. The images were acquired with a FOV of 13.5 mm $\times$ 4.5 mm $\times$ 4.5 mm and 384 voxels $\times$ 128 voxels $\times$ 128 voxels in the $z$-, $x$- and $y$-directions respectively, yielding 3D images with an isotropic resolution of 35.2 µm. It is important to note that because of the XY phase cycle [156, 157] used in this experiment, the datasets of odd and even echoes were acquired separately thus the acceleration factor is not equal to $N_{RF}$ as in conventional RARE, but instead is $N_{RF}/2$. During image acquisitions, a constant flow rate of water of 0.03 ml min$^{-1}$ was imposed, which corresponds to an interstitial flow velocity ($v_i$) of 91 ± 3 ft day$^{-1}$ where the estimate of $v_i$ is based on the macroporosity of the Ketton sample between 13–14%. Note that if we assume the characteristic length of this system, $l_c$, to be equal to the typical grain diameter of approximately 0.5 mm, the Reynolds number, $Re = \frac{l_cm v_i}{\nu_f}$, where $\nu_f$ is the kinematic viscosity of fluid, is $Re = 0.16$. Given that $Re \ll 1$, the flow is in the Stokes regime at the given flow rate.

The velocity map of the packed bed was acquired using a fully-sampled (no under-sampling) PGSE-RARE experiment. The duration of the hard 90° excitation and 180° refocusing r.f. pulses were 78 µs and 156 µs, respectively. The flow imaging parameters were $g = 0.5$ T m$^{-1}$ ($g_i = 1.0$ T m$^{-1}$), $\delta = 0.586$ ms, and $\Delta = 6$ ms. 4 scans were acquired with $N_{RF} = 32$, $t_e = 2.1$ ms (SW = 400 kHz), and $t_{RD} = 0.6$ s, yielding an experimental time of 41 min for a single velocity component. To correct for the velocity offsets, a no-flow image was also acquired. The FOV was set to 8.00 cm $\times$ 4.00 cm $\times$ 4.00 cm with 256 voxels $\times$ 128 voxels $\times$ 128 voxels in the $z$-, $x$-, and $y$-directions, respectively, giving a 3D image with an isotropic resolution of 312.5 µm. During flow imaging experiments, a constant flow rate of water of 9.5 ± 0.5 ml min$^{-1}$ was imposed using a Cole-Parmer Masterflex® peristaltic pump. The estimated interstitial flow velocity was $v_i = 94 \pm 5$ ft day$^{-1}$.

### 3D Spatially-Resolved Propagators

For the acquisition of the spatially-resolved propagators, an under-sampled APGSTE-RARE experiment (Fig. 6.3) was used with the following parameter settings. The duration of the hard 90° excitation and 180° refocusing r.f. pulses were 6 µs and 12 µs, respectively. The number of echoes acquired in each echo train was $N_{RF} = 8$ with $t_e = 4.2$ ms, and the spectral width was set to 400 kHz.
Two different spatially-resolved propagators were acquired with different observation times \( \Delta \), namely \( \Delta = 150 \text{ ms} \) and \( \Delta = 900 \text{ ms} \). Between the two experiments, the imposed interstitial flow velocity, \( v_i \), was scaled as the inverse of observation time, so that the total interstitial displacement, \( v_i \Delta \), is identical between the two experiments and the effects of self-diffusion can be observed. For the observation time of 150 ms, a fluid flow rate of 0.03 ml min\(^{-1}\) (\( v_i = 91 \pm 3 \text{ ft day}^{-1} \)) was imposed, hence the experiment with an observation time of 900 ms was performed at a flow rate of 0.005 ml min\(^{-1}\) (\( v_i = 15 \pm 1 \text{ ft day}^{-1} \)).

Displacement encoding was achieved by two pairs of bipolar gradients \( g \) of duration of \( \delta/2 = 0.14 \text{ ms} \) and maximum amplitude of \( g = 2.8 \text{ T m}^{-1} \) for \( \Delta = 150 \text{ ms} \) and \( g = 1.3 \text{ T m}^{-1} \) for \( \Delta = 900 \text{ ms} \). The 3D spatially-resolved propagators were acquired with a FOV of 13.5 mm \times 4.5 mm \times 4.5 mm and 144 voxels \times 48 voxels \times 48 voxels in the frequency- (z) and both phase-encoding directions (x and y), respectively, yielding 3D images with an isotropic resolution of 93.8 \( \mu \text{m} \). In q-space, 65 points were acquired, leading to a FOV in the displacement direction of 1.0 mm. The displacement direction was chosen to be parallel to the superficial flow direction (z).

For k,q-space under-sampling, a 3D q-k\( \_\text{phase} \)-space under-sampling pattern was generated with a sampling fraction of 0.25, using the approach described in Section 6.2.2. Using \( t_{RD} = 2 \text{ s} \), and acquiring 16 signal averages at a sampling fraction of 0.25 of k,q-space, the acquisition time of the spatially-resolved propagators was 4 days for the \( \Delta = 150 \text{ ms} \) experiment and 5 days for the \( \Delta = 900 \text{ ms} \) experiment – this is 32 times faster than a fully-sampled, simple spin echo MRI experiment at the given SNR. The sample remained in the same position for both the velocity mapping and spatially-resolved propagator experiments.

### 6.3.4 Image Processing

#### 6.3.4.1 Compressed Sensing Reconstructions of Under-Sampled Flow Data

CS reconstructions of under-sampled MRI flow data follow a CS approach as described in Chapter 4. More specifically, CS images were recovered using Eq. 4.6 (Section 4.4.2.2). TV was used as the regularisation functional. The value of the regularisation parameter \( \alpha \) was chosen on the basis of Morozov’s discrepancy principle [108], as is described in Chapter 4.

#### 6.3.4.2 Generating Velocity Maps

First, the individual under-sampled k-space datasets of odd and even echoes with the pump switched on and the pump switched off were reconstructed separately to yield complex-valued MRI images. The complex-valued MRI images were then converted into phase maps by calculating the phase angle for each voxel in the images. To correct for the velocity offsets,
the phase maps acquired under no-flow conditions were subtracted voxel-wise from the phase maps acquired under flow-conditions. Then, the phase difference maps for odd and even echoes were calculated by voxel-wise subtraction of the offset-corrected phase images of both q values. The resulting phase difference maps of odd and even echoes were recombined by voxel-wise averaging for improved accuracy [154] of the velocity maps. The echo-combined phase maps were then converted to velocity maps using Eq. 2.40. Lastly, the magnitude images of the complex-valued no-flow MRI datasets were averaged to generate a binary mask which was multiplied by the velocity maps to null the background noise in the velocity maps. The magnitude image was binarized using the watershed-based segmentation algorithm [84] in Avizo 2019.4 (FEI Visualisation Sciences Group, USA). The velocity maps were processed in Matlab (Mathworks, USA).

It is noted that the watershed-based segmentation algorithm was chosen for image binarization as it can effectively deal with the partial volume effects (i.e., voxels located at the pore-grain interfaces). Inevitably, some voxels in the final masked velocity image will still contain both fluid and rock matrix phases. However, the flow data will not be intrinsically adversely affected, unless the SNR becomes too low, which can happen if only a very small part of the voxel contains fluid. In this work, the flow measurements were shown to be accurate overall, as there was excellent agreement between the imposed flow velocities and velocities estimated from flow data (see Section 6.4).

6.3.4.3 Structure-Transport Correlations of Velocity Maps

To obtain structure-transport correlations in the Ketton rock, the binarized magnitude (structural) image and the velocity map of flow through the rock acquired in the superficial flow direction (z) were analysed in Avizo. The pore space of the binarized structural image was separated into individual pores using a Chamfer distance transform and marker-based watershed algorithm. The structural image and the velocity map were used to correlate the flow properties for the individual pores. Equivalent effective pore body radii (i.e., the radius of a sphere with the same volume as a pore) and coordination numbers of the labelled pores were obtained using the “Generate Pore Network Model” module [13].

6.3.4.4 Image Co-Registration

Image co-registration of the MRI and µCT datasets was performed in Avizo using the “Register Images” module. The alignment of the µCT image relative to the reference image (i.e., the magnitude image of the acquired MR data) was optimised using an automatic image registration based on rigid transformations and the normalised mutual information. The
optimisation procedure was performed in steps at different spatial resolutions for more time-efficient co-registration. During the coarsest-resolution optimisation, MRI and µCT data were down-sampled by a factor of 2 and 14, respectively. Extensive Direction and Quasi Newton optimizers were used for the coarse resolution and the finest resolution images, respectively [79]. Once the registration process was completed, the co-registered µCT dataset was resampled onto the MRI data coordinate system using a Lanczos filter [89]. This allowed for the MRI flow maps and µCT images to be compared on the same grid. For the co-registration of the spatially-resolved propagator, a higher-resolution MRI image of the rock acquired with the exact same sample position was used as a reference image. The resampled µCT image and MRI data were then visualised as a combined (fused) dataset.

6.4 Results and Discussion

This section is structured as follows. First, in Section 6.4.1, the pore-scale resolution 3D velocity map of flow through the Ketton plug is presented and characterised. It is also described how the map is co-registered and fused with the high-resolution µCT image of the same rock sample, and visualised as a single dataset to correlate structure and flow information. In Section 6.4.2, it is shown how a 3D spatially-resolved propagator acquired for flow through the Ketton plug is segmented into the representative flowing and stagnant components and then fused with an aligned µCT image. The effects of using different observation times on the shape of a spatially-resolved propagator are also discussed.

6.4.1 Velocity Map

6.4.1.1 Characterisation of 3D MRI Flow Fields in Ketton Rock

Figure 6.4a shows the magnitude map of the combined z-, x-, and y-velocity components for flow of water in Ketton rock at the imposed flow velocity of $v_i = 91 \pm 3\text{ ft day}^{-1}$ (0.32 ± 0.01 mm s$^{-1}$). By visually inspecting the flow map, two characteristics are observed. First, it is seen that most water in the pore space of Ketton rock has low mobility, with a typical speed $< 0.2$ mm s$^{-1}$. Nearly 70% of the voxels in this region of the rock contain fluid flow with lower speed than the mean absolute flow speed of approximately 0.5 mm s$^{-1}$. Second, the flow is heterogeneous and is concentrated in a few high-velocity flow channels. These observations are consistent with the results obtained from flow MRI measurements in glass bead packs [144, 145] and micron-scale flow simulations in carbonate rocks [158]. They are also consistent with the notion that the conductance of a pore scales as the pore radius to the power of four, which, in a porous medium with a distribution of pore sizes, leads to the
6.4 Results and Discussion

Figure 6.4 (a) Pore-scale 3D magnitude flow map generated from the x-, y-, and z-velocity components showing the main flow channels through the Ketton rock plug. Velocity distributions of (b) z- and (c) y-velocity components; the x-velocity component has a similar distribution of velocities to the y-velocity component.

flow being concentrated in a number of critical paths which carry most of the flow [159, 160]. The velocity distributions of \( v_z \) and \( v_y \) components are shown in Fig. 6.4b and Fig. 6.4c; the velocity distribution of the \( v_x \) component is not shown but is similar to the distribution of the \( v_y \) component. The distribution of \( v_z \) exhibits a long positive tail, a significant intensity at \( v_z = 0 \) mm s\(^{-1}\) which represents stagnant water, and some negative flow or backflow, represented by negative velocities. The long positive tail illustrates the heterogeneity in the flow through Ketton rock with the highest velocities extending to \( \sim 50 \) times the modal velocity of \( v_z \) \( \sim 0.08 \) mm s\(^{-1}\). The mean velocity along the superficial flow direction (z) was calculated
to be \( v_z = 0.32 \text{ mm s}^{-1} \) (91 ft day\(^{-1}\)), which is in excellent agreement with the imposed interstitial flow velocity in the macropores. The occurrence of backflow in flow through porous media has been identified both in flow computations [161, 162] and physical (MRI) flow experiments [140, 143, 155, 163] and is believed to be caused by re-circulating flow patterns in the immediate vicinity of surfaces, or vortex-like structures at the meeting points of streamlines. Backflow has been observed in experimental studies of flow through a variety of bead packs with different bead geometries and sizes [140, 163] and at various flow rates (Re > 1) [140]. It has also been predicted using the lattice Boltzmann method simulations in a bead pack for a range of Re = 0.6–30 [162] that the degree of backflow is dependent on Re and increases with increasing Re. In this work, the backflow phenomenon is present even at a relatively low Re of 0.16, i.e., during Stokes flow. This is perhaps not entirely surprising, since Saeger et al. [161] demonstrated, by solving the Navier-Stokes equation, that re-circulating flow patterns, which represent backflow, are identified for Stokes flow in bi-continuous porous media. The distribution of \( v_y \) is symmetrically distributed around \( v_y = 0 \text{ mm s}^{-1} \) (i.e., zero net flow) with velocities up to \( v_y \sim \pm 2 \text{ mm s}^{-1} \). It was found that the positive and negative parts of the distribution of \( v_y \) are described well by a single-exponential function, which is consistent with findings elsewhere [164].

To analyse in more detail how the flow is distributed across the pore space of Ketton rock, structure-transport information was extracted from the velocity component acquired in the direction of superficial flow (\( z \)) and from the pore segmented structural image; the analysis was performed on the 3D region of the image of size 7.2 mm \( \times \) 4.5 mm \( \times \) 4.5 mm shown in Fig. 6.4a. Figure 6.5 summarises aspects of the structure-flow relationships extracted from the \( z \)-velocity component of the image shown in Fig. 6.4a. Figure 6.5a shows the fraction of the total flow \( (v_z^{\text{sum}}(i)/v_z^{\text{sum, tot}}) \) as a function of the fraction of the number \( (N_p(i)/N_p^{\text{tot}}) \) and volume \( (V_p(i)/V_p^{\text{tot}}) \) of those pores that carry this flow. It is seen that more than half of the flow (\( \sim 53 \% \)) is carried by just 10 % of the pores which represent approximately 36 % of the pore volume in the rock. This analysis is consistent with the flow map in Fig. 6.4a, in which it is seen that only a few flow channels carry a large proportion of flow through the rock. Figure 6.5b shows the mean \( z \)-velocities within pores \( (v^{\text{m}}_z) \) averaged over pores with the same coordination number, i.e., the average mean velocity within a pore, \( \bar{v}_z^{\text{m}} \), plotted as a function of the average radius of these pores for different coordination numbers ranging from 2 to 8; the size of the red dots represents coordination numbers from 2 to 8 in ascending order (i.e., the smallest dot represents pores with coordination number = 2). First, it is seen that the average pore size (as characterised by average pore radius) increases with the coordination number of the pore. A similar positive correlation between the pore size and coordination number in porous sandstone rocks has been reported elsewhere [165], which is expected because larger
6.4 Results and Discussion

Figure 6.5 Structure-flow correlations in Ketton rock. (a) The fractional summed $z$-velocities (in the superficial flow direction) within pores with a summed $z$-velocity equal to or greater than (the parametric variable) $i$, $v^\text{sum}_z(i)/v^\text{sum, tot}_z$, plotted as a function of the fraction of the number of pores, $N_p(i)/N_p^\text{tot} (\cdots)$, and the volume of pores, $V_p(i)/V_p^\text{tot} (\cdots)$, carrying this flow. (b) The average mean $z$-velocities, $\bar{v}_z^m$, within pores plotted as a function of the average radius of these pores for different coordination numbers; the size of the red dots represents coordination numbers from 2 to 8 in ascending order. (c) Correlation between the average mean pore velocities, $\bar{v}_z^m$, and coordination numbers for all pores. (d) Correlation between the average mean pore velocities, $\bar{v}_z^m$, and coordination numbers for pores with local Reynolds numbers greater than the mean local Reynolds number of 0.064. The solid blue lines represent the regression fits to the data.

Pores are more likely to have more throats feeding into them. Second, larger pores tend to have greater values of mean pore velocity, $v^m_z$. Performing coordination number-independent
analysis of the data, it was estimated that the average ± standard error (standard deviation) of \(v_m^z\) of the pores with pore radii smaller and greater than the mean pore radius of 120 µm are 0.25 ± 0.02 (0.40) mm s\(^{-1}\) and 0.31 ± 0.01 (0.25) mm s\(^{-1}\). Figures 6.5c and 6.5d consider the flow through the pores as a function of their coordination number. In Fig. 6.5c, data for all pores with coordination numbers 2–8 are shown. The trend in the data suggests that mean flow velocity through a pore increases with the coordination number of the pore with average mean \(z\)-velocities within the pores increasing from 0.27 ± 0.03 mm s\(^{-1}\) for a pore coordination of 2, up to 0.45 ± 0.07 mm s\(^{-1}\) for a pore coordination number of 8. In Fig. 6.5d, only the data for pores in which the local Reynolds number (\(Re_l\)) is greater than the mean local \(Re\) are shown, where the local \(Re\) is defined as \(Re_l = \frac{A v_m^z}{\nu_f} \) [144], where \(A\) is the cross-sectional area of a pore calculated from its radius, and \(v_m\) is the kinematic viscosity. It was estimated that the \(Re_l\) in the Ketton rock at \(v_i = 91\) ft day\(^{-1}\) (0.32 mm s\(^{-1}\)) are all smaller than 1, therefore all the pores locally exhibit Stokes flow behaviour. Within the Stokes regime, the flow field scales with global flow rate, and so to separate out those pores which carry most of the flow, it is justified to use the mean \(Re_l\) as a cut-off value – the result of the following analysis will not change with global flow rate. The mean \(Re_l\) is 0.064; approximately 36 % of the pores (by number) are considered in this analysis. The mean flow velocity through a pore is now seen to decrease with increase in coordination number. Figures 6.5c and 6.5d are worthy of further inspection. It is seen that at the higher coordination numbers the pores have similar values of mean pore velocity. In contrast, at low pore coordination number – and, in particular, coordination of 2 – the pores carrying flow greater than the mean \(Re_l\) are associated with flow velocities more than double those seen in Fig. 6.5c; i.e., 0.65 mm s\(^{-1}\) compared to 0.27 mm s\(^{-1}\). This observation is consistent with some of the pores identified as having a coordination number of 2 effectively being narrow constructions between high volume pores which are carrying the majority of the flow through the bed. Indeed, interrogation of the image shown in Fig. 6.4a shows that some of the small regions associated with highest fluid velocities (indicated by red voxels) are correlated with the pores with low coordination number and a higher-than-average \(Re_l\).

Figure 6.6 shows the equivalent data recorded for a packing of 4-mm-diameter glass spheres. Qualitatively the trends remain the same as those shown in Fig. 6.5, suggesting that there are similarities in the flow behaviour between a sphere pack and Ketton rock, the microstructure of which does indeed approximate a packing of spherical grains as is seen in Fig. 6.7, although it has a lower porosity than the sphere pack. Figure 6.6a shows a similar shape to Fig. 6.5a and shows that 48 % of the flow is carried by 10 % of the pores which represent approximately 35 % of the pore volume in the sphere pack. The data in Figs. 6.5a and 6.6a are also consistent with data reported earlier for 2D imaging of structure-flow relationships [144] in a packing of 5-mm-diameter spheres in which it was observed that 10 % of the pores carried ∼ 42 %
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Figure 6.6 Structure-flow correlations in a pack of spherical beads. (a) The fractional summed $z$-velocities (in the superficial flow direction) within pores with a summed $z$-velocity equal to or greater than (the parametric variable) $i, \frac{v_{z}^{\text{sum}}(i)}{v_{z}^{\text{sum, tot}}}$, plotted as a function of the fraction of the number of pores, $N_p(i)/N_p^{\text{tot}} (-)$, and the volume of pores, $V_p(i)/V_p^{\text{tot}} (\cdots)$, carrying this flow. (b) The average mean $z$-velocities, $\bar{v}_z^m$, within pores plotted as a function of the average radius of these pores for different coordination numbers; the size of the red dots represents coordination numbers from 2 to 10 in ascending order. (c) Correlation between the average mean pore velocities, $\bar{v}_z^m$, and coordination numbers for all pores. (d) Correlation between the average mean pore velocities, $\bar{v}_z^m$, and coordination numbers for pores with local Reynolds numbers greater than the mean local Reynolds number of 0.82. The solid blue lines represent the regression fits to the data.

of the flow. Similar to the correlations seen for Ketton in Figs. 6.5b and 6.5c, Figs. 6.6b and 6.6c show that the mean pore velocity increases with increasing pore radius and coordination.
number for all pores with coordination numbers 2–8, although the dependency between these quantities appears to be slightly weaker for the bead pack in terms of the slope of the regression fit; for the bead pack data in Fig. 6.6c, average mean z-velocities within the pores increase from 0.27 mm s\(^{-1}\) to 0.36 mm s\(^{-1}\) for coordination numbers 2–8 (vs. 0.27–0.45 mm s\(^{-1}\) for the same range in coordination numbers in Ketton rock). Figure 6.6d shows that the mean flow z-velocity through a pore decreases with increasing pore coordination number for pores with \(Re_l\) greater than the mean \(Re_l\) of 0.82; a correlation which is again consistent with the Ketton data (Fig. 6.5d).

### 6.4.1.2 Co-Registration of High-Resolution MRI Velocity Maps and \(\mu\)CT Images of Ketton Rock

Figure 6.7 shows a 3D visualisation of the combined z-, x-, and y-velocity components co-registered with the 3D \(\mu\)CT image of Ketton rock. The magnitude and colour of the arrows

**Figure 6.7** A 3D section of 1 mm\(^3\) extracted from the co-registered 3D MRI velocity vector map and \(\mu\)CT image of Ketton rock. The displayed 3D velocity vectors were obtained by combining z-, x-, and y-velocity components; arrows represent the direction of flow, and the size and colour of these arrows represent the magnitude of the flow. The superficial flow direction was along the z-axis.
6.4 Results and Discussion

Figure 6.8 (a,b) 2D xy-slice images extracted from 3D co-registered z-velocity map and µCT image of Ketton rock. Four regions have been highlighted by the red boxes which identify different flow patterns in the rock: (1) adjacent positive and negative flow in a large pore; (2) stagnant water in a moldic pore; (3) high-velocity flow channel in a large pore; and (4) concentrated flow in the narrow parts of pores. Regions (c) 1 and (d) 3 are also visualised as co-registered 3D velocity (x, y, z) vector maps.

Represent the speed of the fluid flow, and the direction of the arrows indicate the direction of the fluid flow through the rock. It can be seen in Fig. 6.7 that the speed of flow is higher upstream and downstream from the large ooid in the centre of this rock section and that the high-velocity pore downstream from this ooid has a high coordination number and is associated with high fluid velocity, consistent with the analysis shown in Fig. 6.5c. In Fig. 6.8, 2D xy-slice images and 3D sections obtained from the 3D co-registered MRI and µCT dataset are shown; the 2D velocity maps represent fluid flow velocities acquired in the superficial flow direction (z), while the 3D velocity maps represent all three orthogonal velocity components. The high spatial resolution of the co-registered dataset enables us to identify different flow patterns in the rock.
and to correlate these patterns with the microstructure of the rock matrix. For example, in region 1 (Fig. 6.8a) complex flow behaviour can be observed in a large pore where backflow, which is characterised by negative velocities along the superficial flow direction, has developed adjacent to relatively high-velocity forward-flow channels. A 3D visualisation of this region is shown in Fig. 6.8c. It can be seen that the backflow occurs because the flow in z-direction is obstructed and diverted by the rock grains. In region 2, a moldic pore can be seen, in which water appears to be stagnant; moldic pores are carbonate-specific microstructural features, developed by the dissolution of a pre-existing constituent of a rock, such as a shell or grain. It was verified that this moldic pore has very restricted and narrow openings. In Fig. 6.8b region 3, a wide, high-velocity flow channel can be seen in a macropore, which is also illustrated in Fig. 6.8d in the 3D velocity vector map. In the 2D velocity maps shown in Fig. 6.8, it can be seen that the flow velocity of fluid becomes increasingly high when it passes through narrow pore spaces formed by the tightly packed Ketton ooids, some of which are labelled as region 4.

6.4.2 Spatially-Resolved Propagators

The 3D spatially-resolved propagator data are four-dimensional – with three spatial dimensions and a displacement dimension. Such data are therefore amenable to two different types of analysis. The first type of analysis is image-based and is related to the fact that for each of the displacement points on the propagator, a 3D intensity image exists which shows where the fluid is located which has displaced over that particular distance during the observation time $\Delta$. The second type of analysis is propagator-based and is related to the fact that in each of the voxels in the spatially-resolved propagator a local propagator can be found, which contains information about the distribution of displacements that the fluid molecules in that location have undergone during the observation time $\Delta$. Some of the molecules that are located within a particular voxel after $\Delta$ has elapsed may have started in another voxel and moved to the voxel of which the local propagator is being inspected. Because both the duration of the observation time and the flow rate can be chosen freely, this effect will be stronger for higher flow rates and longer observation times; in such cases, the propagator contains information about flow processes upstream of that particular voxel.

The data were also used to explore whether or not the sample studied was sufficiently large to constitute a representative elementary volume (REV), which was based directly on the flow properties of the rock. To do this, the shape of the local propagator was compared to that of the global propagator across different length scales by spatially averaging the local propagators between adjacent voxels.

An example of an image-based analysis is shown in Fig. 6.9. The spatially-resolved propagator was used to segment the pore space into stagnant and flow-carrying components.
The global, non-spatially resolved propagator, obtained by summation of all 331,776 individual, per-voxel propagators, is shown in Fig. 6.9a. The flow observation time, $\Delta$, was 150 ms, at an interstitial flow velocity of 91 ft day$^{-1}$. The global propagator shows that a significant amount of fluid is stagnant or near-stagnant, whilst a much smaller amount of fluid is significantly displaced during $\Delta$. A cut-off between “flowing” and “stagnant” water, which is indicated by the grey vertical line in Fig. 6.9a, was chosen based on the expected Gaussian shape of the propagator for water molecules in the absence of flow (the self-diffusion coefficient, $D$, is $2 \times 10^{-9}$ m$^2$ s$^{-1}$ at room temperature). The cut-off was applied at the right-hand tail of the distribution, which water molecules would have a less than 1% chance of reaching on the basis of self-diffusion (i.e., under no-flow conditions). The stagnant and flowing water was then spatially-resolved, as shown in the two complementary images in Fig. 6.9b. The data were co-registered and fused with a µCT image of the same rock. In contrast to the co-registered images in Fig. 6.8, the colourmap in Fig. 6.9b indicates the amount of fluid in each voxel which is either stagnant or flowing, whereas Fig. 6.8 represents the average velocities of fluid flow through rock. Overall, the trends seen in Fig. 6.9b are consistent with those observed in velocity maps—the proportion of the fluid that has a significant displacement that can be attributed only to the imposed flow is carried by a small fraction of the pore space. This simple workflow can therefore be used to obtain an estimate of the fraction and spatial
distribution of the flow-carrying porosity. Because the spatial and displacement resolutions in a spatially-resolved propagator can be chosen independently, this approach can also be used with larger rock core samples at coarser spatial resolutions in order to identify flow-carrying porosity.

In Fig. 6.10, a propagator-based perspective is taken on the data. In this case, the effect of observation time, $\Delta$, on the shape of individual, per-voxel propagators is investigated. The results of two separate experiments are shown – recall that between the two, the product of observation time and interstitial flow velocity was kept constant, such that the global mean fluid displacement within the rock during observation time, $\Delta$, is identical. The idea behind this approach is that this gives insight into the extent of diffusive coupling between stagnant and flowing zones on the length scale of a single voxel, rather than on the global level, as was the subject of earlier work [166]; because the mean displacement is the same between the two experiments, the flow dispersion in the absence of self-diffusion would be identical, assuming that the streamlines are identical between the two cases.

Figure 6.10a shows two spatially-unresolved (global) propagators normalised to the same area, which are the sum of the 331,776 local propagators in each of the two datasets. The mean displacement in both propagators, which should be identical, is $45 \pm 5 \mu m$ for the $\Delta = 150$ ms and $39 \pm 5 \mu m$ for the $\Delta = 900$ ms dataset – this corresponds to interstitial flow velocities of $85 \pm 9$ and $12 \pm 2$ ft day$^{-1}$, respectively (to be compared with the imposed flow velocities of $91 \pm 3$ and $15 \pm 1$ ft day$^{-1}$). The measurement is therefore quantitative to within the error margin, with the slightly larger percentage deviation from the expected flow velocity for the $\Delta = 900$ ms experiment probably due a lower SNR for that experiment, because of the longer observation time, $\Delta$. It is seen that although the mean displacement between the two experiments is the same, the propagator of the $\Delta = 900$ ms experiment is much broader due to additional self-diffusion and flow dispersion relative to the $\Delta = 150$ ms experiment. This can be seen also from the Péclet numbers (Eq. 6.4), which equal 80 for the higher flow rate and 13 for the lower flow rate. These numbers confirm that the fluid transport through the rock is significantly less dominated by advective transport at the lower flow rate. In both cases, the propagators are positively skewed, which is typically seen in the regime where the mean displacement is significantly smaller than the characteristic length (grain size) within the porous medium, so that the propagators are still close to being a projection of the distribution of short-time velocities [139]. Only at long time scales will the propagator transition back to a fully dispersive, Gaussian shape, as has been shown in various studies by different groups [139, 147, 158, 166, 167].

The spatially-resolved approach shown in this work allows zooming into the regions where most of the flow and therefore flow dispersion occurs. In these regions, significant flow dispersion is observed which is not readily seen in the global propagator. Figure 6.10b–f
6.4 Results and Discussion

Figure 6.10 (a) Global propagators, obtained by summation of all 331,776 local propagators of the $\Delta = 150$ ms ($\rightarrow$) and $\Delta = 900$ ms ($\leftarrow$) datasets. (b–f) Five examples of local, per-voxel propagators, plotted on the same scale as the propagators in (a).

shows five examples of local propagators taken from the 3D dataset; note that the displacement axis of the propagators is broader (1 mm) than the underlying voxel resolution (94 $\mu$m), so that the starting positions of the fluid molecules in each voxel may lie outside of a particular voxel. A comparison is again made between local propagators from the same voxel at $\Delta = 150$ ms and $\Delta = 900$ ms – their integrals are the same because the fluid content of the voxel is the same in both cases. It can be seen that the local propagators assume various shapes that are different from the shape of the global propagator. For example, in Fig. 6.10b, the propagator is taken from a region where the fluid is stagnant – the propagators are symmetric Gaussians centred around zero displacement. The propagator for $\Delta = 900$ ms is broader due to additional self-diffusion compared to the one at $\Delta = 150$ ms. At short time scales, most of the local propagators have this simple, Gaussian shape centred around zero displacement, because much of the water in the rock is stagnant as was shown in Fig. 6.4a. Figure 6.10c shows local propagators taken for a voxel in which there is significantly different behaviour at the two observation times. At $\Delta = 150$ ms, the propagator is clearly indicative of stagnant water;
however, for $\Delta = 900$ ms the mean displacement has clearly shifted to a positive value. This effect may be counter-intuitive, because the mean displacement between the total propagators for $\Delta = 150$ ms and $\Delta = 900$ ms is the same. However, the shift in mean displacement on a local level is expected since in the limit of very long $\Delta$, the local propagators must resemble the global propagator due to fluid mixing throughout the rock sample; mixing takes place due to self-diffusion and additional dispersion between voxels. Therefore, the mean displacement within a single voxel must change with $\Delta$. The propagators shown in Fig. 6.10d–f are examples where the propagator is bimodal at $\Delta = 150$ ms, indicating that those single voxels contain two fractions of fluid that are associated with two different flow rates, i.e., two fluid streams that have not diffusively exchanged. At the longer observation time, diffusive exchange has taken place and the propagators have merged into unimodal but skewed distributions.

The fact that in the limit of very long $\Delta$, where complete mixing will have taken place, all local propagators must be identical, can be exploited to track the progress of mixing on a local level from the spatially-resolved propagator. To capture the essential properties of the local propagators, $\bar{P}(\mathbf{R}, \Delta)$, as simple statistical descriptors, the mean ($\mu$) and standard deviation ($\sigma$) of displacement were extracted. The mean is given by:

$$\mu = \frac{\int P(\mathbf{R}, \Delta)d\mathbf{R}}{\int P(\mathbf{R}, \Delta)d\mathbf{R}}, \quad (6.5)$$

and the standard deviation is given by the square root of the variance of the propagator as:

$$\sigma = \sqrt{\frac{\int P(\mathbf{R}, \Delta)(\mathbf{R} - \mu)^2d\mathbf{R}}{\int P(\mathbf{R}, \Delta)d\mathbf{R}}}, \quad (6.6)$$

where $\mathbf{R}$ is the displacement over observation time $\Delta$.

Figure 6.11 shows two 2D histograms for $\Delta = 150$ ms (Fig. 6.11a) and $\Delta = 900$ ms (Fig. 6.11b), wherein the mean and standard deviation of all local propagators in the rock sample are collected. Both mean and standard deviation are rescaled using the values calculated for the global propagator. The red dot indicates the position $\mu / \mu_{\text{global}} = 1$ and $\sigma / \sigma_{\text{global}} = 1$, onto which all propagators should converge at long $\Delta$; at long time scales, the flow rate is negligible, and the propagators will be fully dominated by self-diffusion. The colour intensities, $I_c$, in both histograms represent the total sum of fluid in each position (bin) of $\mu / \mu_{\text{global}}$ and $\sigma / \sigma_{\text{global}}$. The exact positions of 0.1% of the local propagators randomly picked from the dataset are also shown, indicated by the black dots – which helps to guide the eye.
6.4 Results and Discussion

Figure 6.11 2D histograms showing the mean and standard deviation of all local propagators in the rock, for (a) $\Delta = 150$ ms and (b) $\Delta = 900$ ms. Both mean and standard deviation are rescaled using the values calculated for the global propagator at the given $\Delta$. The colour scale corresponds to the $\log_{10}$ of the total integral $I_c$ of all the propagators within each bin. The black dots show the exact position of 0.1% of the total number of local propagators, randomly picked from the dataset. The red dot indicates the position $\mu/\mu_{\text{global}} = 1$, $\sigma/\sigma_{\text{global}} = 1$ for reference.

For $\Delta = 150$ ms (Fig. 6.11a), it is seen that many propagators are concentrated close to $\mu/\mu_{\text{global}} = 0$ and $\sigma/\sigma_{\text{global}} = 0.3$. All these propagators are located within stagnation zones and have not had sufficient time to couple into the flow through diffusive exchange, so that the propagators are purely self-diffusive, as in Fig. 6.10b. The tail of the distribution extends towards large values of $\mu/\mu_{\text{global}}$ and $\sigma/\sigma_{\text{global}}$; these data are associated with the propagators from within or close vicinity to the flow channels identified in Figs. 6.4a and 6.9b. At this relatively short time scale, the molecules in these areas have not yet significantly exchanged with the water in the stagnation zones. The expectation value for self-diffusive displacement of a fluid molecule equals $\sqrt{2D\Delta}$, which equals 24 $\mu$m for water after 150 ms and 60 $\mu$m after 900 ms. The effects of this additional mobility can be seen in Fig. 6.11b. The distribution of points around $\mu/\mu_{\text{global}} = 1$ has become significantly narrower, whilst, at the same time, the distribution of $\sigma/\sigma_{\text{global}}$ has shifted towards higher values. Many of the propagators, which represented stagnant water at $\Delta = 150$ ms, have shifted towards $\mu/\mu_{\text{global}} = 1$ and $\sigma/\sigma_{\text{global}} = 1$.

At this longer time scale, the effects of Taylor dispersion [124] are seen whereby molecules which were in stagnant zones at short time scales will have moved across the streamlines of the flowing zones at longer time scales. This mixing between the fluid molecules in flowing and stagnant zones within a single voxel leads to the local flow propagator identifying greater dispersion than the global propagator. However, as was already evident from the global
Figure 6.12 Rescaled mean $\mu/\mu_{\text{global}}$ and standard deviation $\sigma/\sigma_{\text{global}}$ of per-voxel propagators at different coarse-grained spatial resolutions. The highest resolution of 94 µm (●) equals that of the acquired data. The acquired data have been coarse-grained to 562 µm (■), 1.125 mm (◇) and 2.25 mm (♦) isotropic spatial resolutions. The result for 2.25 mm spatial resolution represents a single voxel and is therefore found at position (1,1).

A final look at the spatially-resolved propagator is aimed at answering the question whether the data can be used to determine which voxel size equals an REV [7] for the observed flow phenomena in the rock. As is seen in the flow maps and spatially resolved propagators in Figs. 6.8 and 6.9, flow pathways are sparsely distributed across an axial cross section of the rock and therefore the question arises whether the flow properties of this rock have already averaged out at a 4-mm scale. In the context of spatially-resolved propagators, an REV can be identified by finding the smallest volume element which has an associated propagator that is not significantly different from the total propagator of the entire region of interest. For this analysis, a cubic volume containing $24^3$ voxels (total volume $2.25^3 \text{ mm}^3$) was selected from a region within the rock. The propagator with $\Delta = 150 \text{ ms}$ is used because at this time scale, the flow field is less dominated by diffusion than for the experiment at $\Delta = 900 \text{ ms}$. This volume was successively coarse-grained to an array containing $4^3$, $2^3$ voxels, and finally to a single volume. Mean and standard deviation were calculated for each of the voxels in the different data sets.
and rescaled using the “global” result obtained for the single volume (voxel); the results of this analysis are shown in Fig. 6.12. It is seen that the going from the smallest voxel size (●) to the global result  at $\mu/\mu_{\text{global}} = \sigma/\sigma_{\text{global}} = 1$ (●), the distributions of mean and standard deviation become increasingly narrow and approach the global result. Nevertheless, even at the second lowest resolution (▼, $2^3$ voxels), there still exists significant variation of $\mu/\mu_{\text{global}}$ and $\sigma/\sigma_{\text{global}}$ between the different voxels, relative to the global result (●). It is therefore likely that the global result does not yet equal that of an REV for this sample of Ketton rock. Since spatial resolution and displacement resolution can be chosen independently in the acquisition of spatially-resolved propagators, it would also be possible to carry out this analysis on larger rock core plugs at coarser spatial resolutions without significantly increasing the image acquisition time, in order to identify flow-characterising REVs at a much larger length scale.

6.5 Conclusions

In this chapter, quantitative, 3D velocity maps and spatially-resolved propagators acquired at a pore-scale resolution have been presented and analysed to study flow-structure correlations for a single-phase flow through a 4-mm-diameter Ketton limestone rock core plug. The high spatial resolution of flow MRI achieved in this work enabled the detail of flow structure in the rock to be studied.

First, a compressed sensing PGSE-RARE sequence was used to acquire quantitative, 3D spatially-resolved velocity maps at 35 µm spatial resolution, which is about one order of magnitude higher than has been reported using more conventional MRI flow methods. Using 3D visualisation and quantitative analysis of the pore-scale MRI flow fields, it was shown that flow in Ketton limestone rock is carried by only a few flow channels which mainly consist of large pores; it was found that 53 % of the flow is carried by just 10 % of the pores. Furthermore, it was demonstrated how co-registration and visualisation of MRI flow fields and µCT images can be exploited to correlate complex flow phenomena, such as backflow, with the microstructural characteristics of the rock. In particular, the correlation of local flow velocities with pore size and coordination number was studied. It was also shown that the structure-flow characteristics of Ketton rock were well-approximated by flow through a packing of spheres.

Second, an under-sampled APGSTE-RARE experiment was used to acquire spatially-resolved propagators at 94 µm spatial resolution. Two 3D spatially-resolved propagators, containing 331,776 voxels, each of which contains a local propagator, were acquired using observation times of 150 ms and 900 ms. Based on the segmentation of the global propagator acquired at the shortest observation time, stagnant and flowing water images were generated and co-registered with the high-resolution µCT image of Ketton rock. This analysis demonstrated
that stagnant and flowing water co-exists in some large pores. A comparison between the propagators acquired at the short and long observation times provided a view on fluid dispersion at the pore scale. Flow dispersion was observed by quantifying the changes in mean and standard deviation of each of the local propagators as a function of observation time.

Although these MRI techniques were developed for studying rock samples in the context of DR technology, they are not limited to only this application, but are generic and can be used to obtain flow information in any porous material. In the next chapter, these single-phase MRI flow methods will be employed to validate DR simulations, but in Chapter 8 these methods will be used as a basis for developing multi-phase MRI techniques.
Chapter 7

Integrating Pore-Scale Flow MRI and µCT for Validation of Digital Rock Simulations

7.1 Introduction

In Chapters 5 and 6, MRI methodology based on rapid data acquisition techniques was developed and demonstrated for the acquisition of high-resolution MRI structural and flow images in rocks. In this chapter, these methods are employed to acquire MRI flow images in porous rock plugs at pore-scale resolution in order to validate Digital Rock (DR) flow simulations, performed directly on the X-ray µCT images of the pore space of rock core plugs.

To recap, DR physics is concerned with the computation of petrophysical properties of sedimentary rocks on the basis of high-resolution images of the pore space [4–6, 169, 170]. The aim of DR technology is to complement and augment conventional, laboratory-based rock core analysis. A major focus of DR technology is to accurately simulate fluid flow behaviour within the pore space in order to predict, in particular, the permeability of the sample. One of the most powerful approaches for simulating single- and multi-phase flow directly on pore space images of rocks is the lattice Boltzmann method (LBM) [6, 9, 10, 170, 171]. LBM simulation, which has originated from the lattice gas automata method [172], belongs to a class of computational fluid dynamics (CFD) methods for simulating fluid flow. LBM simulates the streaming and collision of microscopic particles over a discrete lattice mesh, and then evaluates the macroscopic pressure gradient and velocity, from which the permeability of a porous material can be estimated; it can be shown that the averaged behaviour of the LBM simulation approximates the Navier-Stokes equation (Eq. 6.1 in Chapter 6) [9, 10]. Compared
to other, conventional CFD methods, the main advantages of LBM are that it is easy to code and is well-suited for parallel computing [10]. Furthermore, LBM enables flow through complex geometries, such as the pore space of porous media, to be relatively easily modelled.

Before DR simulators, which often employ LBM to simulate flow fields, can be used as a predictive tool, it is necessary to validate their output against experimental data. A natural choice of method to benchmark flow simulations is flow MRI, because of its ability to quantitatively and non-invasively measure 3D spatially-resolved fluid flow fields in rocks, as has been demonstrated in Chapter 6 and elsewhere [107, 151, 152]. By looking at the experimental spatially-resolved flow velocity fields, it is possible to identify whether the microscopic flow phenomena which will determine the core-scale petrophysical properties are correctly simulated. Furthermore, as was already demonstrated in Chapter 6, spatially-resolving flow properties provide fundamental insight into the degree of spatial heterogeneity and dispersion of the flow across the rock sample.

Some earlier studies have compared NMR measurements to direct simulations of flow in porous materials [6, 139, 147, 158, 173–175]. However, many of these studies have focused on investigating model porous systems (i.e., packed beds) and/or have used non-spatially resolved NMR measurements. In one of these studies, Bijeljic et al. [173] simulated flow on 3D images of a millimetre-sized bead pack, a Bentheimer sandstone, and a Portland carbonate, and compared the simulated flow fields to non-spatially resolved NMR propagator measurements acquired on the same types of porous materials [176]; the flow fields were computed by solving the Navier-Stokes equations. Excellent agreement between the simulated and experimental propagators was shown, in particular because the flow fields in each of the systems studied exhibited different behaviour. It was demonstrated that in the Portland carbonate rock, which has the most complex geometry of the three samples, the flow was highly heterogeneous with a wide spread of local velocities and (at longer observation times) exhibited a large peak representing stagnant fluid and a small concentration secondary peak representing mobile water. In the bead pack and Bentheimer sandstone, which have simpler pore space structures, more homogeneous flow was observed. Other computational [6, 158] and experimental (Chapter 6) studies have also identified that the flow in the pore space of carbonates is heterogeneous with the flow concentrated in a few high-velocity flow channels.

Several other authors have compared flow simulations to spatially-resolved MRI velocity maps acquired on packed beds [147, 174, 175, 177]. Manz et al. [147] acquired a 2D velocity map (central slice of the packed bed) on a packed bed comprised of 1-mm-diameter spherical beads and compared it to an LBM simulation run directly on the pore space image obtained from a 3D MRI structural image acquired on the same packed bed. Although good qualitative agreement was shown between the experimental velocity map and the simulation, they noted
that the LBM simulations tend to overpredict large axial (in the superficial flow direction) velocities, but underpredict low axial velocities. Mantle et al. [174] studied single-phase fluid flow through a packed bed of mm-sized alumina catalyst particles using LBM simulations, 3D MRI velocity mapping, and 3D MR structural imaging. By combining the information from the pore space analysis, in which the pore space of the MRI structural image was partitioned into individual pores, and velocity data, they were able to obtain flow characteristics for each individual pore. Based on this analysis, they found that there is a good agreement between the simulated and experimental velocity maps at the pore scale. Sullivan et al. [175] benchmarked LBM simulations against 3D MRI velocity maps for flow of different viscosity single-phase fluids through a random packing of 5-mm-diameter spherical glass beads. 2D slice images extracted from the 3D experimental and simulated velocity maps showed very good agreement, with small differences occurring in some of the pores. Voxel-by-voxel comparison between the LBM and MRI data also showed good agreement between the simulated and experimental datasets with no systematic variation. In a more recent work, Yang et al. [177] acquired a 3D velocity map for a single-phase flow through a 0.5-mm-diameter spherical polystyrene beads at impressive 39 µm spatial resolution and compared the measured data to 3D CFD simulations of Navier-Stokes flow that were performed on the high-resolution MRI image of the same packed bed. They concluded that the experimental and simulated velocity fields overall exhibit similar spatial patterns at the pore scale; the largest discrepancies were observed in the high-velocity flow channels, where LBM in general exhibited lower velocities compared to MRI. Although the MRI velocity maps were acquired at a high spatial resolution of 39 µm, this was achieved by using a doped (Gd\(^{3+}\) ions) water solution that reduced MR signal relaxation time, thus allowing shorter repetition time to be used in the experiments, which in turn shortened the image acquisition time significantly. However, using doped solutions in rocks needs to be avoided because dopants tend to strongly adsorb on the rock surface, which can potentially alter fluid-rock surface characteristics [178, 179].

The above examples included a few cases where spatially-resolved MRI flow experiments have been used to benchmark LBM simulations in porous media. However, these spatially-resolved velocity data were acquired using conventional MRI flow imaging pulse sequences, with typical spatial resolutions of one to two hundred microns; the only exception was the study carried out by Yang et al. [177] where 39 µm spatial resolution was achieved using dopants. Although spatial resolutions of a few hundred microns are sufficient to resolve the pore space in packed beds comprised of millimetre-sized particles, such spatial resolutions would be too coarse for adequately capturing pore-scale information in porous rocks. Therefore, MRI images need to be acquired at spatial resolutions that would be compatible with the pore-scale LBM simulations.
In Chapter 5, it was demonstrated that by using a combination of micro-MRI equipment in combination with data under-sampling and CS techniques, it is possible to acquire high-resolution structural CS-MRI images of a Ketton carbonate rock at spatial resolutions down to 17.6 µm. In Chapter 6, this pore-scale CS-MRI capability was integrated with a flow MRI experiment, which enabled acquisition of a 3D spatially-resolved fluid velocity map during water injection into a Ketton limestone plug at a spatial resolution of 35 µm. At this resolution, pore-scale flow features could be observed clearly. It was further shown that, at such spatial resolutions, it is opportune to co-register the fluid velocity maps with X-ray µCT images of the grain space. Co-registration of the MRI velocity maps with the µCT images therefore makes it possible to correlate local flow velocities directly with the microstructure of the grain space. Furthermore, because flow simulations are often based on segmented X-ray µCT images (i.e., binarized X-ray µCT images partitioned into the pore- and grain-space phases), co-registration provides an opportunity to compare flow simulations to the MRI velocity fields on a voxel-by-voxel basis. X-ray µCT images of small rock plugs are acquired routinely at resolutions of ∼ 1 µm, i.e., an order of magnitude higher than the currently accessible resolution with high-resolution flow MRI. The spatial resolutions of the flow simulations will therefore also be higher than that of the high-resolution MRI velocity maps. However, because magnetic resonance determines an ensemble-average of the properties of individual molecules that carry NMR-active nuclei (such as \(^1\)H), the average fluid velocity of each voxel within the MRI velocity map is an accurate average velocity of all molecules contained within that voxel. So, despite the disparity in spatial resolution, quantitative, voxel-by-voxel comparisons can be made between experimentally acquired MRI velocity flow maps and (coarse-grained) µCT-image-based flow simulations.

However, flow simulations based on segmented X-ray µCT images do suffer from the resolution limit of that imaging method, which may lead to incorrect results. In particular for heterogeneous carbonate rocks, the smallest (micro)pores are still significantly smaller than the voxel size currently accessible with X-ray µCT. The areas in the rock where microporosity is present will have a lower average X-ray absorption because of the globally lower mass density of that area; however, a microporous area cannot be distinguished from a non-porous area with a lower mineral density because the X-ray absorption can be very similar. Using µCT the only way to differentiate the regions of microporosity is to saturate the rock with a doped fluid [180]. In the present work, co-registration of µCT and MRI images makes it possible to non-invasively differentiate between these two, because MRI is sensitive only to fluids and will therefore reveal only the fluid-saturated micropores, but not the areas of solid rock in which no fluid is located – although this may be limited by the effect of the magnetic resonance signal relaxation, i.e., NMR signal disappears faster for fluid in smaller pores.
7.2 Materials and Methods

In the context of DR physics, a key research question is to what extent these smaller pores actually contribute to the overall flow of fluid through the rock, and therefore to what extent a simulation of the flow field based on a µCT-derived pore space is accurate. Although in many cases the microporosity of the rock is not expected to carry significant flow, some regions of the microporous rocks (especially carbonates) can be connected only by microporosity, in which case the contribution to flow by micropores can become significant [122]. It has already been demonstrated [181] via direct flow simulations in combination with mercury injection porosimetry (MIP) and X-ray µCT differential imaging [180] with fluid doping that microporous regions can significantly contribute to the total permeability in heterogeneous carbonate rocks. In fact, Soulaine et al. [182] showed that even in a sandstone rock with only 2.6 % microporosity (2 % sub-voxel porosity), the microporosity can significantly influence the computed permeability values, because microporous regions often serve as bridges between macropores, hence influencing the flow behaviour in the rock. In this work, this question is addressed by comparing single-phase flow simulations, run on segmented 3D µCT images of Ketton and Estaillades limestone rock core plugs, with high-resolution MRI velocity maps that are capable of non-invasively capturing flow information in pore space. The results of the flow simulation will be directly compared to the MRI flow map by co-registration and coarse-graining of the simulation down to the same resolution as the flow MRI data.

This chapter is structured as follows. In Section 7.2, the experimental details of high-resolution MRI flow velocity experiments and direct, pore-scale LBM simulations are given. Qualitative and quantitative comparison between the experimental and simulated velocity fields in rocks is reported in Section 7.3. First, in Section 7.3.1, the analysis of the experimental and simulated velocity maps is demonstrated for the relatively homogeneous Ketton limestone rock. This analysis includes qualitative comparison of the 2D velocity maps extracted from the 3D MRI and LBM datasets, and quantitative comparison between the data on a voxel-by-voxel and pore-by-pore basis. Then, in Section 7.3.2, the benchmarking was extended to compare the MRI and LBM velocity data for the more heterogeneous Estaillades limestone rock. The contribution of microporosity to the total flow rate through the rock is also quantified.

7.2 Materials and Methods

7.2.1 Sample Preparation

A Ketton limestone core plug, 3.84 ± 0.01 mm in diameter and 11.10 ± 0.37 mm in length, and an Estaillades limestone core plug, 3.92 ± 0.02 mm in diameter and 12.65 ± 0.13 mm in length, were used in this study as representative samples of reservoir rocks; 3D sections of these
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Figure 7.1 3D sections extracted from the high-resolution µCT images of (a) Ketton and (b) Estaillades limestone rock core plugs. Overall, the rock plugs were cylindrical, with a diameter of ∼4 mm and length (z) of ∼10 mm.

Table 7.1 Pore network properties of the connected pore space images of the Ketton and Estaillades rock core plugs. To obtain these properties, the grayscale µCT images of the rocks were denoised and then segmented into the pore and grain space images. The properties were then computed from the pore network models, as generated from the connected pore space images. Connected \( \phi_{\text{µCT}} \) refers to the porosity of the connected pore space computed from the µCT image. Image processing was performed in Avizo. The spatial resolution of the images was 7 and 3 µm for Ketton andEstaillades rocks, respectively.

<table>
<thead>
<tr>
<th>Rock</th>
<th>Connected ( \phi_{\text{µCT}} ) (%)</th>
<th>Mean pore radius (µm)</th>
<th>Mean throat radius (µm)</th>
<th>Mean coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketton</td>
<td>14</td>
<td>111</td>
<td>41</td>
<td>4.7</td>
</tr>
<tr>
<td>Estaillades</td>
<td>6</td>
<td>35</td>
<td>15</td>
<td>3.6</td>
</tr>
</tbody>
</table>

rock samples are shown in Fig. 7.1. After drying the samples in an oven overnight at 70 °C and acquiring µCT images, the rock samples were vacuum-saturated with deionised water. The gravimetric porosities, \( \phi_g \), of the water-saturated Ketton and Estaillades rock samples were determined to be \( \phi_g = 21 \pm 4 \% \) and \( \phi_g = 25 \pm 1 \% \), respectively. Further properties of the samples are summarised in Table 7.1.

For flow MRI experiments, the rock samples were placed in an Adtech FEP heat shrink tubing which was used to connect the sample to an inlet and outlet FEP flow line, and to provide confinement. In the case of Estaillades rock, before placing the sample in the heat shrink tubing, two layers of Teflon tape with thickness of 75 µm were applied around the plug to minimise
7.2 Materials and Methods

fluid by-passing through vugs and cracks on the surface of the rock during flow experiments. A constant flow rate of water at 0.03 ml min$^{-1}$ was imposed using a Vindum VP-6 metering pump.

7.2.2 X-Ray Micro-Computed Tomography

7.2.2.1 Ketton Rock

3D µCT data of the dried Ketton rock sample were acquired using a Bruker SkyScan 1172 µCT scanner (Bruker Micro-CT, Belgium) at an isotropic spatial resolution of 5.00 µm. Image acquisition was performed using a source voltage of 60 kV, a source current of 165 µA, and an Al (0.5 mm) filter. 802 projection images were acquired by rotating the sample in angular increments of 0.25$^\circ$ over 200.5$^\circ$ with 10 scans per angular increment, yielding a total acquisition time of 11.4 h. Projection images were reconstructed using the NRecon package (Bruker) to give 2666 cross-sectional slices. To generate a 3D µCT image of the rock sample, all 2D cross-sectional slices were successively stacked.

7.2.2.2 Estaillades Rock

The Estaillades sample was imaged using a Bruker SkyScan 2214 µCT scanner (Bruker Micro-CT, Belgium) at an isotropic spatial resolution of 3.00 µm. Imaging was performed using a source voltage of 90 kV and source current of 70 µA, with an Al (1 mm) filter. To image the entire sample, acquisitions were performed at 5 different scanning positions along the longest dimension of the sample. For each position, 3601 projections were acquired by rotating the sample in angular increments of 0.1$^\circ$ over 360$^\circ$ with 6 scans per angular increment, yielding an acquisition time of 4.26 h. Thus, the total acquisition time was 21.3 h. Projection images from all 5 scanning positions were stitched together and reconstructed using the NRecon package (Bruker) to give 4319 cross-sectional slices. A 3D µCT image was generated by stacking the 2D cross-sectional slices.

7.2.3 Flow MRI

MRI velocity maps were acquired on a 7.0 T vertical-bore magnet controlled by a Bruker BioSpin Avance III HD spectrometer. A Bruker Micro5 tri-axial magnetic field gradient system with a maximum gradient amplitude of 2.9 T m$^{-1}$ was used to achieve the spatial resolution in the three orthogonal z-, x-, and y-directions. An 8 mm r.f. saddle coil tuned to a resonance frequency of 299.84 MHz ($^1$H) was used for spin excitation and signal detection.
Flow velocities through the rock samples were measured along the superficial flow direction, here defined as the $z$-direction.

### 7.2.3.1 Ketton Rock

The main details of the MRI methods employed for the acquisition of velocity maps of Ketton rock are summarised below.

The under-sampled velocity maps of Ketton were acquired using the PGSE-RARE pulse sequence described in Chapter 6. Under-sampling schemes for $k$-space acquisitions were generated using the µCT-VDS approach with a $k$-space sampling fraction of 0.25. The duration of the hard 90° excitation and 180° refocusing r.f. pulses were 6.0 µs and 12.0 µs, respectively. A RARE factor of $N_{RF} = 8$ with an echo spacing of $t_e = 2.2$ ms (SW = 400 kHz) was used to acquire $N_{RF}$ successive lines of $k$-space for each excitation pulse. To achieve velocity encoding, a pair of unipolar gradients $g$ of amplitude $g = 2.0$ T m$^{-1}$ ($g_i = 4.0$ T m$^{-1}$) and duration of $\delta = 0.132$ ms were used, separated by an observation time $\Delta = 4$ ms. With 32 scans for signal averaging and $t_{RD} = 1.1$ s, the acquisition time of the velocity map was 20 h. Velocities were encoded along the $z$-direction, i.e., along the superficial flow direction. Images under no-flow conditions were also acquired to correct for the velocity offsets. Thus, the total acquisition time of the velocity image with velocities encoded in the superficial flow direction was 40 h. The images were acquired with a FOV of 13.5 mm $\times$ 4.5 mm $\times$ 4.5 mm and 384 voxels $\times$ 128 voxels $\times$ 128 voxels in the frequency- ($z$) and phase-encoding ($x$, $y$) directions, respectively, yielding a 3D velocity map with an isotropic resolution of 35.2 µm.

After acquisition, the under-sampled data were reconstructed using an in-house Matlab toolbox, OOMFIP, for which the implementation was presented in [106]. Further details of data reconstruction and image processing can be found in Chapter 6.

### 7.2.3.2 Estaillades Rock

The under-sampled velocity maps of the Estaillades rock plug were acquired using the same PGSE-RARE pulse sequence. Under-sampling schemes were generated using µCT-VDS with a $k$-space sampling fraction of 0.3125. Hard 90° excitation and 180° refocusing r.f. pulses were used with durations of 6.6 µs and 13.2 µs, respectively. The number of echoes in the RARE echo train was $N_{RF} = 8$ with an echo spacing of $t_e = 2.2$ ms (SW = 400 kHz). The velocity imaging parameters were $g_i = 2.3$ T m$^{-1}$, $\delta = 0.132$ ms, and $\Delta = 4$ ms. 32 scans were acquired for signal averaging with $t_{RD} = 1.375$ s, giving an acquisition time of 31.3 h. The total acquisition time of the offset-corrected velocity map was $\sim 63$ h. The velocity maps were acquired with a FOV of 13.5 mm $\times$ 4.5 mm $\times$ 4.5 mm and 384 voxels $\times$ 128 voxels $\times$ 128
voxels in the z-, x-, and y-directions, yielding a 3D velocity map with an isotropic resolution of 35.2 µm. The under-sampled velocity data of Estaillades were reconstructed using the OOMFIP package.

7.2.4 Direct Numerical Pore-Scale Flow Simulations

In this work, LBM simulations were performed directly on the µCT images of the pore space of Ketton and Estaillades carbonate rocks. This section describes the details of image processing used to prepare the µCT data for use as the porous structure upon which the LBM simulations were performed, and the LBM simulations that were performed.

For a more detailed description of the general theory of LBM, the reader is referred to [9, 10].

7.2.4.1 µCT Image Processing

In order to run LBM simulations, a binarized image that represents the structure of each rock sample is required. To achieve this, the acquired µCT intensity images of rocks were denoised, segmented into grain and pore spaces, and masked; for Ketton rock, the µCT image was first coarsened to 7.0 µm using a Lanczos filter [89] due to the data size limitations of the LBM code used (see Section 7.2.4.2). First, the acquired 3D µCT images of rocks were denoised using a non-local mean filter [78]. The denoised images were then binarized using the watershed-based segmentation algorithm [84]. Next, binary cylindrical masks were applied to the grain space images to ensure that the voxels belonging to the grains within the rock and regions outside the rock plug have the same binary intensity value (i.e., intensity = 1), thus guaranteeing that only the pore space has the other binary intensity value (intensity = 0). Lastly, by computing the complement image of the masked grain space image, the pore space image can be obtained on which the fluid flow simulations can be performed.

For Estaillades rock, the binary mask was generated such that ~ 75 µm (one layer of Teflon tape) of the outer portions of the rock are radially removed from the rock plug in the final pore space image. Although this removes some sections of the rock matrix, it also partially accounts for the fact that some of the surface pores in the Estaillades sample were partly blocked by the Teflon tape during the flow experiment, so that the simulation is more structurally consistent with the experimentally acquired MRI data.

7.2.4.2 LBM Simulations

Two LBM algorithms were used in this work to simulate single-phase flow in rocks. In Ketton rock, the fluid flow was computed using an energy-based LBM (eLBM) simulator [170, 171]
which utilises the multiple-relaxation-time (MRT) model as a momentum-balance solver. In Estaillades, the flow was simulated using an MRT-LBM algorithm [183] based on the same MRT solver.

The reason for using a different simulator for each of the different rocks is that for Estaillades rock significant stability issues with eLBM were observed, which is why it was necessary to use MRT-LBM for flow simulations in the Estaillades case. It is important to note that owing to its underlying multi-phase flow formulation and the use of (open) buffers to impose velocity boundary conditions, eLBM is relatively more random-access memory (RAM) intensive than MRT-LBM. Moreover, the velocity boundary condition is more sensitive to the underdiscretization of narrow throats in the digital rock images. Although an attempt was made to simulate flow in Estaillades rock using eLBM, which required coarsening of the Estaillades image to satisfy the eLBM’s memory requirements, it was observed that the resulting image contained a significant amount of underdiscretized narrow throats as well as some pore throats were completely closed to flow due to coarsening. Consequently, significant stability issues with eLBM were observed, and the MRT-LBM code was utilised for flow simulations in Estaillades rock. On the other hand, the MRT-LBM code has a smaller memory footprint due to its underlying single-phase flow formulation. It requires less or no coarsening of the image (depending on the image size) because of its more compact and effective memory management. Moreover, the use of body-force boundary conditions to drive flow in MRT-LBM renders it significantly less sensitive to the presence of narrow throats in terms of stability of flow simulations. Further details of the eLBM and MRT-LBM codes used with respect to their implementations in this work are given below.

eLBM

eLBM is a direct pore-scale visco-capillary flow simulator, which is based on the numerical solution of the Helmholtz free-energy-minimising phase-field model [170, 171]. An MRT model is implemented in eLBM as the collision operator (relaxation term) to represent the particle collision processes. The distributed parallel general-purpose graphics processing unit (GPGPU) code implementation of the eLBM code enables pore-scale simulations to be efficiently run directly on large 3D µCT images of rocks. The implementation of the eLBM code is performed in Compute Unified Device Architecture (CUDA) programming language to take maximum advantage of accelerated computing multi-node GPGPUs. According to [170], eLBM is the first industry-grade distributed parallel implementation of an energy-based LBM which takes advantage of multiple GPGPU nodes.

In eLBM, fluid is injected from the inlet buffer layer into the pore space with a constant prescribed velocity boundary condition. The outlet boundary condition is the gradient-free
boundary to mimic the situation where the porous medium behaves in such a way that is larger than the simulated domain size (i.e., the fluids that are exiting the domain behave as if the domain is continued in a halo cell at the outlet). Loop boundary conditions are imposed on the surfaces of the domain that are perpendicular to the main flow direction [183]. However, if the image naturally has solid walls at the outer surfaces of the domain that are normal to the main flow direction, the loop boundary condition implementation automatically reduces to the closed (no-flow) boundary conditions (i.e., the fluids cannot exit on one side and enter in the other side with no-slip boundary conditions on solid surfaces). In fact, for the velocity vector, the no-slip boundary condition is imposed on all fluid-solid boundaries including the no-flow boundaries on the external surfaces of the global domain. In this work, eLBM is run in single-phase mode by initializing the pore-space with a single-phase fluid and injecting the same phase at the inlet. Therefore, a diffuse interface does not emerge in these simulations. In other words, eLBM can be seen as MRT-LBM [183] with constant velocity inlet and gradient-free outlet boundary conditions. Further details of eLBM are documented in references [170, 171].

MRT-LBM

The MRT-LBM algorithm used in this work is based on the MRT model and a precise treatment of body force that drives the flow [183]. The Boltzmann equation is discretized in space, velocity (momentum), and time coordinates using a 3D 19-velocity grid (D3Q19 scheme), which provides the optimal compromise between accuracy and computational efficiency. The conventional approach of representing particle collision (or relaxation towards an equilibrium state due to collision) is based on the single-relaxation time Bhatnagar-Gross-Krook (BGK) model [184], where a single relaxation time is employed to describe the relaxation processes. However, this model has several deficiencies, such as numerical instabilities at relatively high Reynolds numbers [183]. In the MRT model [185], the velocity distribution function is transformed into moment space, where individual moments can be relaxed at individual rates. Overall, the MRT model has several advantages over the conventional single-relaxation time BGK model, and those include: (1) enhanced numerical stability, (2) independent bulk and shear viscosities, and (3) viscosity-independent, non-slip boundary conditions [183]. The drawback of the MRT model is that it is slightly more computationally demanding compared to the BGK model. This minor hurdle is easily overcome through a GPGPU implementation of the MRT model for eLBM and MRT-LBM. Furthermore, similar to eLBM, the implementation of MRT-LBM code is performed in CUDA programming language to take maximum advantage of GPGPUs.

In MRT-LBM, fluid is driven by a body-force term by imposing a loop boundary condition on the inlet and outlet faces of the domain. The same body force is used for the fluid that leaves
the domain at a given domain-boundary surface (e.g., the outlet face of the domain) and enters the domain at the opposite boundary surface (e.g., the inlet face of the domain). A precise treatment of body-force is required to eliminate errors in velocity gradients. For the velocity vector, the zero-slip boundary condition is imposed on the surfaces between rock grains and fluid within the pore space. More information on MRT-LBM can be found in the following reference [183].

**Simulation details**

Simulations were performed on large 3D µCT images with a size of 1671 voxels × 643 voxels × 643 voxels (in the z, x, and y directions) at an isotropic spatial resolution of 7.0 µm for the Ketton rock plug, and 4279 voxels × 1500 voxels × 1500 voxels (in the z, x, and y directions) at an isotropic spatial resolution of 3.0 µm for the Estaillades rock plug. Experimental details of eLBM and MRT-LBM are given below.

A multi-relaxation-time algorithm was used in both MRT-LBM and eLBM [170, 171, 183]. The relaxation time associated with the single-phase fluid was selected to model a fluid with a viscosity of 1.0 cp in the simulations, i.e., water. Assuming a density of 1.0, lattice spacing of 1.0, and lattice time step of 1.0 (all in lattice units), the relaxation time can be computed as 3.5 (Eq. 16 in Alpak et al. [170]). A body force of $1.0 \times 10^{-5}$ in lattice units was used to drive the (initial) flow in the main flow direction in MRT-LBM. On the other hand, fluid flow was driven by a constant flow rate of $2.0 \times 10^{-5}$ in lattice units into the inlet buffer in eLBM. Simulations were terminated after steady-state flow conditions were attained both in MRT-LBM and eLBM applications. Two criteria need to be satisfied to characterise the steady-state flow in this implementation: (1) the change in the mean velocity should be less than $1.0 \times 10^{-7}$%; and (2) the change in the variance of the velocity field should be less than $1.0 \times 10^{-7}$ %. It was observed that the steady-state velocity field does not have a strong dependence on the boundary conditions and convergence criteria as long as reasonable values that do not violate the underlying assumptions of MRT-LBM and eLBM are used [170, 171, 183].

MRT-LBM and eLBM simulations were performed on a Linux based central processing unit-GPGPU (CPU-GPGPU) high-performance computing (HPC) cluster. All simulations were performed using eight cluster nodes each with two Tesla K80 GPGPU cards each. The technical specification of each CPU-GPGPU node is as follows: HP Proliant XL250a Gen9, 24 Cores - Intel(R) Haswell - Xeon(R) CPU E5-2680 v3 @ 2.50 GHz, 256 GB DRAM, 0.8 TB /scratch, 10 Gbps Ethernet, 56 Gbps Fully Non-Blocking FDR (FBB) Infiniband, 2 Tesla K80 GPGPU cards per node. It is important to note that each Tesla K80 card has $\sim 5000$ CUDA cores and 24 GB of RAM. Simulations utilized 100% of the GPGPU nodes’ processing potential. In other words, no two simultaneous simulation jobs were submitted to the same GPGPU nodes.
In order to be able to quantitatively compare the LBM and MRI velocity data, the velocities of the high-resolution LBM simulations were scaled such that the mean slice-by-slice flow rate of the LBM simulations was equal to the imposed flow rate of 0.03 ml min$^{-1}$. The flow rate for each slice was calculated by multiplying the sum of all velocities within the slice with the cross-sectional area of each voxel. In the case of Estaillades rock, the high-resolution simulation data were first coarse-grained (Lanczos filter) to 6.0 µm spatial resolution for more efficient image registration and data manipulation. For all quantitative analysis, the simulated data were down-sampled (Lanczos filter) to 35 µm spatial resolution to enable direct comparison with the acquired MRI velocity data.

### 7.2.5 Image Co-Registration

Image co-registration was performed in Avizo using the “Register Images” module. The aim of the image co-registration was to spatially align MRI velocity maps and μCT-based LBM simulations in order to be able to qualitatively and quantitatively compare the flow fields of both methods. MRI intensity images, obtained by calculating the magnitude of complex-valued no-flow MRI datasets, and μCT grayscale intensity images, used to generate the pore space for simulations, were used as inputs for image registration. The main steps of image registration process are now discussed. First, the μCT intensity image (model image) was manually pre-aligned with the MRI intensity image (reference image). Next, the alignment of the model image relative to the reference image was optimised using rigid transformations with the normalised mutual information [86, 87] as a metric for the goodness of image alignment. In the optimisation procedure, the data were down-sampled, and the image registration was performed in steps at increasing spatial resolutions for more efficient image registration. Extensive direction and Quasi Newton optimizers were used for the co-registration of the coarse-resolution and the finest-resolution images, respectively. After the image co-registration process was completed, the resulting transformation of the μCT intensity image was applied to the LBM simulation. Last, the co-aligned μCT intensity image and LBM simulation were resampled onto the MRI data coordinate system using a Lanczos filter [89], which enables MRI flow maps and μCT-based images, including LBM simulations, to be visualised and compared on the same grid.

### 7.3 Results and Discussion

In this section, the LBM simulations and MRI velocity data for Ketton and Estaillades rock core plugs are compared. This includes a qualitative comparison of 2D image slices extracted
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from the 3D datasets and a quantitative voxel-by-voxel and more macroscopic, pore-by-pore comparison between the LBM and MRI data. First, this analysis was carried out for the Ketton limestone rock. Ketton rock represents a case where both methods, MRI and µCT, capture predominantly the macroporosity of the rock (i.e., large, intergranular pores). In the case of MRI, the information from the fluid in the micropores is not captured due to the rapid NMR signal decay (short transverse relaxation times) of the water molecules in the intragranular pores within the Ketton ooids. Second, the simulation and experimental data are compared for the Estaillades limestone rock, which has much more complex pore geometry and has more poorly connected rock structure than Ketton rock. In this case, MRI also reveals the flow information about fluids in the micropores due to the slower signal decay in the pores which enabled fluid information to be captured by MRI.

7.3.1 Ketton Rock

Figure 7.2 shows 2D (xy) slice images extracted from the 3D high-resolution LBM simulation at 7 µm spatial resolution and MRI velocity map at 35 µm spatial resolution, co-registered with the µCT structural image of the same Ketton rock sample. The images shown in Fig. 7.2 represent the velocity component in the superficial flow direction (z). Good agreement is observed between the LBM simulation and MRI velocity data. Essentially all characteristics of the flow behaviour present in the MRI flow maps in Ketton are reproduced by the LBM simulation. This includes the location of high-velocity flow channels and the occurrence and location of the regions with backflow (i.e., negative (z) velocities). As is evident from the difference map in Fig. 7.2, the magnitude of simulated velocities is also in a good agreement with the acquired MRI velocities, although LBM seems to underestimate the magnitude of velocities in the high-velocity flow channels of the rock. This observation is in agreement with the results (obtained on a packed bed) reported by Yang et al. [177], but contradicts those reported by Manz et al. [147] who reported that LBM overpredicts large velocities in a beadpack composed of spherical beads; the latter could be due to a different LBM code used to simulate flow. Standard deviation calculated from the middle section of the 3D difference flow map is 0.37 mm s$^{-1}$. Overall, both the simulated and MRI data show that the flow in Ketton rock is highly heterogeneous with the flow being carried by a few high-velocity flow channels.

To further investigate the agreement between the experimental and simulated flow data, more quantitative analysis was performed by comparing the velocity distributions and voxel-by-voxel velocities of the two datasets; the results of this analysis are shown in Fig. 7.3 and Fig. 7.4, respectively. Figure 7.3 shows that the (original) simulated (green dotted line) and experimental (black line) distributions of $v_z$ are significantly skewed and have a long positive tail, which extends far beyond the modal velocity of each distribution, and a considerable degree
Figure 7.2 Comparison between the LBM simulation and MRI velocity map in Ketton rock. Three different 2D slice images extracted from the 3D co-registered MRI and µCT dataset are shown. Good agreement is observed between the simulation and MRI experiment. The difference map ($v_z^{(MRI)} - v_z^{(LBM)}$) was obtained by calculating the difference between the coarse-grained LBM simulation and MRI flow map. The velocity maps shown represent the velocity component in the superficial ($z$) flow direction.

of backflow, which is represented by negative velocities. The experimental and simulated distributions also show that a significant amount of fluid in the pore space of Ketton rock is stagnant or near stagnant with velocities around $v_z = 0$ mm s$^{-1}$. This observation is consistent
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Figure 7.3 Velocity distributions of LBM simulation (⋯) and MRI velocity map (—) of Ketton rock. The velocity distribution of LBM simulation convoluted with a noise-related Gaussian distribution with standard deviation of 0.15 mm s\(^{-1}\) is also shown (−−−).

with the visual inspection of velocity maps in Fig. 7.2, where fluid in the majority of pores appears to be near stagnant. However, there also are noticeable differences between the two velocity distributions. In terms of the shape of the distributions, the two main discrepancies are the location and population of the modal velocity peak and the distribution of backflow. Compared to the MRI velocity distribution with the modal velocity of \(v_z \approx 0.08\) mm s\(^{-1}\), the modal velocity peak of the simulated dataset is located at a lower velocity of \(v_z \approx 0.02\) mm s\(^{-1}\). MRI velocity measurements are, of course, affected by experimental noise, which can decrease the sharpness of the modal velocity peak and, in general, lead to broadening of the velocity distribution. The noise-related uncertainty in the MRI velocity measurements can be estimated from the intensity images since error in measured velocities is reciprocally proportional to the SNR of the images [148, 152]. It was estimated that in this case the noise-related velocity errors in pores fully-saturated with water are on the order of 0.03 mm s\(^{-1}\), relative to the measured velocities. However, in the voxels at the edges of grains, these errors can be as large as \(\sim 0.2\) mm s\(^{-1}\) because of lower SNR due to partial volume effects. To investigate the effect of noise on the MRI measurements, the LBM velocity distribution was convoluted with a noise-related Gaussian distribution with a standard deviation of 0.15 mm s\(^{-1}\), the result of which is represented by the red dashed line in Fig. 7.3 (the standard deviation of 0.15 mm s\(^{-1}\) is the upper limit of the noise-related uncertainty in MRI velocity measurements). It can be seen in Fig. 7.3 that there is now excellent agreement between the simulation and experimentally-acquired data.
Voxel-by-voxel comparison between the simulated and experimental velocity maps is shown in Fig. 7.4. Overall, good agreement is observed between the two datasets, as most voxels lie close to the straight reference line (white dashed line) with a slope of unity. Significant differences between the MRI and simulated velocities are observed for a relatively small number of voxels (note the logarithmic scale of the color bar). It can be also seen in Fig. 7.4 that a number of voxels which represent stagnant or near-stagnant liquid in the LBM simulation exhibit a range of positive and negative velocities significantly greater than $v_z = 0$ mm s$^{-1}$ in the MRI velocity map. This can be partly explained by the experimental noise, especially at the pore-grain interfaces where noise can compromise the accuracy of the measured velocities due to partial volume effects. It is also important to recognize that while the pore-grain interface phenomena occur at the molecular (angstrom) scale, the simulation model is constructed at the pore (micron) scale. The simulation model imposes zero velocity boundary condition at the pore-grain interface, whilst the precise location of this interface is inevitably affected by the voxel resolution, and so this may also lead to deviations in the velocity close to the interface assuming that experimental data is resolving/capturing a large portion of the physical phenomena in this neighbourhood. This physical vs. simulation discrepancy in pore-grain interface representation and its implications on the velocity field is largely a localised effect unless the voxel resolution is unreasonably low in the simulation. As such, these localised errors in the immediate vicinity of the physical interface do not accumulate and propagate in the simulation.
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Figure 7.5 Pore-scale comparison between the LBM simulation and MRI velocity map of the Ketton rock core plug. (a) Pore-by-pore correlation between the experimental and simulated mean $z$-velocities within a pore, $v_m^z$. The black dashed line represents a reference line with a slope of unity, but the solid blue line represents the regression fit to the data. (b) The fractional summed $z$-velocities within pores with a summed $z$-velocity equal to or greater than (the parametric variable) $i$, $v_{z}^\text{sum}(i)/v_{z}^\text{sum, tot}$, plotted as a function of the fraction of the number of pores, $N_p(i)/N_p^{\text{tot}}$, carrying this flow for velocity data representing MRI (——) and LBM (---).

The experimental and simulated velocity data were further analysed using a pore-scale approach, wherein velocity information was obtained for each individual pore in the images and then compared between the two datasets. To achieve this, a (combined) binarized structural image was first generated from the individual binary masks of the MRI and LBM datasets by only selecting the voxels that are shared between the two datasets. This is done so that the same pores consisting of the same number of voxels can be later identified using pore labelling. The pore space of the structural image was then separated into individual, labelled pores using a Chamfer distance map and marker-based watershed algorithm [84] in Avizo. The labelled structural image and each velocity dataset separately (MRI or LBM) were then used as inputs in the labelled pore analysis to extract and correlate the flow properties for individual pores. The results of this analysis are shown in Fig. 7.5. Figure 7.5a shows a pore-by-pore comparison between the simulated and experimental velocity data; the black dashed line in the plot represents a reference line with a slope of unity, but the blue line is a regression fit to the data. Although there is a good overall agreement between the two datasets, the general trend is that the LBM simulation slightly underpredicts large pore velocities, but overpredicts small and negative pore velocities; inspection of Fig. 7.2 and Fig. 7.4 also reveals a similar trend. This observation, however, cannot be fully explained by the experimental noise. In
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Fig. 7.5b, the fraction of the total flow \( \frac{v_{\text{sum}}(i)}{v_{\text{sum, tot}}} \) is plotted as a function of the fraction of the number \( \frac{N_p(i)}{N_p^{\text{tot}}} \) of pores that carry this flow for both datasets. As can be seen, agreement between experiment and LBM simulation is excellent. An interesting aspect of the data shown in Fig. 7.5b is the indication that the flow field in Ketton rock exhibits significant heterogeneity on the pore scale with 10 % of the pores carrying \( \approx 50 \% \) of the flow. These results are consistent with the heterogeneity seen in the velocity fields in Fig. 7.2.

7.3.2 Estaillades Rock

7.3.2.1 Benchmarking of the LBM Simulation

To illustrate both the fluid-saturated microporous and macroporous regions in Estaillades rock, the magnetic resonance intensity image of the rock sample, generated from the complex-valued MRI data, was co-registered with a \( \mu \)CT image of the rock; a 2D (\( xy \)) slice image of the co-registered MRI and \( \mu \)CT dataset is shown in Fig. 7.6, where the blue and green colour intensities represent the amount of water in the micropores and macropores of the rock, respectively. Figure 7.6 shows that microporosity occupies large regions of the rock, whereas only a few macropores can be identified in the rock structure; the latter are likely to carry most of the flow through the rock. It can also be seen that no water is present within the dense calcitic grains of the Estaillades formation.

**Figure 7.6** 2D (\( xy \)) slice image extracted from the 3D co-registered MRI intensity and \( \mu \)CT images of the Estaillades carbonate rock plug. The four red boxes labelled a, b, c, and d represent a microporous grain, a non-porous calcitic grain, a mesh of medium-sized pores, and a large macropore, respectively. The MR signal intensity is proportional to the local water content in the rock.
Figure 7.7 Comparison between the LBM simulation and MRI velocity map in Estaillades rock. Three different 2D slice images extracted from the 3D co-registered MRI and μCT dataset are shown. The difference map \( (v_z^{(MRI)} - v_z^{(LBM)}) \) was obtained by calculating the difference between the coarse-grained LBM simulation and MRI flow map. The velocity maps shown represent the velocity component in the superficial \((z)\) flow direction. Three regions, namely a, b, c, and d, have been highlighted by the red boxes which identify interesting flow patterns in the rock.

The flow MRI data of the Estaillades rock sample are now discussed, along with the comparison with the LBM flow simulations. Figure 7.7 shows 2D \((xy)\) slice images of Estaillades rock obtained from the 3D LBM simulation at 6 \(\mu\)m spatial resolution and MRI velocity map at
35 µm spatial resolution, co-registered with the µCT dataset of the rock; the images represent the velocity component in the superficial flow direction (z). Considering the complex structure of the Estaillades formation, good qualitative agreement is observed (ignoring microporous regions) between the three image slices of the LBM and MRI datasets, with some local deviations in some of the pores. Similarly to Ketton rock, it can be seen in both LBM and MRI data that the flow in Estaillades rock is highly heterogeneous with a few high-velocity flow channels. MRI flow maps also reveal that the fluid is stagnant or near-stagnant in the microporous regions of the rock (i.e., dark grey µCT image intensities). To further inspect the flow fields, four regions in Fig. 7.7 have been highlighted by red boxes. Region “a” (top slice) represents a large pore where the LBM predicts the formation of a high velocity flow channel with \( v_z \gtrsim 5 \text{ mm s}^{-1} \) and a diameter extending to about half of the width of the pore, whereas the MRI velocity map shows lower velocities in the same pore. Interestingly, the acquired MRI velocity map indicates that two relatively small high-velocity channels have formed in region “a”, instead of one, as predicted by LBM. In the other large pores in this image slice with significant flow, LBM tends to underestimate the flow velocity, as is evident from the difference map. Fig. 7.7 region “b” shows another high-velocity flow channel in the middle of a relatively large pore – in this case the LBM has accurately predicted the location and velocity of the flow field. In region “c”, a microporous rock grain can be seen. No flow information was obtained from this region using the LBM simulation, because the pore size was below the imaging resolution of X-ray µCT. However, using MRI the average flow velocity can be accurately measured at voxel sizes much greater than the pore size of the fluid-saturated rocks [151, 152]. In this case, the MRI flow map indicates that the microporous grain contains stagnant or near stagnant fluid. Lastly, region “d” shows complex flow behaviour with adjacent positive and negative flow channels in a large macropore. This complex flow behaviour has been relatively accurately predicted by LBM, as good qualitative agreement in this region is observed between the MRI and LBM velocity data.

Visual inspection of Fig. 7.7 reveals that although in some of the pores complex flow patterns are predicted well by the LBM simulation, in some pores significant differences between MRI and LBM data can be seen. To investigate these discrepancies in more detail, a more quantitative analysis similar to that carried out for the Ketton sample was performed on a pore-by-pore basis. This analysis was carried out for the macroporous regions of the rock that are shared between the binarized (structural) images of the MRI and LBM datasets. The results of this analysis are shown in Fig. 7.8; note that this analysis resulted in a large number of small pores (consisting of a few voxels), hence for clarity only pores with radius greater than 35 µm are shown. Figure 7.8a shows that there is a much greater scatter of the points and deviation from the reference line of slope unity relative to the data observed for the Ketton sample (Fig. 7.5a). However, as with the Ketton data, the LBM simulation generally
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Figure 7.8 Pore-scale comparison between the LBM simulation and MRI velocity map of the macroporosity in the Estaillades rock core plug. (a) Pore-by-pore correlation between the experimental and simulated mean $z$-velocities within a pore, $v^m_z$. The black dashed line represents a reference line with a slope of unity, but the solid blue line represents the regression fit to the data. (b) The fractional summed $z$-velocities within pores with a summed $z$-velocity equal to or greater than (the parametric variable) $i$, $v^\text{sum}(i)/v^\text{sum, tot}$, plotted as a function of the fraction of the number of pores, $N_p(i)/N^\text{tot}_p$, carrying this flow for velocity data representing MRI (—) and LBM (—-).

underestimates large pore velocities, but overestimates negative pore velocities. As can be seen in Fig. 7.8a, there is a large number of pores in the MRI velocity map with significant negative and positive mean pore $z$-velocities, $v^m_z$, which have $v^m_z \sim 0 \text{ mm s}^{-1}$ in the LBM simulation. A close inspection of the LBM simulation shown in Fig. 7.7 also reveals a similar trend as the LBM simulation predicts more highly localised flow than is seen in the MRI velocity data. This observation is also supported by the plot shown in Fig. 7.8b, where, based on the LBM data, approximately 94 % of the flow in the Estaillades rock is carried by just 10 % of the pores. Similarly, data extracted from the acquired MRI velocity map indicate that the flow through the macroporous regions of the rock is highly heterogeneous with 10 % of the pores carrying $\approx 80$ % of the flow. Compared to Ketton rock, where 50 % of the flow was carried by 10 % of the pores, $\sim 60$ % more flow is passing through the same percentage of pores in the Estaillades formation, which is an indication of its highly heterogeneous rock microstructure.

There are several sources of error that may contribute to the error in the experimental and simulated velocity maps and lead to the discrepancies between the two datasets. As was already discussed in Section 7.3.1, one source of error is the experimental noise present in the MRI velocity data. In the flow MRI data of Estaillades rock, the noise-related velocity errors are estimated to be on the order of 0.06 mm s$^{-1}$ and 0.2 mm s$^{-1}$ for the macroporous and
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microporous regions (green and blue regions in Fig. 7.6), respectively. Noise-related velocity errors of $\sim 0.2 \text{ mm s}^{-1}$ are also present in the voxels at the interfaces between the macropores and rock grains. In the microporous regions of the rock, where the typical fluid velocities are $< 1 \text{ mm s}^{-1}$, the uncertainty of $\sim 0.2 \text{ mm s}^{-1}$ can significantly influence the accuracy of the measured velocity on a per-pixel basis (microporous regions were excluded from the analysis shown in Fig. 7.8). These errors are larger than those estimated from the MRI images of Ketton rock. Two other possible sources of error in the MRI flow velocity measurements include the internal gradient effects and asymmetry of the intravoxel displacement distribution, which were discussed in detail in Chapter 3 and Chapter 6, respectively. These two types of errors could, in principle, be minimised by generating a velocity map from APGSTE-based spatially-resolved propagator measurements; however, at 35 µm spatial resolution, spatially-resolved propagator data would take prohibitively long time to acquire. One of the main sources of error in both the experiment and simulation is the partial volume effect, which increases with decreasing spatial resolution of the images [97, 186]. In MRI, partial volume effects reduce the signal available in voxels that contain both fluid and rock matrix phases, which results in larger velocity errors in those voxels due to lower SNR. An additional loss of signal in such voxels is caused by shorter $T_2$ relaxation times, relative to voxels that contain only fluid. In terms of the LBM simulations, it has been demonstrated that the uncertainty in the computed single-phase flow properties increases with increasing voxel size [7, 67] for a given rock type as limited by the typical pore throat size. Another limitation of the LBM simulation is that it is run on a segmented µCT image that represents only the connected pore space of the rock that can be resolved at the imaging resolution used, which can lead to further inconsistencies between the experiment and the simulation. These types of errors are expected to be greater in the case of Estaillades than in Ketton due to its smaller pore throat size to voxel size ratio (Ketton: 6, Estaillades: 5), lower connected porosity (connected $\phi_{\mu CT}$), and its more complex rock geometry [7, 67].

7.3.2.2 The Contribution of Microporosity to the Total Flow in Estaillades Rock

The qualitative analysis of Fig. 7.7 indicated that the fluid-saturated micropores mainly exhibit low flow velocities. However, as is evident from Fig. 7.6, microporosity occupies a large proportion of the total porosity in Estaillades rock (in Fig. 7.7 only parts of microporous regions were displayed for clearer visualisation of velocity maps). In fact, microporosity can constitute more than half of the total rock porosity in the Estaillades formation [98, 187]. To investigate the extent to which these fluid-saturated micropores, which occupy a significant portion of the total porosity, affect the global flow rate, quantitative analysis was performed on the MRI velocity map with velocities encoded in the superficial flow direction ($z$). For this analysis, the flow rate, $Q_z$, for each axial ($xy$) image slice was calculated by summing the $z$-velocities
Figure 7.9 Calculated flow rate, $Q_z$, for each image slice in the middle region of the Estaillades rock core plug. The black, blue, and green lines represent the total porosity (—), macroporosity (—), and microporosity (—) of the rock. The red dashed line (---) represents the flow rate, which was imposed during MRI experiments, i.e., at $Q_z = 0.03 \text{ ml min}^{-1}$.

of each voxel within a given slice and then multiplying by the cross-sectional area of a single voxel. This analysis was performed for three separate images, namely the total porosity image, the macroporosity image, and the microporosity image. To generate an accurate value of $Q_z$ for each image slice, the velocity map was first multiplied by two masks, which were generated by manual thresholding of the MRI intensity image (Fig. 7.6). The first mask is needed to null the background noise and to separate the macroporous regions and the microporous regions; in the context of this analysis, the macroporous regions are defined as the regions with large and medium-sized pores that are coloured in green in Fig. 7.6 (i.e., ~ the pores that can be captured by µCT, as shown in Fig. 7.7), but the microporous regions, in the context of this study, are defined as regions with pore sizes well below image resolution – these are coloured in blue in Fig. 7.6. The second mask, which is computed by averaging multiple binary masks at different threshold values, is required to account for the partial volume effects and the fact that the majority of voxels are only partially saturated by water in order to make an accurate estimate of $Q_z$. The plot of $Q_z$ as a function of the position of the image slices for the three different porosity images in the middle region of the rock is shown in Fig. 7.9. It can be seen that although most of the flow goes through macropores, the microporous regions also noticeably contribute to the total flow rate through the Estaillades plug. For example, for the region of the rock from ~ 0.5 to 1.3 mm along the $z$-direction, the macroporous and microporous regions have approximately the same contribution to the total flow through the rock. The average contribution of microporosity to flow in this region of the rock was estimated to be $36 \pm$
5% relative to the average total \( Q_z \) (the uncertainty was estimated by varying the manual segmentation threshold value by ±10% relative to the chosen threshold). Given the significant flow through the micropores in Estaillades rock, it is not perhaps surprising to observe some discrepancies between the MRI and LBM velocity fields, since the LBM simulations were run on the macropore network of Estaillades rock. Note that in the MRI velocity image of Ketton rock, the macropore network alone (as shown in Fig. 7.2) accounted for the total \( Q_z \) in the rock, so the contribution of micropores to the flow is expected to be minor. These results are somewhat similar with the previous findings reported by Bijeljic et al. [181] who, based on the methodology of direct flow simulations, MIP, and differential X-ray imaging (30% KI dopant solution was used), demonstrated that microporosity in Ketton and Estaillades rocks contribute approximately 17 and 39%, respectively, to the overall computed permeabilities (the micropores were defined as the pores with sizes below the imaging resolution of 5 µm). This simple analysis indicates that microporosity plays an important role in the fluid flow and transport processes in microporous carbonate rocks.

### 7.4 Conclusions

In this chapter, high-resolution MR flow velocity imaging at 35 µm spatial resolution has been used to provide a robust benchmark of the DR single-phase LBM simulations in two carbonate rocks, namely the Ketton and Estaillades limestone. In order to be able to qualitatively and quantitatively compare the simulated and experimental velocity data, the velocity maps were co-registered with the high-resolution µCT structural images of the same rock core plugs, on the basis of which the LBM simulations were run.

First, the results were demonstrated for the simplest of the two cases – Ketton limestone rock, which is a relatively homogeneous carbonate sample with large macropores. Inspection of the velocity maps indicated that the LBM simulation used was able to accurately predict the location of high-velocity flow channels and backflow, and, in general, also the magnitude of the velocities. Excellent agreement between the MRI and LBM data was observed in various plots which quantitatively compare the two datasets. It was also observed that the LBM tends to underpredict large flow velocities in some of the pores.

Second, the experimental and simulated velocity maps for the more heterogeneous Estaillades rock were presented and analysed. Estaillades is a heterogeneous carbonate rock with a more complex rock microstructure and smaller pores than Ketton rock, hence presented a more challenging case for simulation. Comparison of the 2D visualisations extracted from the 3D co-registered velocity and structural images revealed that the LBM can reproduce many complex flow patterns in the Estaillades formation. However, in some pores noticeable
differences between the MRI and LBM velocity maps were observed, which was also reflected in a quantitative comparison between the two datasets. Furthermore, it was demonstrated that the flow in Estaillades rock is highly heterogeneous with approximately 80% of the flow being carried by just 10% of the pores; in the Ketton core plug ≈ 50% of the flow was carried by the same percentage of the pores in the rock. Analysis of the MRI velocity map revealed that approximately one third of the total flow through theEstaillades formation is carried by microporosity.
Chapter 8

Chemically-Selective High-Resolution MRI

8.1 Introduction

One of the key aims of DR technology is to be able to predict multi-phase displacement processes in porous rocks at the pore-to-core scale, although the long term goal is to use this technology to simulate macroscopic processes at the reservoir scale in order to evaluate reservoir production potentials [6, 188, 189]. Compared to single-phase flow simulations, pore-scale simulations of multi-phase flow are much more challenging. This is because in multi-phase flow the challenge is to track the complex dynamics of fluid-fluid interfaces and to account for the behaviour of contact angles (wettability), which is also inherently complex and sensitive to heterogeneities in physical and chemical properties of rocks. One way of how to account for the complexity of these systems in modelling is to integrate multi-phase simulations with the experimentally acquired data [6, 190, 191]. The experimental data can not only be used for the validation of multi-phase simulators, but can also provide useful input for multi-phase simulations or pore network models. For example, multi-phase images could be used to initialise relative permeability predictions or to provide information on the pore-scale displacement mechanisms or likely contact angles in the multi-phase system of interest that can be exploited to improve DR modelling capabilities.

To date, the two most widely employed techniques that have been used to great effect to investigate multi-phase flow in porous rocks are X-ray μCT [6, 8, 15, 190, 192] and MRI [17, 26, 101, 193]. As has been mentioned in the previous chapters, the advantage of X-ray μCT is its capability to routinely produce high spatial resolution images with resolutions on the order of a few microns. However, the drawback of using μCT for imaging multi-phase systems is that
a doping agent is typically required to obtain sufficient contrast between fluid phases of similar densities (e.g., oil and water), which can potentially alter the properties of the system. Although the spatial resolution of routine MRI acquisitions is on the order of a few hundred microns, the advantage of MRI is that it provides a range of different non-invasive contrast mechanisms which enable information about various fluid phases in the system to be independently acquired.

The most common non-invasive contrast mechanisms that are exploited in MR to discriminate between different fluid phases include $T_1$ and $T_2$ weighting, diffusion weighting, detection of specific NMR-active nuclei (e.g., $^1$H, $^{23}$Na), and spectroscopic chemical shift sensitivity. The choice of the contrast mechanism used in the MRI experiment depends on the nature of the experiment and the system (i.e., types of fluids and rocks used) under investigation. The use of these contrast mechanisms for the petrophysical applications are briefly reviewed below.

One of the contrast mechanisms that has been widely utilised to discriminate between the aqueous and oil fluid phases in porous materials is relaxation weighting, i.e., the relaxation time differences between fluids. Hall and Rajanayagam [194] incorporated an inversion-recovery pulse sequence into a 3D imaging sequence which allowed them to acquire separate 3D water and oil images of a sandstone sample based on the differences in the $T_1$ relaxation times of the water and oil fluid phases. $T_1$ contrast was also employed by Davies et al. [195] who developed a saturation-recovery-based MRI method to acquire 2D images of water and oil at 0.8 mm spatial resolution in a chalk reservoir rock. $T_2$-based fluid phase discrimination of aqueous and oil phases was demonstrated by Mitchell et al. [193] who used 1D spatially-resolved $T_2$ maps to monitor oil recovery in a microporous limestone core plug during a brine flood. Oil and brine specific 1D saturation profiles were determined by integrating the signal intensities of the respective $T_2$ regions of the fluid phases in the $T_2$-distribution along the length of the plug. Vashaee et al. [196] utilised both $T_1$ and $T_2$ relaxation times to acquire spatially-resolved (slice-selective) $T_1$-$T_2$ distributions in a Bentheimer sandstone saturated with crude oil and brine during different oil saturation stages. They showed that oil and brine saturations, which were calculated from the $T_1$-$T_2$ distributions according to the $T_1$-$T_2$ cut-off, are in quantitative agreement with the direct volumetric saturations of oil and brine. Alternatively, MR methods that exploit the differences of fluid diffusion coefficients can also be used to distinguish between the oil and water fluid phases. Of relevance to the present work, both spatially-unresolved [24, 25] and spatially-resolved [197] (1D) $D$-$T_2$ correlations have been successfully used to quantify and discriminate between water and oil phases during core flooding experiments in rocks. However, a successful use of relaxation time and diffusion-based contrast MR methods rely on clear separation of the relaxation or diffusion properties of the fluids studied. In cases where there is not a clear separation of the inherent NMR properties, the addition of doping agents may be required in order to enhance the fluid phase contrast [193].
Another method that can be used to discriminate between multiple fluid phases in porous media is based on a nuclear-specific NMR signal detection. Of course, in order to separate fluid phases based on the detection of a specific nucleus, for example, in a two-phase system, this specific nucleus needs to be present in only one of the two phases. In the context of petrophysical laboratory measurements, $^{23}$Na MRI is a popular choice [21, 198], because sodium-containing brine is present in many reservoirs and, for this reason, is also often used in laboratory core flood experiments. A successful application of $^{23}$Na MRI was demonstrated by Washburn and Madelin [198] who used a $^{23}$Na spin-echo MRI method to acquire 2D images of the aqueous (brine) phase in a Bentheimer sandstone saturated with brine and mineral oil. Other nucleus-specific MRI methods have been demonstrated to acquire images of fluid-saturated rock core plugs, such as $^7$Li MRI [199], which is a great alternative to $^{23}$Na MRI for imaging aqueous phases, and $^{19}$F MRI [21, 199], which could be used for imaging fluorinated hydrocarbons. The disadvantage of using the nucleus-specific MR methods is that they only provide direct information about the fluid phase that contains this nucleus, but not about other phases. In addition, MR measurements of nuclei such as $^{23}$Na and $^7$Li are much less sensitive compared to $^1$H MRI, which makes the acquisition of high-resolution MRI images more time-consuming.

If, for a multi-phase system, the hydrocarbon and aqueous phases can be resolved in a single NMR spectrum, discrimination between the two phases can also be achieved using spectroscopic chemical shift sensitivity. When a spectroscopic chemical shift sensitivity NMR measurement, which independently isolates the signal from the two fluid phases, is integrated in an imaging experiment, we obtain an MRI experiment that is capable of imaging fluid phases independently of one another; here, for simplicity, this method will be referred to as chemically-selective MRI. Of relevance to the present study, the use of chemically-selective MRI has been demonstrated previously to image oil and aqueous phases in rocks. Dechter et al. [200] showed that using a slice-selective, chemically-selective presaturation MRI method aqueous brine and refined oil phase images in carbonate (dolomite) and sandstone (Bentheimer) rocks can be obtained at a spatial resolution of 0.6 mm. The (one-pulse) presaturation stage, or also known as the preconditioning stage, was used to null the undesired phase (i.e., oil or water) before the imaging part of the experiment was executed. In a more recent work, Ramskill et al. [26] used a chemically-selective 3D CS-RARE technique to discriminate between oil (dodecane) and water phases during a dynamic core flood experiment in a carbonate (Estaillades) core plug. Similar to the aforementioned study by Dechter et al., in this work chemical selectivity was also achieved using a (one-pulse) preconditioning method. Although this method gave quantitative results and had a sufficient temporal resolution to monitor multi-phase displacement processes dynamically, the spatial resolution was limited to 0.4 mm, which is much greater than the size of the pores in the rock sample studied. In this chapter, some ideas from this study are combined with the
methods developed as part of the DR project to generate pore-scale, chemically-selective MRI techniques.

One requirement for using chemical shift sensitivity as a contrast mechanism to study multiphase systems is that the hydrocarbon and aqueous signals in an NMR spectrum must have sufficient chemical shift separation to enable accurate discrimination of the two fluid phases. In clay-rich rocks, such as sandstones, chemical shift separation can be poor due to spectral line broadening caused by magnetic susceptibility induced internal gradients, but in carbonates the chemical shift separation of fluid phases is expected to be better. The nature of fluids used to saturate the pore space of rocks also influences the spectral separation of phases, e.g., crude oil, which is a complex mixture of hydrocarbons, is expected to give broader line shapes than a single-component hydrocarbon [26]. An advantage of using chemical shift sensitivity in MRI experiments is that it is relatively straightforward to implement in an imaging pulse sequence, and the parameters optimised and used for a simple chemically-selective experiment (e.g., a chemically-selective pulse-acquire NMR pulse sequence) and an imaging experiment do not need to be changed or may only slightly change when combined in a single pulse sequence.

Before discussing the intricacies of high-resolution, chemically-selective MRI method development, it is useful to describe a few concepts related to multi-phase displacement processes in porous rocks that are also relevant to this work. In this chapter, MRI was used to investigate two types of pore-fluid displacement processes, namely spontaneous imbibition and forced imbibition. Technically speaking, the term imbibition refers to a process where a wetting phase is adsorbing into a rock [201]. In practice, however, it is simply used to describe a process where water saturation increases in a rock. The difference between a spontaneous imbibition and a forced imbibition process is that during spontaneous imbibition the adsorption of the wetting fluid relies on capillary forces, whereas in the case of forced imbibition the wetting fluid is drawn into the rock by external forces; an example of forced imbibition is a core flooding experiment in which water (the wetting fluid) is injected in a water-wet rock core plug [201]. The opposite process of imbibition is called drainage, which is a process in which a non-wetting fluid is injected into a porous material; in practice, it refers to a process of increasing oil saturation. The outcome of a spontaneous or forced imbibition experiment highly depends on the wetting state or wettability of the rock. Wettability, which is defined as the tendency of a solid to be in contact with one fluid rather than another immiscible fluid, is controlled by the balance between adhesive (fluid-surface) and cohesive (fluid-fluid) type interactions at the molecular level [201, 202]. Three different wetting states can be distinguished – water-wet, oil-wet, and mixed-wet. A pore-level view of these three cases are shown in Fig. 8.1. In a water-wet rock (Fig. 8.1a), the rock/mineral surface is preferentially coated with water, whereas oil occupies the centre of the pores. The opposite is true in an oil-wet rock (Fig. 8.1b) – in this case,
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Figure 8.1 Schematic representation of the wetting states in the pore space of a porous rock. In a (a) water-wet rock, oil (grey) is located in the centre of the pores. In the case of an (b) oil-wet rock, water (blue) is located in the centre of the pores. A (c) mixed-wet rock is characterised by inhomogeneous wetting.

Oil coats the surface of the rock grains, but water is in the centre of the pores. In a mixed-wet rock (Fig. 8.1c), some surfaces and grains are water-wet, but some are oil-wet. Typically, most reservoirs are water-wet prior to migration of oil [201]. Outcrop rocks, which are typically used as representative reservoir samples in the laboratory core analysis measurements, including this thesis, are also strongly water-wet. If we now imagine a situation where a water-wet rock is fully saturated with a non-wetting fluid (e.g., oil), after which this rock comes into contact with a wetting fluid (e.g., water), water will spontaneously imbibe into the rock and expel oil. Due to capillary forces (which are associated with capillary pressure), water will first be drawn in the smaller pores, followed by the larger pores [122, 201]. This is because the capillary forces (pressure) are inversely proportional to the pore throat sizes in the rock, which, for a water-wet rock, corresponds to stronger capillary forces in the smaller pores compared to the larger pores [122, 201]. As (positive) capillary forces pull the fluid in the pore space, the smaller pores are filled first. The larger pore spaces can be filled with water (i.e., more oil can be produced) by performing a water flood, which forces more water into the rock. However, as the water saturates more and more pore throats that were formerly filled with oil, oil can become trapped in some of the large pores. These trapped oil ganglia may not even be mobilised during the water flood if there is not sufficient mobilisation force to overcome the capillary entry pressure to force the trapped oil ganglia through the now water-saturated pore throats [201]. More of this trapped oil can be recovered using enhanced oil recovery (EOR) methods [3], such as those based on surfactants or polymers.

The aim of this chapter is to develop and demonstrate an MRI toolbox for probing multiphase systems in rocks at the pore scale. This was achieved by integrating chemically-selective MR techniques with rapid MRI pulse sequences, optimised under-sampling and CS techniques, and sensitive MRI equipment. The chemically-selective techniques developed were demon-
Chemically-Selective High-Resolution MRI

strated by acquiring independent 3D images of water and oil phases at 35 µm spatial resolution during spontaneous and forced imbibition experiments in heterogeneous Estaillades rock plugs. Although chemically-selective [26] and non-chemically-selective [101] (used dopants) 3D CS-MRI methods have already been used in the past to investigate multi-phase displacement processes in rocks, these experiments were primarily aimed at increasing the temporal resolution of MRI acquisitions to enable dynamic processes to be captured; the spatial resolution of these MRI experiments was limited to ~ 0.4 mm. The focus of this work is to increase the spatial resolution of chemically-selective MRI methods so that they could potentially be used for validation of multi-phase DR simulators. In this work, the first steps towards integrating multi-phase MRI and µCT images were taken by co-registering the chemically-selective MRI data with high-resolution µCT images of the same rock.

This chapter is structured as follows. First, in Section 8.2, the approach taken to develop chemically-selective high-resolution 3D CS-MRI techniques are discussed. This includes the development of chemically-selective structural and velocity imaging pulse sequences. Then, in Section 8.3, the experimental details of MRI and µCT acquisitions are given. Lastly, in Section 8.4, the chemically-selective MRI methods developed were used to acquire high-resolution 3D images of water and oil phases at 35 µm spatial resolution during spontaneous and forced imbibition experiments. Chemically-selective 3D velocity maps acquired at the end state of the forced imbibition experiment are also presented.

8.2 Pore-Scale Chemically-Selective MRI

In the previous chapters, it was demonstrated that by combining rapid MRI pulse sequences with optimised k-space under-sampling schemes and CS reconstruction techniques, pore-scale structural and flow images with spatial resolutions of up to 17.6 µm and 35 µm, respectively, can be achieved. In this chapter, these methods, in combination with effective chemical suppression schemes and quantitative k-space sampling trajectories, are employed to develop under-sampled MRI techniques for the acquisition of pore-scale chemically-selective images.

8.2.1 Chemically-Selective Pulse Sequences

Chemical shift sensitivity is one of the key advantages of MR, as it allows us to separate signals from different chemical species present in the NMR spectrum; the success of chemical selectivity, of course, relies on good spectroscopic chemical shift separation between these species. The separated NMR signal, which corresponds to different chemical species, can then be spatially-resolved using MRI techniques. Thus, chemically-selective MRI is a combination
Figure 8.2 Schematic of the chemically-selective pulse-acquire experiment. Chemical suppression is based on the WET suppression scheme which consists of four Gaussian-shaped excitation pulses with variable flip angles ($\theta_n$) equal or close to $90^\circ$, each followed by homospoil gradients in all three orthogonal directions ($z$, $x$, $y$) which suppress the selectively excited signal.

of two MR experiments – a chemically-selective NMR spectroscopy experiment, which is used to chemically isolate signals from different chemical species based on their chemical shift separation, and an MRI experiment, which is used to spatially-resolve the separated NMR signals of the different chemical species. Details of how these two MR experiments were combined in order to develop chemically-selective MRI techniques are given below.

In this work, discrimination between chemical species is achieved by means of chemical suppression, which, first, involves selective excitation of the desired NMR signal (i.e., peak in the NMR spectrum), followed by destruction of the excited signal (transverse magnetisation) using homospoil gradients. The unsuppressed NMR signal can then be manipulated using the imaging part of the pulse sequence. Chemical suppression is typically achieved by repeatedly applying one or more selective r.f. pulses in combination with dephasing (homospoil) gradients. In chemically-selective MRI sequences, for an effective chemical suppression, a complete dephasing of the transverse magnetisation and nulling of the longitudinal magnetisation of the species we want to suppress are required at the start of the imaging part of the sequence. Because of these requirements, careful optimisation of r.f. pulse flip angles (dependent on $B_1$) and sequence delays are needed to achieve optimal chemical suppression.

Figure 8.2 shows a schematic of the chemically-selective pulse-acquire NMR experiment; the chemical suppression part of this sequence was implemented in all chemically-selective MRI experiments in this work. This NMR experiment is based on a variant of so-called WET (water suppression enhanced through $T_1$ effects) scheme, which was originally developed from a Bloch equation analysis of the longitudinal magnetisation over the relevant ranges of $T_1$ and $B_1$ [203]. The WET scheme can be optimised, via tuning of the selective pulse flip angles, to be insensitive to $T_1$ differences and/or $B_1$ inhomogeneities across the sample, thus giving excellent chemical suppression of fluid signals [203, 204]. Although it was originally designed as a
Figure 8.3 Schematic of the chemically-selective RARE sequence used to selectively acquire oil and water images. This is achieved by adding the WET-based suppression scheme in front of the RARE imaging module.

suppression sequence for water signal, it can also be used for chemical suppression of much more complex fluid mixtures [204]. As can be seen in Fig. 8.2, the suppression in the WET sequence is achieved by four successive soft r.f. pulses with variable flip angles that selectively excite the (un)desired region of the NMR spectrum, each followed by a homospoil gradient in the $z$, $x$, and $y$-direction that suppresses the selectively excited region. To selectively excite a particular region in the NMR spectrum, the selective r.f. pulses are applied at a specific offset frequency. By optimising the delay after the last set of homospoil gradients (before the non-selective pulse), the WET scheme also minimises the small, inverted peak of the suppressed phase, which has been observed, for example, in chemically-selective MR experiments that use only one selective r.f. pulse [26].

For the acquisition of chemically-selective 3D MRI structural images, a chemically-selective 3D CS-RARE sequence was developed by adding the WET-based suppression scheme, which yields excellent chemical suppression, in front of the 3D RARE imaging sequence [33], which is well-suited for fast imaging in porous media applications, as has been discussed and demonstrated in the previous chapters; a schematic of the chemically-selective 3D RARE sequence used in this work is shown in Fig. 8.3. Although a 3D CS-RARE sequence, in combination with chemically-selective preconditioning stage, has already been demonstrated previously [26] to study multi-phase systems in rocks, the new contributions of the current work include (1) more than 10-fold increase in the spatial resolution, which was achieved by combining optimised $k$-space sampling schemes ($\mu$CT-VDS) and CS reconstructions with the use of a sensitive MRI equipment, and (2) the implementation of the WET-based suppression scheme. In the aforementioned study [26], one selective r.f. pulse, followed by homospoil
gradients, was used for chemical suppression, and a small, inverted peak was observed for the suppressed phase – as will be shown in Section 8.4, the WET-based scheme eliminates the small inverted peak, while maintaining the quantitative nature of the MR experiment.

The WET-based suppression sequence was also implemented in the spatially-resolved flow MR experiment to enable measurement of flow velocities of individual fluid phases in a multiphase system. More specifically, a chemically-selective CS-based PGSE-RARE pulse sequence was developed, which is shown in Fig. 8.4. This sequence combines the WET-based suppression scheme, which is used for chemical suppression of fluid phases, the PGSE sequence for velocity encoding, and the 3D RARE sequence for rapid acquisition of $k$-space data. As can be seen in Fig. 8.4, the chemical suppression scheme is put in front of the PGSE-RARE sequence, which means that one of the fluid phases is first selectively suppressed, followed by spatial encoding of velocities for the other, chemically-unsuppressed fluid phase. Adding chemical selection in front of the sequence was the only feasible option because the magnetisation is stored in the $xy$-plane during the PGSE-RARE pulse sequence after the initial 90° excitation pulse, hence putting the selective excitation pulses anywhere else in the velocity imaging pulse sequence would not be possible in the current structure of the sequence. In the case of an APGSTE-based flow imaging sequence, the chemical suppression scheme could also be added during the $z$-storage interval (i.e., when the magnetization is stored along the $z$-axis); compared to the APGSTE sequence with the chemical selection added in front of the sequence, this pulse sequence configuration would not increase the experimental time and sequence duration. The PGSE sequence was selected over the APGSTE sequence for velocity encoding because the observation time, $\Delta$, is relatively small compared to $T_2$ relaxation time of the rock, and APGSTE inherently suffers from 50% signal loss, as was already discussed in Chapter 6.
8.2.2 k-Space Under-Sampling

An important aspect of chemically-selective CS-RARE acquisitions is the trajectory of k-space data acquisition during the RARE echo trains. Although k-space sampling patterns were generated using the same sampling strategy as in the previous chapters, namely µCT-VDS, a different approach to those used in the previous chapters was used for acquiring data experimentally. In this chapter, the order in which k-space points from the sampling scheme were acquired experimentally was determined using a “centre-out” type sampling approach reported in [26]. This approach is different from the one shown in Fig. 4.5b (for more details, see also [101]), because, instead of approaching the centre of k-space in the middle of the RARE echo train, it samples the central k-space points at the beginning of the echo train and then progressively acquires points further out in k-space; this “centre-out” trajectory is shown in Fig. 8.5. By acquiring the centre of k-space early in the echo train ensures that the overall signal intensity in the image, thus also the quantitative nature of the MRI experiment, is preserved as the signal attenuation due to $T_2$ relaxation is now minimised. This is due to the fact that using the “centre-out” sampling trajectory the effective echo time, $t_{e,\text{eff}}$, is significantly reduced compared to the standard approach shown in Fig. 4.5b; $t_{e,\text{eff}}$ is defined as the duration between the 90° excitation pulse and the acquisition of the signal at the centre of k-space and can be calculated by multiplying the echo time, $t_e$, by the number of echoes acquired prior to the acquisition of the central k-space point following the 90° excitation pulse.

A detailed analysis of how these two sampling approaches influence the quantitative nature of MRI experiments and $T_2$ weighting in the images can be found in [26].

![Figure 8.5](image.png)

**Figure 8.5** Representative trajectories of the “centre-out” sampling approach for $k_x$ and $k_y$ with the echo train length of $N_{RF} = 16$. The black (—), red (---), and blue (-----) lines represent the 1st, 64th, and 384th (last) echo train (i.e., excitation), respectively.
8.3 Materials and Methods

8.3.1 Implementation of High-Resolution Chemically-Selective 3D MRI

8.3.1.1 Materials

An Estaillades limestone rock core plug, 3.90 ± 0.02 mm in diameter and 9.92 ± 0.38 mm in length, was dried in an oven at 70 °C (overnight) and then vacuum-saturated with dodecane (99 %, Acros Organics). Using gravimetric analysis, the porosity of the rock, \( \varphi_g \), was estimated to be \( \varphi_g = 25 \pm 1 \% \). Before acquiring MR data, the sample was submerged in distilled water in a 5-mm-diameter flat-bottom Shigemi NMR tube, with the plunger inserted to remove the water from the top side of the rock sample, and was kept there for more than 48 hours [205].

The typical transverse relaxation times, \( T_2 \), of water and dodecane in the intergranular pores of Estaillades limestone are approximately 180 ms and 230 ms, respectively. The \( T_2 \) relaxation times of water and dodecane in the intragranular pores of Estaillades limestone are on the order of 20 ms.

8.3.1.2 Chemically-Selective NMR Spectroscopy and MRI

All NMR spectra and CS-MRI images of the Estaillades sample were acquired on a 7.0 T vertical-bore magnet controlled by a Bruker BioSpin Avance III HD spectrometer and a Bruker Micro5 tri-axial gradient system with a maximum gradient strength of 2.9 T m\(^{-1}\). For spin excitation and signal detection, a 10 mm r.f. saddle coil tuned to a resonance frequency of 299.84 MHz (\(^1\)H) was used.

Standard (non-chemically-selective) spectra were acquired using the traditional pulse-acquire pulse sequence. The duration of the hard 90° excitation r.f. pulse was 8.7 \( \mu \)s, and the sampling rate was 20 kHz. Chemically-selective spectra were acquired using the WET-based [203, 204] pulse-acquire sequence shown in Fig. 8.2. As already mentioned in Section 8.2, the suppression in this sequence is achieved by four successive soft r.f. pulses with variable flip angles that selectively excite the desired region of the NMR spectrum, each followed by a homospoil gradient in the z-, x-, and y-direction that suppresses the selectively excited region. In this work, four Gaussian-shaped excitation pulses each with a duration of 1504 \( \mu \)s and optimised flip angles equal or close to 90° were used; the excitation bandwidth of these pulses was approximately 1400 Hz. Water or oil signals were selectively excited by applying these pulses at a specific offset frequency in the NMR spectrum, corresponding to either water or oil peaks. To suppress the excited signal, four successive homospoil gradients were applied along all the three orthogonal axes, each with a duration of 2 ms at a strength of 0.23, 0.12, 0.06, and 0.03 T m\(^{-1}\). All NMR spectra were acquired with 4 scans and \( t_{RD} = 5 \) s.
Three images of the water and dodecane saturated Estaillades plug were acquired – the “standard” image, which was acquired using non-chemically selective MRI, and oil and water images, which were acquired using chemically-selective MRI (Fig. 8.3). All three images were acquired using a 3D CS-RARE pulse sequence which combines k-space under-sampling and a 3D RARE imaging sequence [33] for faster image acquisition. For the chemical suppression part of the sequence, the same experimental parameters were used as for the chemically-selective pulse-acquire experiment. For all CS-RARE experiments, a RARE factor of $N_{RF} = 16$, an echo time of $t_e = 2.2$ ms, a spectral width of $SW = 400$ kHz, and hard 90° excitation and 180° refocusing r.f. pulses of duration 8.7 µs and 17.4 µs, respectively, were used. 24 scans were acquired for signal averaging with $t_{RD} = 5$ s and a k-space sampling fraction of 0.375, giving a total acquisition time of approximately 12.8 h for each image. All images were acquired with a FOV of 13.5 mm $\times$ 4.5 mm $\times$ 4.5 mm and 384 voxels $\times$ 128 voxels $\times$ 128 voxels in the frequency- ($z$) and both phase-encoding directions ($x$ and $y$), respectively, yielding 3D images with an isotropic resolution of 35.2 µm.

For data under-sampling, k-space sampling patterns (with a sampling fraction of 0.375) were generated using the µCT-VDS methodology described in Chapter 5. The order in which k-space points from the sampling scheme were acquired experimentally was determined using the centre-out type sampling approach described above in Section 8.2.

After MRI data acquisition, the under-sampled chemically-selective data were reconstructed using the OOMFIP toolbox, for which the implementation was presented in [106]. For all reconstructions, TV was used as a regularisation functional, and the regularisation parameter $\alpha$ was determined using the Morozov’s discrepancy principle.

### 8.3.2 Forced Imbibition
#### 8.3.2.1 Materials

For this study, a different Estaillades limestone core plug was used. The diameter and length of this plug were measured to be $3.92 \pm 0.02$ mm and $10.04 \pm 0.09$ mm, respectively. After drying the rock in an oven overnight at 70 °C, the sample was vacuum-saturated with dodecane (99 %, Acros Organics); the gravimetric porosity of the sample was $\phi_g = 26 \pm 1$ %. Two layers of Teflon tape with thickness of 75 µm and an Adtech FEP heat shrink tubing were applied around the core plug to prevent fluid by-passing and to provide confinement. The sample was then placed in a Zeus dual-shrink polytetrafluoroethylene (PTFE)/FEP tubing which was used to connect the sample to an inlet and outlet FEP tubing and to provide additional confinement. Dodecane was injected in the system at $0.03 \text{ ml min}^{-1}$ using a Harvard apparatus 22 syringe pump to re-saturate the sample, which was required because some dodecane was
removed from the sample while applying the heat shrink tubing. Water was then injected in the system at a constant flow rate of 0.005 ml min$^{-1}$ using a Vindum VP-6 metering pump. The imposed flow rate of water of 0.005 ml min$^{-1}$ corresponds to an interstitial flow velocity ($v_i$) of $v_i \sim 20$ ft day$^{-1}$; the estimate of $v_i$ is based on the flow-carrying porosity (see Chapter 7) of the water phase in the Estaillades rock sample.

### 8.3.2.2 X-Ray Micro-Computed Tomography

The (dry) Estaillades sample was imaged using a Bruker SkyScan 2214 µCT scanner (Bruker Micro-CT, Belgium) at an isotropic spatial resolution of 3.00 µm. The source voltage and current were set to 90 kV and 70 µA, respectively. The X-ray beam was filtered using a 1-mm-thick Al filter. To acquire an image of the entire sample, acquisitions were performed at 4 different scanning positions along the longest dimension of the rock plug. For each scanning position, 3601 projections were acquired by rotating the sample in angular increments of 0.1° over 360° with 6 scans per angular increment, yielding an acquisition time of 5 h. Therefore, the total acquisition time was 20 h. Projection images from all 4 scanning positions were stitched together and reconstructed using the NRecon package (Bruker) to give 3566 cross-sectional slices. The final 3D µCT image of the rock was generated by stacking the 2D cross-sectional slices.

### 8.3.2.3 Chemically-Selective MRI Structural Imaging

MRI images were acquired on a 7.0 T vertical-bore magnet controlled by a Bruker BioSpin Avance III HD spectrometer. The spatial resolution was achieved using a Bruker Micro5 tri-axial gradient system with a maximum gradient strength of 2.9 T m$^{-1}$. A 10 mm r.f. saddle coil tuned to a resonance frequency of 299.84 MHz ($^1$H) was used to excite and detect NMR signal.

High-resolution chemically-selective and non-chemically selective 3D MRI structural images were acquired at the end state of the forced imbibition experiment, i.e., at the residual oil saturation. As with the “static” imaging experiment (Section 8.3.1.2), three images of the water and dodecane saturated Estaillades plug were acquired, namely the “standard” image and chemically-selective images of water and dodecane. The images were acquired using the standard and chemically-selective 3D CS-RARE imaging sequences, which are illustrated in Fig. 4.3 and Fig. 8.3, respectively. For data under-sampling, k-space under-sampling schemes with a sampling fraction of 0.375 were generated using the µCT-VDS approach; the under-sampling trajectory was designed based on the centre-out approach shown in Fig. 8.5. To achieve chemical suppression, four Gaussian-shaped excitation pulses each with a duration of
1504 µs and optimised flip angles equal or close to 90° were used; the excitation bandwidth of these pulses was approximately 1400 Hz. The duration and the strength of the homospoil gradients were 2 ms and 0.23, 0.12, 0.06, and 0.03 T m⁻¹, respectively. All CS-RARE images were acquired with \( N_{\text{RF}} = 16, t_e = 2.2 \) ms, SW = 400 kHz, and hard 90° excitation and 180° refocusing r.f. pulses of duration 9.75 µs and 19.5 µs, respectively. 24 scans were acquired for signal averaging with \( t_{\text{RD}} = 2 \) s, thus the total acquisition time for each image was \( \approx 5.1 \) h. The images were acquired with a FOV of 13.5 mm × 4.5 mm × 4.5 mm and 384 voxels × 128 voxels × 128 voxels (frequency\( (z) \) × phase \( (x) \) × phase \( (y) \)), which gave an isotropic spatial resolution of 35.2 µm.

The chemically-selective MRI structural images of oil and water phases presented in this chapter represent the initially dodecane-saturated Estaillades rock core plug at the end state of a forced imbibition experiment. The initial plan, however, was to acquire a series of 3D water and oil images of the rock sample during water injection at a flow rate of 0.0004 ml min⁻¹ using an “inject-stop-acquire” approach [26]. Although an attempt was made to inject water at 0.0004 ml min⁻¹ using the inject-stop-acquire approach, this proved to be very challenging due to the extremely small pore volume of the plug (\( \sim 0.03 \) ml) and the slow system response to the fluid injection in the system. This in turn meant that the acquisition of multiple 3D images in a systematic, step-wise manner was not possible; alternative options for future improvements of this experiment will be briefly described in Section 8.4.2. To ensure that no more oil is produced during the velocity mapping experiment (Section 8.3.2.4), the flow rate of water was increased to 0.005 ml min⁻¹ (i.e., the same flow rate as used during velocity imaging), after which the pump was switched off and the structural water and oil images were acquired using the WET-based and standard CS-RARE sequences; these images were used to represent the end state of the forced imbibition experiment, in which the Estaillades rock was at the residual oil saturation. By comparing the relative amount of water and oil (determined from MR measurements) before the structural images were acquired and after the velocity imaging experiment, during which thousands of pore volumes of water were injected in the system, the amount of residual oil in the system decreased only by approximately 1–2 percentage points.

8.3.2.4 Chemically-Selective Velocity Mapping

3D velocity maps of oil and water phases were acquired using the chemically-selective CS-based PGSE-RARE pulse sequence, shown in Fig. 8.4. For \( \mathbf{k} \)-space under-sampling, sampling schemes with a sampling fraction of 0.3125 were generated using the \( \mu \)CT-VDS methodology. For chemical selectivity, the same optimised parameters as described in Section 8.3.2.3 were used. To achieve velocity encoding of the unsuppressed fluid phase, the following experimental parameters were used: \( g = 2.46 \) T m⁻¹ \( (g_i = 4.91 \) T m⁻¹\), \( \delta = 0.15 \) ms, and \( \Delta = 5 \) ms. The
duration of the hard 90° excitation and 180° refocusing r.f. pulses were 9.75 µs and 19.5 µs, respectively. 32 scans were acquired with $t_{RD} = 2$ s, $N_{RF} = 8$, and $t_e = 2.2$ ms (SW = 400 kHz), giving an acquisition time of 45.5 h for one velocity image (i.e., oil or water velocity image). Velocities were encoded along the superficial flow direction, i.e., $z$-direction. Velocity maps under no-flow conditions were also acquired to correct for the velocity offsets. Thus, the total acquisition time of the velocity image for one fluid type (oil or water) acquired in the superficial flow direction was 91 h. The FOV and the number of voxels in the $z$, $x$, and $y$ dimensions were 13.5 mm $\times$ 4.5 mm $\times$ 4.5 mm and 384 voxels $\times$ 128 voxels $\times$ 128 voxels, respectively, yielding 3D images with an isotropic resolution of 35.2 µm. The velocity imaging experiment was performed after acquiring the structural images (Section 8.3.2.3) on the same Estaillades rock sample.

Details on how under-sampled velocity data are reconstructed and processed can be found in Chapter 6.

8.4 Results and Discussion

This section is divided into two parts. First, the chemically-selective MRI methods are used to study an initially dodecane-saturated Estaillades rock sample submerged in an NMR tube containing water. The primary aim of this experiment is to assess the quantitative nature of the chemically-selective 3D MRI techniques developed. In the second part of this section, the MRI techniques developed are employed to image oil/water distributions at the end state of the forced imbibition experiment (i.e., at the residual oil saturation) in an Estaillades limestone core plug. The chemically-selective 3D velocity imaging experiment is also used to study flow phenomena for water flow in the Estaillades plug at the residual oil saturation.

8.4.1 Implementation of High-Resolution Chemically-Selective 3D MRI

To validate and test the quantitative nature of the WET-based chemically-selective pulse sequences, a 4-mm-diameter Estaillades rock core plug was saturated with dodecane, after which it was submerged in an NMR tube containing water and studied using standard and chemically-selective NMR and MRI techniques.

Figure 8.6 shows the standard and chemically-selective spectra of water and dodecane in the initially dodecane-saturated Estaillades sample. The water and oil peaks in the NMR spectrum (Fig. 8.6a) are located at the offset frequencies of approximately 4.8 ppm and 1.2 ppm, respectively. Good chemical shift separation is seen between the water and oil phases. Figure 8.6b and Fig. 8.6c show that using the WET-based pulse-acquire experiment excellent
suppression of the dodecane and water peaks is achieved while preserving the desired peaks. Furthermore, in contrast to the previous study carried out by Ramskill et al. [26], where small inverted peaks were observed in the chemically-selective NMR spectra for the suppressed phases (probably as a result of using only one selective r.f. pulse, followed by homospoil gradients), for the spectra shown in Fig. 8.6, the baselines are flat with only approximately 1% residual signal left for the suppressed peaks.

To assess the quantitative character of the chemically-selective pulse-acquire method, relative water ($S_w$) and oil ($S_o$) saturations were determined from the NMR spectra by integrating water and oil peaks from the cut-off at 3 ppm using the following equations:

$$S_w = \frac{HI \times I_w}{HI \times I_w + I_o}, \quad (8.1)$$

$$S_o = \frac{I_o}{HI \times I_w + I_o}, \quad (8.2)$$

where $I_w$ and $I_o$ are the integrated signal intensities of the water and dodecane fluid phases and HI is the hydrogen index of the dodecane, which has been measured experimentally [26] as HI = 1.03 ± 0.01 (hydrogen index is the density of hydrogen nuclei in a fluid relative to that of water). The relative water and oil saturations were determined as $S_w = 0.58 \pm 0.02$ and $S_o = 0.42 \pm 0.02$ for the chemically-selective NMR spectra, and $S_w = 0.57$ and $S_o = 0.43$.
(error less than 0.005) for the non-chemically-selective spectrum. For the chemically-selective spectra, the uncertainties in relative saturations are associated with the imperfections caused by chemical suppression and were determined by comparing the integrals of dodecane and water peaks in the chemically-selective spectra to the integral of the respective peaks in the standard spectrum; uncertainties related to the measurement of HI and the chosen cut-off value were also included in the error computation. Overall, these results demonstrate that the quantitative nature of the data is preserved in the chemically-selective pulse-acquire experiment.

The next step was to experimentally implement and benchmark the chemically-selective MRI pulse sequence used for the selective acquisition of structural oil and water images. Water/oil, water, and oil CS-MRI images at 35 µm spatial resolution acquired using the non-chemically-selective and chemically-selective CS-RARE sequences are shown in Fig. 8.7. By visually comparing all three images shown in Fig. 8.7a, it can be seen that water and dodecane phases are effectively suppressed. For closer inspection of the images, close-ups of two regions extracted from the 2D image slices of the Estaillades rock are shown in Fig. 8.7b. As can be seen, excellent chemical suppression and high spatial resolution enable water- and oil-containing microstructural features in the rock to be distinguished. It can be clearly seen that oil is primarily located in the macropores (higher signal intensity; yellow), whereas water has predominately misplaced oil from and has imbibed in the micropores (lower signal intensity; orange) of the rock; the latter is driven by spontaneous imbibition processes. The black regions correspond to dense calcitic grains where no water or oil is present. The same trends can be observed in Fig. 8.7a. The most powerful aspect of these images is that we can now physically visualise, without the use of dopants, where oil and water in porous rocks are located using the high-resolution MRI techniques developed.

The visual inspection of the images in Fig. 8.7 revealed that qualitatively excellent chemical suppression is achieved using the new, chemically-selective CS-RARE sequence. In order to test the quantitative nature of the experiment, and hence the relative oil and water saturations in the rock, the experimental MRI data need to be benchmarked. To achieve this, one should, ideally, compare the fluid saturations determined from the images (or spectra) to the volumetrically determined values, but due to the extremely small pore volumes of the 4-mm-diameter Estaillades plugs, which are typically on the order of 0.03 ml, this was not a feasible option. Instead, the relative saturations determined from the MRI images can be compared to the data obtained from the spectra. This is because in the NMR spectroscopy measurements, where the pulse-acquire pulse sequences are used, the dead time is on the order of microseconds, hence the signal attenuation due to relaxation is negligible, even in the fluid-saturated rock samples.
Figure 8.7 (a) 2D (zy) slice images taken from the 3D MRI images of the dodecane and water saturated Estaillades rock sample acquired using the standard (non-chemically-selective) CS-RARE sequence and the chemically-selective CS-RARE sequence. (b) Close-ups of two regions of size 1.4 mm × 1.4 mm extracted from these image slices are shown. The yellow, red/orange, and black colours represent macroporous regions, microporous regions, and dense calcitic grains in the rock, respectively.
Therefore, the measured NMR signal intensity is a true representation of the spin density, which is proportional to the amount of fluid in the rock. To determine the relative saturations of the fluid phases from the MRI data, the signal intensities of the respective entire CS-MRI images were integrated. Using Eq. 8.1 and Eq. 8.2, the relative saturations of water and dodecane were determined to be $S_w = 0.56 \pm 0.01$ and $S_o = 0.44 \pm 0.01$, which are in excellent agreement with the relative saturations determined from the spectra, i.e., for the non-chemically selective spectrum, $S_w = 0.57$ and $S_o = 0.43$; the uncertainty in the calculated relative saturations was estimated by comparing the summed intensities of the chemically-selective oil and water images to the intensity of the standard image (the error associated with HI was also included in the calculations of the overall uncertainties). These results demonstrate that the quantitative nature of the MRI measurement is retained and is not severely influenced by $T_2$ weighting. These relative saturations, however, represent the entire water and oil content in the NMR tube, which includes oil and water within the rock plug and the bulk fluids surrounding the plug (see Fig. 8.7). By integrating the signal intensities of the regions within the rock plug, the relative water and oil saturations were determined to be $S_w = 0.45 \pm 0.03$ and $S_o = 0.55 \pm 0.03$. This means that approximately 45 \% of the oil has been displaced in the Estaillades formation by a spontaneous imbibition process of water.

For the NMR and MRI experiments discussed in this section (Section 8.4.1), a recycle delay of $t_{RD} = 5$ s was used in each scan to enable magnetisation to recover. However, the spin-lattice relaxation times of bulk water and dodecane are approximately $T_1 = 2.7$ s and $T_1 = 1.4$ s, respectively. Given that the sample contained bulk water and dodecane and the recycle delay of $t_{RD} = 5$ s is less than $5 \times T_1$ for both fluids, it is important to assess the effects of $T_1$ relaxation on the quantification of relative saturations, $S_w$ and $S_o$. To analyse these effects, chemically-selective spectra with a shorter recycle delay of $t_{RD} = 2$ s and a longer recycle delay of $t_{RD} = 12$ s were acquired and analysed to determine the $S_w$ and $S_o$ values. For $t_{RD} = 2$ s, the relative saturations were determined to be $S_w = 0.57$ and $S_o = 0.43$, but, for $t_{RD} = 12$ s, these values were $S_w = 0.59$ and $S_o = 0.41$. Comparing these saturations to the ones obtained for the $t_{RD} = 5$ s case (i.e., $S_w = 0.58$ and $S_o = 0.42$), it can be concluded that the $T_1$ weighting does not significantly influence the accuracy of the measurements since there is little variation in the calculated fluid saturations among the spectra acquired using the three different recycle delays. The time savings gained by using a shorter recycle delay probably outweigh the accuracy of MR data acquired at a longer recycle delay. Furthermore, the typical spin-lattice relaxation times of water and dodecane in Estaillades are $T_1 \lesssim 1$ s, hence even less variation in the relative water and oil saturations due to $T_1$ weighting is expected, e.g., between $t_{RD} = 2$ s and $t_{RD} = 12$ s, when estimated for the fluids within the pore space of the rock.
8.4.2 Forced Imbibition

The chemically-selective high-resolution MRI methods validated in Section 8.4.1 were further utilised to study water and dodecane distributions in an initially dodecane-saturated Estaillades core plug during a forced imbibition experiment. Here the focus is on the oil and water structural images acquired at the end state of the forced imbibition experiment, i.e., at the residual oil saturation. In the second part of this section, the novel chemically-selective PGSE-RARE sequence is demonstrated by acquiring velocity maps of water and oil phases separately at 35 µm spatial resolution for water flow through the same rock plug that has undergone forced imbibition of water.

8.4.2.1 Chemically-Selective Structural Imaging at 35 µm Spatial Resolution

Figure 8.8 shows 2D (zy) slice images extracted from the high-resolution 3D MRI data that were acquired using the standard and chemically-selective CS-RARE sequences at the end of the forced imbibition experiment. By visually comparing the images, excellent chemical selectivity (suppression) of water and oil phases can be seen. Compared to the validation

![Figure 8.8](image-url)
8.4 Results and Discussion

Figure 8.9 Relative water and oil saturations in the Estaillades core plug at the residual oil saturation: (a) the total intensity image of the plug showing the locations of regions 1 and 2; (b) relative water, $S_w$, and oil, $S_o$, saturations in the rock plotted along the $z$-direction, i.e., the superficial direction of the injected water flow; (c) regions 1 and 2 extracted from the 3D images with different $S_w$ and $S_o$ values.
experiment described in Section 8.4.1, where water had spontaneously imbibed primarily in the micropores, it can be observed that in this case water has also imbibed in many large pores, as well as in micropores. The relative oil saturation in the rock was determined to be $S_o = 0.44 \pm 0.07$ (the relative water saturation was $S_w = 0.56 \pm 0.07$), which is approximately by 0.1 saturation units lower than the relative oil saturation determined for the same rock type in the case of spontaneous imbibition (see Section 8.4.1). Similar relative oil saturation of $S_o = 0.40 \pm 0.05$ was obtained in an analogous study carried out by Ramskill et al. [26], where water was injected in an initially dodecane-saturated 4-cm-diameter Estaillades core plug at 0.4 ft day$^{-1}$, and the core flooding process was monitored using chemically-selective MRI at more than 10 times coarser spatial resolution.

To highlight the strength of the high-resolution chemically-selective MRI techniques developed, the acquired water and oil images were analysed in more detail; the results of this analysis are shown in Fig. 8.9. Fig. 8.9b shows a plot of the relative water and oil saturations of the rock along the superficial flow direction ($z$-direction) in which water was injected. It can be seen in the saturation profiles that almost along the entire length of the Estaillades formation in the $z$-direction most pores are saturated with water, i.e., $S_w \sim 0.6$. The only exception is the outlet section of the plug, which contains approximately 20 percentage points more oil than the rest of the plug. This discrepancy in fluid saturation between the outlet of the rock plug and the rest of the plug can be attributed to the phenomenon known as the end effects, which is widely encountered in core flooding experiments and can arise due to geometric constraints (e.g., inlet or outlet geometry), viscous instabilities, or capillarity [24, 193, 206]. Figure 8.9c shows two regions, region 1 and region 2, with markedly different $S_w$ and $S_o$ values that have been extracted from the chemically-selective 3D water and oil images (note that region 2 is not located in the section of the rock that contains the end effects). As can be seen in Fig. 8.9c, region 1 contains significantly more ($\approx 2.7$ times) water than oil, whereas region 2 has much more even content of both fluids. In the case of the oil images in Fig. 8.9c, it can be seen that region 1 contains many disconnected oil ganglia that are mainly represented by high oil signal intensities (orange/yellow), which means that these oil clusters are located in the high porosity (i.e., macroporous) regions of the rock. By quantitatively analysing the isolated oil clusters located in the macropores in a large section of the rock (i.e., $\sim 5.8$ mm of the $z$-dimension), it was found that the mean ganglia radius is 41 µm ($\sim 15$ voxels in volume), which is similar to the typical macropore radius in Estaillades rock. It was also found that the largest single ganglion contains 681 voxels ($\sim 0.03$ mm$^3$), which constitute about 6 % of the total trapped volume in the rock section analysed. According to [8], if the total trapped volume is one order of magnitude or more greater than the volume of the largest oil cluster, then all ganglia are statistically well represented and the volume of the region that contains these ganglia is greater
Figure 8.10 2D (a) water and (b) oil (xy) slice images extracted from the co-registered 3D MRI and µCT datasets of Estaillades rock.

than the REV. This means that 4-mm-diameter Estaillades rock core plugs can be quite safely used for multi-phase core-flooding experiments with respect to the subsequent quantitative analysis of the data. The visual inspection of Fig. 8.9c also reveals that region 2 contains notably more oil than region 1; this increase in the oil saturation can be mainly attributed to the significant amount of oil that is located in the microporous regions of the rock. The oil that is located in the micropores is of lower local concentration and therefore appears in red. Similarly, in the case of the water images, it can be clearly seen that water is present in both macropores (green) and micropores (blue) of the Estaillades formation.

The distribution of water and oil phases in the Estaillades rock core plug is also illustrated in Fig. 8.10, where the acquired oil and water MRI images are co-registered with the high-resolution µCT image of the same rock sample. The co-registered high-resolution MRI and µCT datasets allow us to more clearly identify oil- and water-containing macropores and micropores in the rock. For instance, it can be seen in Figure 8.10 that some macropores and microporous grains are completely saturated with water or dodecane, but there also are a few pores and microporous grains which are saturated by both fluids.

In this section, chemically-selective 3D structural MRI images of oil and water acquired at the end state of the forced imbibition experiment have been presented. Although these images did provide some useful information about the multi-phase system studied, more detailed insight into the displacement mechanisms, such as pore filling and oil trapping, could potentially be
Chemically-Selective High-Resolution MRI

gained by performing these experiments dynamically at the spatial resolutions achieved in this work. However, at the time when these experiments were planned and carried out, the minimum flow rate of the pump available that was used for water injection was 0.0001 ml min$^{-1}$, which corresponds to $v_i \sim 0.4$ ft day$^{-1}$ (5 mm h$^{-1}$). Given that the typical length of a 4-mm-diameter plug is $\sim 10$ mm and the acquisition time of one 3D MRI image is 5.1 h (based on the current experimental parameters), it would not even be possible to acquire one “snapshot” image before the water breakthrough occurs. By slightly sacrificing the quality of 3D images, i.e., by reducing k-space sampling fraction to 0.25 and increasing the rare factor to $N_{RF} = 32$, one could in principle reduce the image acquisition time to $\sim 1.7$ h, but this would only give sufficient time to acquire one quantitative 3D image at 35 µm spatial resolution. A potential compromise to increase the temporal resolution of the 3D MRI measurements, of course, include decreasing the spatial resolution. So, for example, by decreasing the spatial resolution to 70 µm, which is still considered a relatively high resolution in the context of MRI, and using realistic acquisition parameters (sampling fraction = 0.25, $t_{RD} = 2$ s, $N_{RF} = 64$, and $N_s = 4$), one could reduce the image acquisition time to approximately 2 min. At the injection speed of 5 mm h$^{-1}$, approximately 60 (30 oil and 30 water) chemically-selective 3D snapshot images could potentially be acquired (note that these measurements would introduce some temporal blurring, as the fluid front would move $\sim 2$ voxels during each image acquisition). At this image acquisition rate, the dynamics of the moving fluid front in the rock should be adequately captured [26].

8.4.2.2 Chemically-Selective Velocity Mapping at 35 µm Spatial Resolution

After acquiring the chemically-selective 3D structural images of the Estaillades rock sample at the residual oil saturation, the pump was switched on, and water was injected at 0.005 ml min$^{-1}$. The continuous injection of water was monitored using the chemically-selective 3D PGSE-RARE sequence (Fig. 8.4).

Figure 8.11 shows 2D $xy$-slice images extracted from the chemically-selective 3D $z$-velocity maps and intensity images of water and oil phases of the Estaillades rock plug. As can be seen in Fig. 8.11a, only a few narrow flow channels carry significant flow of water in the rock. The location of these high-velocity flow channels generally correlate well with the high-porosity (orange/yellow pixels in Fig. 8.11c) regions in the rock. It can also be seen that a large proportion of water appears to be stagnant; the stagnant water is mainly located in the microporous regions (lower signal intensity) of the rock (see Fig. 8.11c). Figure 8.11d shows that dodecane is generally located in relatively large pores, represented by the high signal intensities. As is evident from Fig. 8.11b, these dodecane clusters are stagnant, i.e., $v_z \sim 0$ mm s$^{-1}$, and appear to be trapped in the pore spaces they are located. It is interesting
8.4 Results and Discussion

Figure 8.11 2D (xy) slice images taken from the acquired chemically-selective 3D (a) water and (b) dodecane velocity maps and chemically-selective 3D (c) water and (d) dodecane intensity (magnitude) images of Estaillades rock. Velocities were encoded along the superficial flow direction ($z$). The intensity images were generated from the acquired no-flow complex-valued MRI data; the signal intensities in these images correspond to the local fluid content in the rock.

To note that the high-velocity flow paths of water have not formed near the regions where the remaining oil is located.

To support the visual analysis of Fig. 8.11, the velocity ($z$) distributions, extracted from the chemically-selective 3D water and oil images, are shown in Fig. 8.12. The velocity distribution of the water phase (Fig. 8.12a) is slightly skewed to positive velocities along the superficial flow direction ($z$) and exhibits a long positive tail representing the high-velocity flow channels. The fact that the velocity distribution of water exhibits positive skewness is expected since water is the fluid phase that is being injected in the rock. Despite this, it can also be seen that a
Figure 8.12 Velocity ($z$) distributions obtained from the chemically-selective 3D (a) water and (b) dodecane images of Estaillades rock.

A large fraction of water molecules is stagnant. Fig. 8.12b shows that the measured velocities of the dodecane fluid phase are small and are symmetrically distributed around $v_z = 0$ mm s$^{-1}$ (i.e., zero net flow) indicating that the dodecane phase is stagnant or near-stagnant, which is in agreement with the above assessment of the velocity images. The spread of velocities around $v_z = 0$ mm s$^{-1}$ can be partly attributed to phase errors due to noise and partial volume effects (see Chapter 7); the noise-related velocity errors in both water and oil velocity maps were estimated to be on the order of 0.002 mm s$^{-1}$ for the macroporous regions and 0.01 mm s$^{-1}$ for the microporous regions of the rock.

Based on the information in this section and Section 8.4.2.1 and given that the oil recovery factors hardly changed during the course of the imbibition experiment despite the large number of pore volumes injected in the rock, a likely scenario is that some of the oil located in the macropores of the rock (Fig. 8.9c and Fig. 8.11d) became disconnected (Fig. 8.9c) from the rest of the oil phase as the moving water front spontaneously filled the narrow pore openings (one mechanism that controls such processes is called snap-off [207]). Although many more pore volumes of water were injected in the rock, the injection flow rate was constant. As a result, the isolated oil ganglia remained trapped (Fig. 8.11), as there was not sufficient viscous force to overcome the capillary forces and to mobilise the trapped oil. The injected water simply followed the easiest water-filled paths, hence bypassing the pores that contained the remaining dodecane (Fig. 8.11). To overcome the capillary forces and recover more oil, one could increase the injection flow rate of water or employ EOR methods, such as surfactant flooding [3].
8.5 Conclusions

In this chapter, quantitative chemically-selective 3D CS-MRI methods for imaging multiple fluid phases in heterogeneous porous rocks at pore-scale resolution have been demonstrated. The chemically-selective methodology used in this chapter was built upon the rapid CS-RARE imaging and optimal $k$-space under-sampling techniques developed in the previous chapters. By combining these techniques with quantitative experimental implementation of the $k$-space sampling schemes and an effective chemically-selective WET-based pulse sequence, which utilises chemical shift differences between fluids, it was demonstrated that independent quantitative 3D images of the aqueous and hydrocarbon phases in porous rocks can be acquired at 35 µm spatial resolution.

The chemically-selective high-resolution MRI methodology was first validated by placing a dodecane saturated Estaillades limestone in water and then using NMR and MRI methods to determine the relative water and oil saturations. The MRI data were found to be in excellent agreement with the NMR spectroscopy measurements with only 0.01 difference in fluid saturations determined between the two measurement techniques. The visual inspection of images revealed that water has primarily imbibed in the micropores, but oil has remained in the macropores of the rock, consistent with a spontaneous imbibition process in a water-wet rock. The relative oil saturation in the rock was determined to be $S_o = 0.55 \pm 0.03$.

The methods were then employed to study an initially dodecane-saturated Estaillades limestone core plug at the end state of the forced imbibition experiment during which water was injected at 0.005 ml min$^{-1}$ ($\sim$ 20 ft day$^{-1}$). Compared to the spontaneous imbibition experiment, in this case water had also imbibed in a large number of macropores. As a result, the relative oil saturation in the rock was approximately by 0.1 saturation units lower, i.e., $S_o = 0.44 \pm 0.07$. The high-spatial resolution of 3D MRI images, in combination with the co-registered µCT images of the rock, was utilised to identify oil- and water-containing microstructures in the rock. The visual analysis of the 3D oil images revealed that some residual oil appears to exist as disconnected oil blobs.

Lastly, a chemically-selective PGSE-RARE technique was demonstrated by acquiring velocity maps of water and oil phases separately at 35 µm spatial resolution during water injection in the same Estaillades rock plug at the residual oil saturation. The flow of water was highly localised with a few high-velocity flow channels carrying significant amount of flow. The oil clusters that remained in the rock after the water flood were mostly located in macropores and were immobile. The most likely scenario is that these oil clusters were separated from the rest of the oil phase and became trapped during water injection, as water spontaneously filled the narrow pore throats of the pores formerly occupied by oil.
Using the chemically-selective high-resolution MRI techniques developed in this chapter, we can now study structure-transport relationships at pore-scale resolution for multi-phase flow in rocks and potentially provide useful input for multi-phase DR simulators.
9.1 Conclusions

In this thesis, high spatial resolution, quantitative 3D MRI methods were developed for characterising fluid-saturated porous rocks at the pore scale. A particular focus of this work was to utilise these techniques and the 3D MRI images acquired, in combination with high resolution μCT, to study structure-transport relationships for single- and multi-phase flow in porous rocks and to aid the development of DR simulators. The synergy between MRI and μCT played a major role in the development of these techniques and provided more detailed insight into the intricacies of fluid flow within the pore space of rocks than the individual imaging modalities alone. The main conclusions for each of the chapters are given below.

Chapter 1 introduced the concept of DR physics and its importance in the oil and gas industry. The main motivation for using DR technology is to provide fast and cheap analysis of rocks, which has the potential to complement and even possibly replace the slow conventional laboratory core analysis measurements. As part of the DR workflow, X-ray μCT and MRI are the two main imaging modalities used for studying porous rocks and the fluids within them. X-ray μCT is used in DR technology as the primary tool for obtaining μm-scale images of the rock matrix. However, it has limited capabilities in directly and non-invasively studying multi-phase systems and fluid flow and transport processes in rocks. Although the spatial resolution of conventional MRI techniques is lower (a few hundred microns) than that of μCT,
Conclusions and Suggestions for Future Work

it provides a range of different non-invasive contrast mechanisms, based on, for example, fluid type via chemical shift sensitivity and fluid mobility via direct MR measurements of velocity. In this thesis, the spatial resolution of MRI techniques that utilise different contrast mechanisms was increased to a few tenths of microns, which is a resolution at which pore-scale structural and flow features in many rocks can be clearly identified and is also compatible with µCT-based DR simulations.

Chapters 2 and 3 provided an introduction to MR data acquisition and digital image processing techniques pertinent to this thesis. More specifically, Chapter 2 introduced the basic principles of NMR and MRI and explained how these principles can be utilised to acquire NMR spectra, multi-dimensional images, and flow data. Chapter 3 focused on the main digital image processing techniques used for processing high-resolution MRI and µCT images, such as image denoising, image segmentation, and image co-registration.

Chapter 4 laid the foundation for Chapters 5–8 by discussing the main aspects of high-resolution MRI in porous rocks. The first step included the assessment of commercially-available MRI (hardware) technologies, as they impose practical limits on the achievable resolution in MRI. As a result of this analysis, sensitive MRI equipment capable of delivering high spatial resolution images was procured and was used as the main imaging tool in this thesis. An assessment of a range of different rock types was also carried out to determine the most realistic rocks for high-resolution imaging. Among the rock samples studied, Ketton and Estaillades carbonate rocks were found to be the best candidates for high-resolution MRI experiments, and hence were the rock types most extensively studied in this work. The details of rapid MRI data acquisition techniques, namely \( k \)-space under-sampling and the RARE pulse sequence, along with CS reconstruction methods, were also given.

In Chapter 5, a novel, parameter-free \( k \)-space sampling approach that exploits \( k \)-space energy distribution derived from high spatial resolution µCT images, referred to as µCT-VDS, was developed to produce optimal \( k \)-space under-sampling patterns for acquiring high spatial resolution 3D MRI images of rocks. To validate the performance of the new approach, it was benchmarked against other, well-established sampling strategies using simulated MRI data obtained from high-resolution µCT images of rocks. The simulations were performed for a range of different \( k \)-space sampling fractions (0.125–0.375) using images of Ketton rock and for different rock types (Ketton and Estaillades limestones, and Fontainebleau sandstone). The results showed that the new method can be used to generate a bespoke, optimised sampling scheme for each rock type and sampling fraction. The method, in combination with 3D RARE, was also employed to acquire 3D MRI images of a Ketton limestone core plug at (isotropic) spatial resolutions of 35 and 17.6 µm; 17.6 µm is the highest spatial resolution reported for an MRI image of rock samples. Pore space analysis in Avizo was used to benchmark the quality of
the acquired MRI images relative to the µCT image of the same rock by extracting pore space characteristics (i.e., PSDs and CNDs). The PSD of the 17.6 µm MRI image gave excellent agreement with the PSD obtained from the µCT image acquired at 5 µm spatial resolution, while the pore coordination number distribution obtained from the MRI dataset was slightly skewed to lower coordination numbers. Overall, the new approach delivers accurate pore space reconstructions at resolutions that would be difficult to achieve using conventional fully-sampled MRI acquisitions. This method can also be used to accelerate other MRI acquisitions, such as velocity mapping and chemically-selective imaging, which was demonstrated in Chapters 6 and 8, respectively.

Chapter 6 presented quantitative, 3D spatially-resolved flow imaging techniques to characterise structure-flow correlations for a single-phase flow through a Ketton limestone core plug at a pore-scale resolution. This was achieved by using rapid MRI pulse sequences in combination with optimised \(k\)- and \(q\)-space data under-sampling schemes, based on µCT-VDS, and CS data reconstruction techniques. The acquired flow MRI data were co-registered with an X-ray µCT image of the same rock sample, thus allowing microstructural features of the rock to be correlated with local fluid transport properties. Two flow MRI measurement techniques were used – velocity mapping and spatially-resolved propagators. The analysis of 3D velocity maps, which were acquired at 35 µm isotropic spatial resolution, revealed that the flow in Ketton rock was highly heterogeneous, with \(\sim 10\%\) of the pores carrying 53 % of the flow. Structure-flow relationships were found between the local flow velocities through individual pores and the size and topology (coordination number) associated with these pores. It was also demonstrated that the structure-flow characteristics of Ketton rock are consistent with those observed for a packing of spheres. 3D spatially-resolved propagators were acquired at 94 µm isotropic spatial resolution. Flow dispersion within the rock was examined by analysing each of the 331,776 local propagators as a function of observation time. The heterogeneity of flow within the rock was again demonstrated. Quantification of the mean and standard deviation of each of the local propagators showed that enhanced mixing occurs within the pore space of the rock at longer observation times. These spatially-resolved measurements were also used to identify an REV based on the observed flow properties – it was shown that for a 4-mm-diameter plug this length scale is not reached. The spatial resolution at which these flow images were acquired, namely 35 µm and 94 µm, are the highest spatial resolutions reported for the respective flow measurement techniques for flow in porous media.

In Chapter 7, single-phase flow fields in Ketton and Estaillades carbonate rock core plugs were computed at a pore-scale resolution (\(\leq 7\) µm) using LBM simulations, performed on the segmented X-ray µCT images of the rocks, and then benchmarked to quantitative 3D velocity maps acquired at 35 µm isotropic spatial resolution for flow of water through the
Conclusions and Suggestions for Future Work

same rock samples. Co-registration of the 3D experimental and simulated velocity fields and coarse-graining of the simulations to the same resolution as the flow MRI data allowed the data to be directly compared. For Ketton limestone, good qualitative and quantitative agreement was found between the simulated and experimental velocity maps. In Ketton rock, the flow-carrying microstructural features identified by flow MRI were mostly larger than the spatial resolution of the µCT images, so, in this context, the segmented images of Ketton were an adequate representation of the pore space in the rock. In the case of Estaillades limestone, which presents a more heterogeneous case with microstructural features mostly below the spatial resolution of the µCT images, many of the complex flow patterns were also qualitatively reproduced by the LBM simulation, although in some pores, noticeable differences between the LBM and MRI velocity maps were observed. It was also found that only 10% of the pores in the Estaillades formation carry 80% of the flow, which is an indication of the high structural heterogeneity of the rock; in the more homogeneous Ketton rock, ~50% of the flow is carried by 10% of the pores. By analysing the 3D MRI velocity map of Estaillades rock, it was found that approximately one third of the flow through the rock is carried by microporosity – a porosity that is not captured with the resolution of the µCT image. This is the first MRI and LBM benchmarking study performed on porous rocks at such spatial resolutions.

In Chapter 8, novel high-resolution, chemically-selective 3D CS-MRI methods were demonstrated which were applied to record independent 3D images of water and dodecane fluid distributions in heterogeneous Estaillades limestone core plugs during spontaneous and forced imbibition experiments. The chemically-selective MRI methods were developed by combining the techniques demonstrated in the previous chapters with quantitative experimental (centre-out) k-space sampling trajectories and an effective chemically-selective WET-based pulse sequence that achieves chemical suppression based on chemical shift sensitivity. The methods were employed to yield chemically-selective 3D images at 35 µm spatial resolution, which is the highest spatial resolution reported for chemically-selective MR measurements in rocks or any other inorganic porous materials. The methodology was validated by placing a dodecane-saturated Estaillades plug in a water-filled NMR tube and then using NMR and MRI methods to determine relative fluid saturations. Excellent agreement was found between the NMR data and MRI images acquired at 35 µm spatial resolution; NMR was considered as the “ground truth” measurement. Water was found to imbibe primarily in the micropores of the rock, yielding $S_0 = 0.55 \pm 0.03$. The chemically-selective structural MRI and velocity mapping methods were then employed by study an initially dodecane-saturated Estaillades plug at the end state of the forced imbibition experiment during which water was injected at 0.005 ml min$^{-1}$. During the forced imbibition process, oil was forced out of some large pores, as well as a large fraction of micropores, which resulted in about 0.1 saturation units lower
oil saturation in the rock compared to the spontaneous imbibition experiment. Some of the remaining oil was found to exist as disconnected oil ganglia. The velocity maps acquired at 35 µm spatial resolution revealed that the flow of water was highly localised, but the oil ganglia were stagnant, as expected.

In summary, this thesis presented quantitative, spatially-resolved rapid 3D MRI methods that enabled structural and flow properties of fluid-saturated porous rocks to be studied on a pore scale. The synergy between high-resolution MRI and μCT was employed not only to develop new techniques, but also to correlate the measured fluid properties with the microstructure of the rock matrix via image co-registration. The first steps towards benchmarking pore-scale LBM flow fields in rocks were also taken. Overall, the work conducted in this thesis provides a solid background for future use of MRI in the development of DR technology and other related fields.

### 9.2 Suggestions for Future Work

#### 9.2.1 Systematic Study of Structure-Flow Correlations in Rocks

Chapter 6 demonstrated various structure-flow correlations for a single-phase flow in a Ketton limestone rock core plug. This study, however, was conducted only on one rock sample and at one flow rate (one $Re$). It would be beneficial to perform the same experiment on multiple samples and at various $Re$ to identify how universal these relationships are. Furthermore, these studies could be extended to include other rock types, in which pore space features can be discerned at resolutions that can now be achieved using the high-resolution MRI methods developed in this work. Similarly, the statistics of spatially-resolved propagator data, such as mean ($\mu$) and standard deviation ($\sigma$), could be used to provide information on the flow characteristics of various types of porous rock samples. Depending on the outcome of these “fingerprinting” studies, it would then be useful to create a library of the rocks studied and their unique flow characteristics, which would be useful for future studies and could potentially serve as inputs for DR simulations and machine learning algorithms.

#### 9.2.2 Single-Phase Polymer Core Floods

Polymer solutions based on water-soluble polymers, in particular acrylamide-based polymers, are widely used in EOR processes to mobilise the remaining oil in rocks [208]. The addition of polymers is primarily aimed at increasing the viscosity of the injection fluid, which improves the sweep efficiency, and hence minimises the amount of oil that is bypassed during the flood [3, 208]. However, several studies have demonstrated that additional mobilisation of
oil can be achieved by using high molecular weight viscoelastic polymers [209, 210], such as high molecular weight partially hydrolysed poly-acrylamides. Therefore, there exists strong motivation to better understand the flow behaviours of different polymer solutions and the underlying mechanisms that control them. Using the high-resolution imaging methods developed in this work, injection of different polymer solutions in rock plugs could be monitored, either by varying the concentration of the polymer or the type of the polymer (polyacrylamides and polysaccharides) used in the solution. It would then be interesting to compare the pore-scale flow images acquired during the single-phase polymer flood with an identical flow experiment during brine/water injection, which could be conducted, for example, prior to the polymer flood. A similar study has been conducted for a single-phase flow in a bead pack at 180 µm spatial resolution [175].

Note that recently in collaboration with Shell a mini PEEK (polyether ether ketone) rock core holder has been designed and built for holding 4-mm-diameter rock plugs during flow experiments. The advantage of using a core holder is that it provides confining pressure to mimic reservoir conditions, while simultaneously directing flow through the rock and preventing bypassing of fluids. This could be particularly useful for polymer core floods, where relatively high injection pressures are expected, relative to water core floods.

9.2.3 Dynamic Monitoring of a Forced Imbibition Experiment at Pore-Scale Spatial Resolution

In Chapter 8, structural oil and water 3D images were acquired at the end state of the forced imbibition experiment in a heterogeneous limestone core plug using chemically-selective high-resolution MRI techniques. The next step would be to use high-resolution chemically-selective MRI to monitor the imbibition process dynamically. At the time when the aforementioned forced imbibition experiment was performed, the goal was to acquire oil and water images at as high spatial resolution as possible in a reasonable experimental time, which corresponded to 35 µm. As a result, the experiment was performed using an inject-stop-acquire approach, because dynamic information of the forced imbibition process at such spatial resolution could not captured due to insufficient temporal resolution of the high-resolution MRI acquisitions relative to the time it would take for water breakthrough in the rock to occur, i.e., no more than one chemically-selective MRI image could be acquired at 35 µm spatial resolution at the minimum available water injection flow rate of 0.0001 ml min$^{-1}$ (∼ 0.4 ft day$^{-1}$). As discussed in Chapter 7, one solution would be to decrease the spatial resolution to 70 µm, which would yield, by also slightly adjusting the experimental parameters, approximately 60 chemically-selective images during the course of the imbibition experiment, which should be
sufficient to capture the dynamics of the moving fluid-fluid interface [26]. A possibility to increase the spatial resolution of such measurements has recently arisen due to the upgrades to the core flooding system. More specifically, the software of the pump that was used in the initial imbibition experiment (Vindum VP-6) was upgraded to allow control of lower flow rates; the minimum flow rate of the pump now is 0.00003 ml min$^{-1}$ ($\sim$ 0.1 ft day$^{-1}$). At such injection rate and using realistic image acquisition parameters (sampling fraction = 0.25, $t_{RD} = 2$ s, $N_{RF} = 50$, and $N_s = 6$), the spatial resolution of 3D MRI images can potentially be increased to 56 µm to acquire approximately 60 chemically-selective images. By careful fine-tuning of experimental parameters, the spatial resolution could potentially be increased even more.

9.2.4 Further Single- and Multi-Phase LBM Simulations

In Chapter 7, single-phase LBM simulations were benchmarked against MRI flow fields acquired for water flow through limestone core plugs. It would be valuable to extend the benchmarking studies to include polymer (non-Newtonian fluid) flow and two-phase fluid flow in porous rocks. The LBM methodology presented in Chapter 7, more specifically eLBM, can be relatively easily extended to simulate non-Newtonian and two-phase fluid flow. In fact, the eLBM code has already been used for simulating two-phase flow in rocks [170, 171]. The LBM simulations of non-Newtonian fluid flow [175, 211] in porous materials have also been demonstrated. Such single- and multi-phase simulations, of course, have great importance in DR technology.

9.2.5 A Complete EOR Core Flooding Study in Rocks at High Spatial Resolution

Laboratory-scale EOR core flooding studies are performed to gain a deeper understanding of the recovery processes and/or to screen different displacing fluids, thereby providing useful information for field-scale EOR operations. Although MR has been widely used to study EOR core floods in the laboratory [17, 24, 193, 212], it has never been used to probe these processes at pore-scale resolutions. Therefore, it would be valuable to use the high-resolution MRI techniques developed in this thesis to monitor a complete EOR core flooding study. The experiment could comprise two main flooding stages – brine injection followed by chemical flooding (i.e., polymer, surfactant, or a combination of these) – in which aqueous solutions would be injected in an initially oil-saturated core plug. The injection process would be monitored using chemically-selective high-resolution MRI techniques developed in Chapter 8. The exact experimental protocol, of course, would have to be carefully designed; the decisions would have to be made about the rock type to be studied, the type of oil to be used for saturating
the plug, the type of chemical to be used for chemical flooding, the number of pore volumes of
displacing fluid to be injected, injection flow rates, and other factors.
References


References


References


