PORE-SCALE SIMULATION OF NMR RESPONSE IN POROUS MEDIA

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ABSTRACT

Rock properties are usually predicted using 3D images of the rock’s microstructure. While single-phase rock properties can be computed directly on these images, two-phase properties are usually predicted using networks extracted from these images. To make accurate predictions with networks, they must be topologically similar to the porous medium of interest. In this work, NMR response is simulated using a random walk method. The simulations were performed on 3D images obtained from micro-CT scanning and in topologically equivalent networks extracted from these images using a maximal ball algorithm. A comparison of the NMR simulations on a 3D image and an extracted network helps to ascertain if the network is representative of the underlying 3D image.

Single-phase NMR simulations are performed on 3D images and extracted networks for different porous media including sand packs, poorly consolidated sandstones, consolidated sandstones and carbonates, and are compared successfully with experimental measurements. The algorithm developed for the simulation of NMR response in networks was validated using a tuned Berea network that reproduced experimental capillary pressure data in Bentheimer sandstone. Simulation results of the sand packs and poorly consolidated media show that the T2 distributions of the networks are narrower than those of the corresponding micro-CT images and experimental data. This is attributed to the loss of some fine details of the pore structure in the network extraction algorithm. The algorithm developed for single-phase NMR response in networks was extended to two-phase fluids in order to study the effect of wettability on simulated NMR response in networks. While NMR behaviour is influenced pore structure, wettability and phase saturation, it is not possible to determine each of these influences uniquely. The ultimate goal is to have a two-phase simulator that predicts relative permeability, electrical resistivity, NMR response and capillary pressure which will be used to determine the wettability of a porous medium.
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1. Introduction

To make accurate predictions using network models, the wettability of the porous medium must be known, especially if comparison with experimental measurements is desired. NMR response provides information about pore size distribution and wettability, which if combined with other wettability dependent properties like relative permeability, capillary pressure and electrical resistivity can be used to pin down the wettability of a porous medium. As a preliminary step to the simulation of NMR response of two-phase fluid in networks to investigate the effect of wettability, NMR response of single-phase fluid is simulated in networks extracted from the micro-CT images of different porous media ranging from sand packs to carbonates. One of the uses of NMR response is that it can be used to validate how representative a network is, to the micro-CT image or the microstructure from which it was extracted.

The starting point in the prediction of transport properties of reservoir rocks is the generation of 3D images; a detailed literature review of the different methods used in obtaining these images is described in Chapter 2. A review of the different algorithms used in extracting networks from these 3D images is also discussed along with different mathematical methods used for the computation of transport properties in 3D images and networks. Fundamentals of NMR response and the modelling of the different relaxation mechanisms are discussed in Chapter 3, along with a detailed description of the random walk method.

In Chapter 4, the algorithm used for the simulation of NMR response of single-phase fluid in micro-CT images is described and validated. Chapter 5 describes the algorithm developed for the simulation of NMR response of single-phase fluids in networks. The single-phase NMR simulation algorithm is extended to two-phase fluids in Chapter 6. In order to further validate the algorithms developed for the simulation of NMR response in 3D images and networks, sand packs were studied because of their homogeneity.
A detailed comparison of NMR simulation results of sand packs with experimental data is discussed in Chapter 7. These comparisons are further extended to poorly consolidated and consolidated sandstones in Chapter 8. In chapter 9, networks are generated for carbonates from their experimental capillary pressure by tuning the properties of a Berea network to match the measured capillary pressure. NMR response was then simulated in these carbonates networks and are compared with experimental data. Two-phase NMR simulation results for different porous media and the effect of wettability are discussed in Chapter 10. Finally in chapter 11, the important findings of this work are summarized and recommendations for future work are discussed.

The following articles have been either based on material presented in this thesis or used by the simulation code developed in this work.


2. Literature Review

Rock flow properties cannot be predicted without an accurate 3D representation of the rock microstructure. This is most commonly achieved using one of the following three methods: (1) Experimental - (Hazlett, 1995; Arns et al., 2004), (2) Statistical – which involves stochastic microstructural modelling, also known as image reconstruction procedure, (Adler et al., 1990; Liang et al., 1998; Okabe and Blunt, 2004) and (3) Process- or physics-based method, which simulates the rock forming processes (Bryant et al., 1993, Bakke and Øren, 1997; Øren and Bakke, 2003; Jin et al., 2003).

2.1 Methods of generating 3D images of microstructures

Experimental (Micro-CT imaging)

The experimental 3D representation of a rock microstructure involves the use of X-ray computed tomography (micro-CT). This is already an established and rapidly evolving technology which is of significant importance in the image analysis of porous media. It was initially developed for widespread use in the field of medicine; however its use has been extended to a wide variety of fields which include, archaeology, geophysics, oceanography, materials science and astrophysics. X-ray computed tomography is a quick and non-destructive three-dimensional visualization tool used for viewing the internal structure of objects as determined by the variations in density and atomic composition.

It is used efficiently for qualitative and quantitative analysis of internal structures of reservoir rocks especially if those structures are marked by sufficiently great differences in atomic composition and/or density as shown in Figure 2-1. Density transitions usually correspond to boundaries between materials or phases.
The density contrast which is usually observed between fluid phases and grains in reservoir rocks is the basis for the current widespread application of X-ray computed tomography (CT) in the field of petroleum geology, rock mechanics and soil science (Peters et al., 1996). The term microtomography (micro-CT) is often used in imaging reservoir rocks in order to indicate that the pixel sizes of the cross-section are in the µm range.

Figure 2-1: (a) 3D Micro-CT image of porous media (silica sphere pack), imaged at the Australian National University (http://xct.anu.edu.au/network_comparison). (b) Corresponding 2-D cross sectional image.

Until recently, direct imaging of 3D microstructures using X-ray computed microtomography (Dunsmuir et al., 1991; Coles et al., 1994, 1996; Spanne et al., 1994; Hazlett, 1995; Coker et al., 1996), was often time consuming, expensive and not readily applicable to damaged cores and drill cuttings. Hence, it was quite challenging to obtain reliable images of the 3D pore structure. Even with modern machines, the resolution is limited to a few microns which excludes small pores in tight sandstones and carbonates. This limitation has led to the development of statistical methods based on high resolution 2D images.

**Statistical method**

In the past, information about the microstructure of porous materials was often limited to two-dimensional thin section images. Such 2D images have formed the basis for the reconstruction techniques developed to generate 3D microstructures statistically (Joshi, 1974; Quiblier, 1984; Adler et al., 1990, 1992; Roberts, 1997; Hazlett, 1997; Yeong and Torquato, 1998a, b; Manswart and Hilfer, 1998; Okabe and Blunt, 2005).
The reconstruction techniques use the spatial information of 2D thin section images by measuring statistical properties, such as porosity, correlation and lineal path functions on the 2D image. 3D microstructures are then generated such that the measured statistical properties of the 2D thin section images are preserved. Detailed quantitative comparisons of statistically generated microstructures with X-ray tomographic images of sedimentary rocks have shown that statistical reconstructions may differ significantly from the original sample in their geometric connectivity especially for low porosity materials, (Hazlett, 1997; Biswal et al., 1999; Manswart et al., 2000; Øren and Bakke, 2003). This has led into more sophisticated statistical techniques, such as multiple point statistics.

These methods preserve higher-order information, describing the statistical relation between multiple spatial locations. They replicate typical patterns of the void space seen in thin sections thereby capturing the large-scale features of the pore space geometry. The application of multiple point statistics to reconstruct 3D images using 2D image data has successfully been used to reconstruct long-range connectivity of sandstone and carbonate samples (Okabe and Blunt, 2004; Okabe and Blunt, 2005).

**Process-based reconstruction method**

A different approach to the stochastic generation of 3D pore structures is the process-based reconstruction method (Bakke and Øren, 1997), where the main rock forming processes; sedimentation, compaction and diagenesis are simulated. Input data into the simulation are petrographical measurements on BSE images of thin sections such as grain sizes and shapes, porosity, amount of quartz cement, clay and other diagenetic minerals. This method has been used to reconstruct the 3D microstructure of Fontainbleau sandstone (Øren and Bakke, 2002). Transport properties computed in reconstructed microstructures had been compared successfully with those computed on equivalent micro-CT images of similar porosity, Figure 2-2 shows a comparison of a reconstructed microstructure with a micro-CT image of Fontainbleau sandstone. In a similar approach to the process-based reconstruction method, Jin et al., (2003) used a physics-based depositional model to reconstruct natural sedimentary rock, and generated 3D images of the pore space at an arbitrary resolution.
This model provided a detailed microstructure of the rock thereby making it possible to calculate the steady state velocity field in the single-phase fluid flow. The model was used to analyze unconsolidated rocks whose micro-tomographic images cannot be obtained. The effect of compaction and various styles of cementation on the microstructure and permeability of reservoir rock were also studied using this model.

![Image of micro-CT and process based image](image)

**Figure 2-2**: Comparison of a micro-CT image (a) and process based image (b) of Fontainebleau sandstone (Øren and Bakke, 2002).

Among the three methods discussed for the generation of 3D representation of the rock microstructure, X-ray computed microtomography (micro-CT) despite its limitations, is the most promising since it is a direct measurement of the actual microstructure. Process-based reconstructions may be problematic for rocks whose depositional and diagenetic history is complex or unknown such as many carbonates, thus statistical methods are useful in overcoming these limitations of the process-based method.

### 2.2 Network models

The use of network models to study multiphase flow in porous media was pioneered by Fatt (1956a). These models were based on the idea that pore space may be represented as an interconnected network of capillary tubes whose radii represent the dimensions of the pores within a porous medium.
Fatt’s initial network was a $50 \times 50$ lattice of resistors which was used to compute relative permeability and capillary pressure for drainage-type displacement. Although the results of this initial work were qualitative because the networks were regular and two-dimensional which is not representative of a real porous medium, it is still the basis of the current use of networks for the prediction of transport properties. Fatt’s initial network assumed that the bonds’ intersections do not possess any volume of their own. Chatzis and Dullien (1977) later focused on the assumptions made by Fatt (1956a). They used a 3D model that consisted of sites which are connected to each other by bonds. The sites correspond to pore bodies while the interconnecting bonds are analogous to pore throats connecting the pore bodies. Most researchers nowadays attribute the majority of the porosity to the pore bodies. The basis of these network models is that the void space of a porous medium can be represented by a graph of connected sites.

The interconnecting pathways of networks make them structurally similar to porous media. A network of pores and throats preserves the essential topology of the pore space it represents. In addition, if sizes are assigned to the pores and throats in accordance with the sizes of the pore bodies and throats in the porous medium, then macroscopic properties of the resulting network should accurately reflect the properties of the porous medium. For accurate prediction of properties of the porous medium, a network model should replicate both the geometry and topology of pore space as much as possible, so that flow through the network is equivalent to flow through the actual porous medium. Direct replication of a porous medium with network models has proven elusive because the pore space in real granular media is complicated.

The pioneering networks of Fatt (1956a) and Chatzis and Dullien (1977) were based on a regular lattice; however the pore space in a real porous medium is complicated and may not be adequately described by such regular lattice. Chatzis and Dullien, (1977) compared results from these regular cubic networks with experimental mercury intrusion data from sandstones and noted that regular networks combined with circular capillaries did not yield a realistic description of real sandstones.
In order to obtain a network that best describes the complicated structure of a given rock sample, the coordination number of the rock which is typically between 3 and 8 (Jerauld and Salter, 1990) can be matched by removing throats from a regular lattice of higher coordination number. An alternative way of constructing a representative network is to randomly distribute points within the model area and then construct a network from the triangulation of these points. Jerauld et al. (1984a) constructed random networks from Voroni diagrams; these networks had an initial coordination number of more than 15. This was significantly reduced to a coordination number of 6 by removing the longest throats. Little difference was observed in the comparison of the relative permeability of the networks constructed by reducing coordination numbers and networks based on a regular lattice. All the methods of constructing networks fail to capture any of the statistics associated with real porous media, thereby necessitating the need for other network construction methods.

Bryant et al. (1992; 1993a), pioneered the use of networks derived from a real porous medium. The porous medium was formed from a dense random packing of equally sized spheres. The spatial coordinates of every sphere was measured thereby enabling the microstructure of the medium to be completely determined; a network model which replicates the pore space was then extracted. Relative permeabilities were then predicted from the networks which were successfully compared with experimental values measured on sand packs, bead packs and a simple sandstone. In contrast, using a statistically equivalent but uncorrelated network, the permeability was over predicted by a factor of two (Bryant et al., 1993b). This result emphasizes the significance of using geologically realistic networks when predicting flow behaviour.

Other transport properties such as electrical conductivity and capillary pressures have also been compared successfully with experimental results from sand packs, bead packs and a simple sandstone. It is unlikely that most porous media will comprise of equally-sized grains resulting in a constant coordination number, as such the application of the method used for network extraction by Bryant et al. (1992; 1993a; 1993b), to more complex porous media is limited.
2.3 Network extraction

In order to extract a representative network from a real porous medium, an accurate 3D representation of the microstructure is required. This is most commonly achieved using any of the three methods described earlier. A common method of extracting networks from microstructures involves defining the skeleton of the pore space as a set of points (voxels) at equal distances from two or more points of the solid grain (Serra, 1982; Adler, 1992). This skeleton may be regarded as the centre line of the pore network; this line contains points where two or more lines meet. These points are the network nodes which are connected to other nodes through the pore throats.

Skeleton extraction from binarized images is often carried out by means of thinning algorithms (Hilditch, 1969), which are based on deleting or preserving the analysed pixel according to the rules for the binary 1- and 0-pattern of its surrounding neighbour pixels. Lindquist et al. (1996; 1999; 2000) extended a similar thinning algorithm (Lee et al., 1994) in which the pore space is eroded until only the centre-lines remain in order to analyze geometric properties such as connectivity and tortuosity of skeletons generated from various micro-CT imaged rock samples.

An alternative method of skeleton extraction from binary images is the dilation method (Bakke and Oren, 1997) which is the inverse function of the thinning method. In the dilation method, each grain is numbered, and is subjected to ultimate dilation, the border surface between two ultimate dilated grains is a grain-to-grain connection surface. This surface contains the pore network skeleton. The skeleton of the pore network is thus found where two or more such dilated grain border surfaces meet. This skeleton is used as a basis for mapping of pore throats between nodes. For each pore throat skeleton voxel, the pore throat wall is mapped in a plane normal to the local direction of the pore throat. The throat radius is measured with a rotating vector which measures the distance from the skeleton voxel to the pore throat wall in this plane. The area, perimeter and inscribed radius for the narrowest constriction of the pore throat are recorded. The volume of each pore body is calculated using an average radius from the geometrical centre point which is defined by the skeleton node. The geometry of the pore bodies are analysed in a manner similar to that of the pore throats.
An alternative method of generating networks from 3D images without the need to first extract a skeleton is the maximal ball method (Silin et al., 2003; Silin and Patzek, 2006; Al-Kharusi and Blunt, 2007; Dong, 2007). This method involves finding the largest inscribed spheres (maximal ball) that touch grain surfaces. Maximal balls (MB) are the basic elements used to define the pore space and detect the geometrical changes and connectivity. A maximal ball is defined as a set of voxels assembling a largest sphere, as such, a maximal ball must touch the grain surface and it cannot be a subset of any other maximal ball. Every maximal ball possesses at least one voxel that is not contained in any other maximal ball, the aggregate of all maximal balls defines the void space in a rock image.

Figure 2-3: A principal MB absorbs the clusters of smaller neighbours to form multiclusters; maximal balls connected to two clusters define a throat. Pore-throat chains (white arrows) define the topology of the pore space.

The maximal balls fill the entire void space measuring the local apertures in pore central spaces and irregular corners. To define the topology, maximal balls are merged into clusters. Two types of clusters are defined: single and multiclusters. In a single cluster, a principal maximal ball absorbs all its direct smaller neighbours in its domain. Multiclusters are extensions of single clusters; the principal maximal ball absorbs the clusters of smaller neighbours in its domain. The maximal balls are then sorted into interconnected clusters, the common principal maximal ball of each cluster defines a pore.
If a maximal ball is connected to two clusters, then it defines a throat. As shown in Figure 2-3, clusters A and B meet at the throat node indicated; this is referred to as a pore-throat chain. These chains are used to define the topology of the pore space as shown in Figure 2-4. The radius, volume and shape factor of the pores and throats are then calculated. The inscribed radius of an element corresponds to the radius of its principal maximal ball. Their volumes are found by counting the number of pore voxels associated with each element. Shape factor, $G$ is calculated from:

$$ G = \frac{VL}{A_s^2} \quad (2.1) $$

where $V$ and $L$ are the volume and length of the element respectively, $A_s$ is the grain surface area of the element.

![Figure 2-4: (a) Micro-CT image of a sandstone and (b) topologically equivalent network extracted from this image using the maximal ball algorithm.](image)

2.4 **Prediction of transport properties**

Permeability, formation factor and NMR response can be predicted in micro-CT images and extracted networks. Multiphase properties such as capillary pressure and relative permeability can only be predicted in networks.
**Permeability**

Permeability in the 3D images is computed as the mean of the directional permeabilities. These are calculated by applying a macroscopic pressure gradient \((p_1 - p_0)/L\) in the reference direction.

\[
Q_i = \frac{k_i (p_1 - p_0) A}{\mu L}
\]  

(2.2)

\(Q_i\) is the macroscopic flux obtained from the macroscopic pressure gradient, \(\mu\) is the viscosity of the fluid and \(A\) is the cross sectional area perpendicular to the reference direction. The fluid flow is assumed to be governed by the steady state Stokes equations for an incompressible Newtonian fluid subject to a no slip boundary condition at the solid wall, (Øren et al., 2002). Permeability is also calculated in the networks using equation (2.2), \((p_1 - p_0)/L\) in this case, is the applied macroscopic pressure gradient on the network and \(Q_i\) is the total single-phase flow rate through the network which is found by solving for pressure everywhere and imposing mass conservation at every pore (Valvatne and Blunt, 2004).

**Formation factor**

Formation factor is calculated in the 3D images as the harmonic mean of the directional formation factors. The directional formation factors \(F_i\) are defined as the inverse of the macroscopic electrical conductance, \(\sigma_i\) in a given \(i\)-direction:

\[
F_i = \frac{\sigma_w}{\sigma_i}
\]  

(2.3)

where \(\sigma_w\) is the bulk electrical conductance of the fluid that fills the pore space. \(\sigma_i\) is computed from a linear relation between the total electric flux, \(Q_i\), and the applied potential gradient.
\[ Q_i = -\sigma_i \frac{\left( \Phi_i - \Phi_o \right)}{L} A \] (2.4)

The potential \( \Phi_i \) is applied to and inlet face, \( \Omega_i \) of area \( A \), and potential \( \Phi_o \) is applied to and outlet face \( \Omega_o \) separated from \( \Omega_i \) by a distance \( L \) (Øren et al., 2002). Formation factor is calculated in the network by a similar approach invoking Ohm’s law to find the overall conductance (Valvatne and Blunt, 2004).

**Capillary pressure and relative permeability**

Capillary pressure is computed in the network from the maximum local displacement pressure of the invading phase as a function of saturation, (Valvatne and Blunt, 2004). The relative permeability, \( k_{ri} \), is given by:

\[ k_{ri} = \frac{Q_{im}}{Q_{is}} \] (2.5)

where \( Q_{im} \) is the total flow rate in multiphase conditions with the same imposed pressure drop in equation (2.2) while \( Q_{is} \) is the total single-phase flow rate (Valvatne and Blunt, 2004).

**NMR Response**

NMR response is predicted in 3D images and networks by a random walk method, (Ramakrishnan et al., 1998; Øren et al., 2002). This involves the simulation of the Brownian motion of a diffusing particle called the walker. These walkers diffuse within the pore space and when they come in contact with a solid surface, they are killed with a finite killing probability. The life-time distribution of the walkers is the magnetization decay which can be inverted into \( T_2 \) distribution by using a curvature-smoothing regularization method (Chen et al., 1999).
Toumelin et al., (2003) simulated NMR response of two-phase fluids in 3D bimodal pack of spheres which replicates the complex pore structure (microporosity and macro porosity) geometry of carbonate formations. Each grain in the model was defined as a sphere inscribed into a concentric cubic cell. If the sphere does not completely fill its cubic unit, then the complimentary volume is filled with fluids. Fixed blobs centred in the macropore space was included in the model to represent partial saturations of the immiscible nonwetting oil phase, while the microporosity was only filled with irreducible water. The simulations were performed in the presence of constant magnetic gradients to replicate actual well-logging conditions that include the effect of Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences at a microscopic level. Magnetization decay is simulated in each phase and the total decay of the two phases is given by a weighted average of the magnetization decay of each phase.
3. Nuclear Magnetic Resonance

3.1 Basics of NMR response

Nuclear Magnetic Resonance (NMR) is a physical phenomenon based upon the quantum magnetic properties of an atom's nucleus. It is observed when the nuclei of certain atoms are aligned with an applied constant magnetic field and then perturbed using an alternating orthogonal magnetic field. Magnetic nuclei absorb energy when placed in a magnetic field of a strength specific to the identity of the nuclei. When the absorption occurs, the nucleus is described as being in resonance, different atoms within a molecule resonate at different frequencies at a given field strength. The observation of the resonance frequencies of a molecule allows the determination of the structural information about the molecule. This resulting response to the perturbing magnetic field is the phenomenon that is exploited in NMR spectroscopy and magnetic resonance imaging. Only nuclei with a property called spin experience this resonance phenomenon.

3.1.1 Spin

Spin is a fundamental property of nature like electrical charge or mass. Spin comes in multiples of $\frac{1}{2}$ and can be positive or negative. Protons, electrons, and neutrons possess spin. Individual unpaired electrons, protons, and neutrons each possess a spin of $\frac{1}{2}$. Two or more particles with spins having opposite signs can pair up to eliminate the observable manifestations of spin. In nuclear magnetic resonance, it is unpaired nuclear spins that are of importance. The spin property possessed by a proton enables it to be considered as a small magnetic field which will cause the nucleus to produce an NMR signal. The most commonly measured nuclei are $^1$H (Hydrogen 1; the most receptive isotope at natural abundance) and $^{13}$C (Carbon 13), although nuclei from isotopes of many other elements can also be observed. When placed in a magnetic field of strength $B$, a particle with a net spin can absorb a photon, of frequency $\nu$ (Purcell et al., 1946; Bloch et al., 1946).
The frequency \( \nu \) (often referred to as the Larmor frequency) depends on the gyromagnetic ratio, \( \gamma \) of the particle and the magnetic field strength \( B \).

\[
\nu = \gamma B
\]  

For hydrogen (\(^1\text{H}\)), \( \gamma = 42.58 \text{ MHz} / \text{T} \) (Hornak, 1997).

### 3.1.2 Spin packets

It is cumbersome to describe NMR on a microscopic scale. A macroscopic picture is more convenient, (Hornak, 1997). The first step in developing the macroscopic picture is to define the spin packet. A spin packet is a group of spins experiencing the same magnetic field strength. At any instant in time, the magnetic field due to the spins in each spin packet can be represented by a magnetization vector. The vector sum of the magnetization vectors from all of the spin packets is the net magnetization. The external magnetic field and the net magnetization vector at equilibrium are both along the z-axis.

### 3.1.3 Longitudinal relaxation processes

At equilibrium, the net magnetization vector lies along the direction of the applied magnetic field \( B_0 \), and is called the equilibrium magnetization \( M_o \). In this configuration, the Z component of magnetization \( M_z \) equal \( M_o \). \( M_z \) is referred to as the longitudinal magnetization. It is possible to change the net magnetization by exposing the nuclear spin system to energy of a frequency equal to the energy difference between the spin states. If enough energy is put into the system, it is possible to saturate the spin system and make \( M_z = 0 \) as shown in Figure 3-1a. The time constant which describes how \( M_z \) returns to its equilibrium value is called the spin lattice relaxation time \( T_1 \) (Bloembergen et al., 1948). The equation governing this behaviour as a function of the time \( t \) after its displacement is:

\[
M_z = M_o \left( 1 - e^{-t/T_1} \right)
\]
The spin-lattice relaxation time, $T_1$, is the time to reduce the difference between the longitudinal magnetization $M_z$ and its equilibrium value by a factor of $e$.

\[
\frac{2}{T_t} = \ln \left( \frac{M_z}{M_{so}} \right) = 1 - e^{-t/T_1} \tag{3.3}
\]

Figure 3-1: (a) In longitudinal relaxation processes, the net magnetization $M_z$ increases exponentially to the initial value $M_o$ with the time constant $T_1$. (b) For transverse relaxation processes, the net magnetization $M_{xy}$ decreases exponentially to zero from its the initial value $M_{xy}$ with the time constant $T_2$.

### 3.1.4 Transverse relaxation processes

If the net magnetization is placed in the XY plane, it will rotate about the Z axis at a frequency equal to the frequency of the photon which would cause a transition between the two energy levels of the spin. This frequency is called the Larmor frequency. In addition to the rotation, the net magnetization starts to dephase because each of the spin packets making it up is experiencing a slightly different magnetic field and rotates at its own Larmor frequency. The longer the elapsed time, the greater the phase difference. The time constant which describes the return to equilibrium of the transverse magnetization, $M_{xy}$ is called the spin-spin relaxation time or transverse relaxation time, $T_2$.

\[
M_{xy} = M_{xyo} e^{-t/T_2} \tag{3.3}
\]
$T_2$ is always less than or equal to $T_1$. The net magnetization in the XY plane decreases to zero while the longitudinal magnetization increases to $M_o$ along the z-axis.

### 3.2 Relaxation mechanisms

There are three main mechanisms that cause both longitudinal and transverse relaxation during NMR measurements; these are surface relaxation, bulk relaxation and diffusive relaxation.

#### 3.2.1 Surface relaxation

Surface relaxation occurs as a result of Brownian motion which causes fluid molecules to diffuse substantial distance during NMR measurements. From the equation for diffusion:

\[
X^2 = 6D_0t
\]

where $X^2$ is the mean squared distance a molecule diffuses in time $t$, and $D_0$ is the molecular diffusion coefficient which is a property of the fluid and is dependent on temperature and viscosity. During the random motion of molecules in a fluid, the protons in these molecules collide with the pore surfaces and consequently relax thereby contributing to both the transverse and longitudinal relaxation.

The rate at which these protons relax upon contact with a pore surface is dependent on the surface relaxivity of the pore. Surface relaxivity is thus defined as the ability of a surface to relax the magnetization of the protons in the molecules of a given fluid and is often determined from diffusion experiments and is denoted by $\rho_1$ (for $T_1$ relaxation) and $\rho_2$ (for $T_2$ relaxation). Not all surfaces are effective in relaxing proton spins; paramagnetic ions such as iron, manganese, nickel and chromium are powerful relaxers and tend to control the rate of relaxation when they are present.
Carbonates are known to have lower rates of surface relaxivity than sandstones. Surface relaxivity also depends on temperature (Godefroy et al., 2001) and the type of fluid in the pore; surface relaxivities to water are higher than surface relaxivity to oil (Looyestijn and Hofman, 2005). The relaxation time of protons will be short if their molecules are contained in small pores because their diffusion is restricted by the pore sizes. Correspondingly, the relaxation time will be long in large pores because the protons spend an appreciable period diffusing substantial distances before eventually relaxing as shown in Figure 3-2.

![Figure 3-2: Magnetization decays faster in small pores than in large ones](image)

The relaxation time will also be high if only a small amount of surface area is available to relax the protons of a large volume of liquid. As such, relaxation rates, \( \frac{1}{T_{1s}} \) and \( \frac{1}{T_{2s}} \), are dependent on the intrinsic surface relaxivity of the pore surface and its surface area-to-volume ratio (Brownstein and Tarr, 1979; Loren and Robinson, 1970),

\[
\frac{1}{T_{1s}} = \frac{\rho_1 S}{V}
\]

(3.5)

and

\[
\frac{1}{T_{2s}} = \frac{\rho_2 S}{V}
\]

(3.6)

where \( S \) is the surface area and \( V \) is the volume of the pore.
3.2.2 **Bulk relaxation**

Relaxation in bulk reservoir fluids is mainly as a result of fluctuating local magnetic fields that occur due to the random motion of neighbouring spins. Bulk relaxation is important when a fluid is prevented from coming in contact with a solid surface, for example a droplet of oil or gas at the centre of a pore without having any contact with the surface. Bulk relaxation is a property of the fluid alone and is independent of any property of the formation in which it resides; it does however depend on fluid temperature and viscosity. Whenever bulk relaxation is dominant, longitudinal relaxation time $T_1$ is equal to transverse relaxation time $T_2$.

3.2.3 **Diffusive relaxation**

The Carr-Purcell-Meiboom-Gill (CPMG) sequence is often used for transverse relaxation measurements; any radio frequency pulse at the Larmor frequency causes the net proton magnetization to undergo pure rotation. The CPMG sequence starts with a pulse producing a 90° rotation, so that any longitudinal magnetization now becomes transverse and produces a precession signal detected by the radio-frequency coil (Meiboom and Gill, 1958). This signal decays very quickly if the magnetic field is very inhomogeneous and in consequence the precession of individual protons quickly dephase.

A subsequent pulse produces a 180° rotation which reverses the dephasing, and produces a second signal called the “spin echo”. Each subsequent 180° pulse produces an additional spin echo, and the sequence of amplitudes of successive spin echoes is recorded. The sequence of these spin echo amplitudes is affected by inhomogeneities in the permanent magnetic field when protons are diffusing. When water or hydrocarbon molecules diffuse, the refocusing is no longer a perfect mirror image of the dephasing, the molecules have probably diffused into a region of different magnetic field strength and in consequence their protons now precess at different frequency. The global relaxation rate due to diffusion in such magnetic field gradients is given as (Kleinberg and Vinegar, 1996);
\[
\frac{1}{T_2^D} = \frac{\gamma^2 G^2 T_E^2 D}{12}
\] (3.7)

where \( D \) is the molecular diffusion coefficient, \( G \) is the magnetic gradient strength in \( \text{T/m} \), \( T_E \) is the time between spin echoes in the CPMG sequence and \( \gamma \) is the gyromagnetic ratio of the proton.

### 3.2.4 Relaxation due to all mechanisms

In summary the relaxation mechanisms described all act in parallel and as such their rates add up, (Bloembergen et al., 1948). For transverse relaxation;

\[
\frac{1}{T_2} = \frac{1}{T_{2S}} + \frac{1}{T_{2B}} + \frac{1}{T_{2D}}
\] (3.8)

where \( 1/T_{2S} \) is the surface contribution, \( 1/T_{2B} \) is the bulk contribution and \( 1/T_{2D} \) is the diffusion in field gradient contribution (Kenyon, 1997). The corresponding equation for longitudinal relaxation is,

\[
\frac{1}{T_1} = \frac{1}{T_{1B}} + \frac{1}{T_{1S}}
\] (3.9)

### 3.3 Modelling of NMR response

In order to model NMR response, each of the relaxation mechanisms - surface relaxation, bulk relaxation and relaxation due to diffusion in a magnetic field gradient must all be modelled independently since they all occur independently and simultaneously. The reaction-diffusion equation is the basis for the modelling of surface relaxation and bulk relaxation mechanisms of NMR response.
3.3.1 The reaction-diffusion equation

Senturia and Robinson (1970) proposed that the NMR response of a porous medium assuming no magnetic gradient can be modelled by a reaction-diffusion equation. This diffusion model is based on a random-walk picture in which the protons in the molecules of a liquid at the surface of a confining region experience an enhanced relaxation probability per unit time. This reaction-diffusion equation is;

\[
\frac{\partial [M]}{\partial t} = D \nabla^2 [M] - \frac{[M]}{T_2 b} \tag{3.10}
\]

with initial and boundary conditions,

\[
[M] = [M_0] \text{ at } t = 0 \quad \text{and} \quad Dn.\n[M] = \rho[M]
\]

where \([M]\) is the magnetization per unit volume, \(\rho\) is the surface relaxivity and \(D\) is the diffusion coefficient. The magnetization profile can be obtained by solving the differential equation. The total magnetization \(M(t)\) at a given time can be calculated by integrating the magnetization over the whole volume. If the structure of the porous medium is known then a direct solution of equation (3.10) can be used to estimate the magnetization decay.

The reaction-diffusion equation (3.10) can be solved by finite-difference method or the random walk method. The finite difference approach may require large computer memory and long computation time especially if the porous medium has a complicated geometry. For simply shaped pores, such as a sphere, a cylinder, cube, or rectangular parallelepiped, analytical solutions can be derived for the magnetization decay. An analytical solution for the magnetization decay of a fluid in a spherical pore has been proposed by Crank (1975). The magnetization decay as a function of time in a spherical pore of radius \(r\) is given as:

\[
M(t) = M_0 \exp \left( -\frac{t}{T_2 b} \right) \sum_{n=1}^{\infty} \frac{6L^2 \exp\left(-\frac{\rho n^2 Dt}{r^2}\right)}{B_n^2(B_n^2 + L^2 - L)} \tag{3.11}
\]
where $\beta_n$ is the root of $\beta_n \cot \beta_n + L - 1 = 0$ and $L = \rho r / D$. In the fast diffusion limit where $(L \ll 1)$, the magnetization follows a single exponential decay (Senturia and Robinson, 1970), i.e.

$$M(t) = M_0 \exp \left( -\frac{t}{T_2} \right)$$

(3.12)

$M_0$ is the initial transverse magnetization at time $t = 0$ and the decay rate $T_2$ is given by,

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + \frac{\rho S}{V}$$

(3.13)

which is a combination of the bulk and surface relaxation mechanisms. $S/V$ for a sphere is $3/r$, equation (3.13) is also valid for other simply shaped pores. From equation (3.13), for a spherical pore, we have;

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + \frac{3\rho}{r}$$

(3.14)

the surface area to volume ratio $(S/V)$ is a measure of pore size, thus the transverse relaxation time, $T_2$ is directly proportional to pore size. In reality, a porous medium will comprise of several interconnected pores of different sizes and shapes, as such, a multiexponential expression representing a distribution of $T_2$ constants is much more suitable for describing the magnetization decay of a real porous medium (Kenyon, 1997).

$$M(t) = M_0 \sum_{i=1}^{n} a_i \exp \left( -\frac{t}{T_{2i}} \right)$$

(3.15)

$a_i$ is the volume fraction of pores of size $i$ that decay with relaxation time $T_{2i}$. Usually a logarithmic mean is used to determine the mean transverse relaxation time, $T_{2\text{lm}}$. 

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\[ T_{2\text{im}} = \exp \left( \frac{\sum a_i \log T_{2i}}{\sum a_i} \right) \] (3.16)

### 3.3.2 Modelling surface relaxation

The reaction-diffusion equation (3.10) was solved by a random walk method (Ramakrishnan et al. 1998). This method is based on simulating the Brownian motion of diffusing particles called the random walkers. Initially, the walkers are placed randomly in the pore space. At each time step, the walkers diffuse from their initial position \([x(t), y(t), z(t)]\) to a new position \([x(t + \Delta t), y(t + \Delta t), z(t + \Delta t)]\) on the surface of a sphere with radius, \(s\) centred on their initial positions. The time it takes to diffuse this distance \(s\) is given by;

\[ \Delta t = \frac{s^2}{6D} \] (3.17)

The new position of the walkers after each time step is given by;

\[ x(t + \Delta t) = x(t) + s \sin \phi \cos \theta \] (3.18)

\[ y(t + \Delta t) = y(t) + s \sin \phi \sin \theta \] (3.19)

\[ z(t + \Delta t) = z(t) + s \cos \phi \] (3.20)

the angle \(\theta\) is randomly selected in the range \((0 \leq \theta \leq 2\pi)\) and \(\phi\) is randomly selected in the range \((0 \leq \phi \leq \pi)\). If the walker encounters a solid surface, it is killed with a finite killing probability \(\delta\). The killing probability \(\delta\) is related to the surface relaxivity (Bergman et al. 1995) by;

\[ \delta = \frac{2\rho s}{3D} \] (3.21)
If the walker survives, it simply bounces off the surface and returns to its previous position and time is advanced by the time step given in equation (3.17). Since the walkers move with equal probability in all directions, this algorithm is valid because there is no magnetic gradient in the system. At each time step, a record of the fraction of the walkers alive \( P(t) \) is kept.

\[
P(t) = \frac{N_t}{N_0}
\]  

(3.22)

\( N_t \) is the number of walkers alive at time \( t \) and \( N_0 \) is the initial number of walkers at time \( t = 0 \). \( P(t) \) is analogous to the normalized amplitude due to surface relaxation mechanism in NMR measurements, as such:

\[
P(t) \equiv \frac{M(t)}{M_0}
\]  

(3.23)

The random walk solution method can be validated with the analytical solution for the magnetization decay of a fluid in a spherical pore. The analytical solution for the magnetization decay as a result of surface relaxation mechanism alone of a fluid in a spherical pore in fast diffusion limit \( L << 1 \) is given by:

\[
\frac{M(t)}{M_0} = \exp\left(-\frac{3\rho t}{r}\right)
\]  

(3.24)

A direct substitution of the surface relaxivity, \( \rho \) and the radius, \( r \) of the spherical pore into equation (3.24) gives the magnetization decay as a function of time. For the random walk solution, the diffusion coefficient of the fluid contained in the pore is required in addition to the radius and surface relaxivity of the pore. Using a spherical pore of radius 5µm, surface relaxivity of 20µm/s, a fluid diffusion coefficient of \( 2.5 \times 10^{-9} \text{m}^2/\text{s} \) and an initial number of 10,000 walkers, the magnetization decay is simulated using the random walk solution method. The ratio of the number of walkers alive to the initial number of walkers, \( P(t) \) was recorded at each time interval.
A plot of this ratio $P(t)$ against time ($t$) is the magnetization decay due to surface relaxation mechanism alone. The dimensionless constant $L$ defined as $L = \rho r / D$, in this analytical solution above is 0.04. From Figure 3-3, it is evident that the random walk solution is consistent with the analytical solution thereby validating the random walk solution method. A further advantage of the random walk solution method is that it is not only limited to simple geometrical shapes, it can be used to simulate magnetization decays in highly complicated geometries as we have in the complex pore spaces of 3D images.

### 3.3.3 Modelling bulk relaxation

Bulk relaxation is modelled by multiplying the magnetization decay due to surface relaxation mechanism and relaxation due to diffusion in magnetic gradients by the exponential decay;

$$b(t) = \exp \left( -\frac{t}{T_{2B}} \right)$$  \hspace{1cm} (3.25)
3.3.4 Modelling diffusive relaxation

The additional decay of the amplitudes of spin echoes as a result of diffusion in magnetic field gradients depends on the time interval between these spin echoes $2\Delta t$. This additional decay can be expressed as a function of time and as a multiplicative factor, (Kenyon, 1992);

$$g(t) = \exp\left(-\gamma^2 G_s^2 D_0 (\Delta \tau)^2 t\right)$$  \hspace{1cm} (3.26)

where $t$ is time, $D_0$ is the molecular self-diffusion coefficient of the fluid, $\gamma$ is the gyromagnetic ratio of the proton and $G_s$ is the spatial gradient of the magnetic field intensity. This decay becomes rapid as the spacing of the echoes $2\Delta t$ increases. When the echo spacing is very short, relaxation due to diffusion in magnetic field gradients is negligible. In order to incorporate this relaxation mechanism in NMR simulations, the experimental values of the spatial gradient of the magnetic field $G_s$ and the echo spacing $\Delta \tau$ must be known. This is required if comparison of simulation results with experimental data is desired.

3.3.5 Modelling relaxation due to all mechanisms

Since all the relaxation mechanisms occur simultaneously and independently, the total magnetization amplitude as a function of time is given as (Kenyon, 1992);

$$M(t) = M_0 \left[P(t)g(t)b(t)\right]$$  \hspace{1cm} (3.27)

where $P(t), g(t)$ and $b(t)$ are given by equations (3.22), (3.26) and (3.25) respectively.
4. Simulation of NMR response in 3D images

The capability of the random walk method to simulate magnetization decay in complex pore geometries has enabled the pore scale simulation of NMR response in discretized images of reservoir rocks. Simulation of magnetization decay using the random walk method is significant when surface relaxation mechanism is dominant because the random walk simulation method only simulates the surface relaxation mechanism of the NMR response. Bulk relaxation and relaxation due to diffusion in magnetic gradients are independent of the diffusion paths of the random walkers. Hence, if these relaxation mechanisms are dominant, then NMR response may not offer good insight about the pore size distribution of the porous medium. Discretized images obtained from micro-CT imaging have to be processed to enable the grains to be clearly differentiated from pores. A suitable method of achieving this is to convert the image in gray scale into binary format and denote the pores as 0 and the grains as 1 or vice versa as shown in Figure 4-1. In order to ensure that the discretized image is representative of the whole sample from which it was taken, its porosity can be compared to the porosity of the parent sample.

Figure 4-1: (a) Micro-CT image in gray scale is converted to a binary format (b) where pores are clearly distinguished from grains.
4.1 Geometry of the micro-CT image

The geometry of the pore spaces in micro-CT images are quite complex. These complexities are captured by the resolution of the micro-CT images. The inputs into the simulation code are the resolution of the image and the binarized image where 0 and 1 represents the pore and grain voxels respectively. The porosity of this binarized image is determined by simply counting the number of pore voxels and dividing by the total number of voxels in the image.

4.2 Initialization of walkers in the micro-CT image

Each pore voxel is assigned a unique identification number; equal numbers of walkers are then placed randomly in each pore voxel so as to ensure a uniform coverage of the entire pore space of the image. Assigning a high number of walkers to each pore voxel can be computationally expensive; for example, a $300^3$ voxel image of porosity 33% will have 9 million pore voxels and if 1 walker is assigned to each pore voxel, we will have 9 million walkers. This will result in longer simulation time. Alternatively, we can limit the number of walkers to be assigned to the pore voxels - in this case the walkers are assigned to randomly selected pore voxels.

4.3 Diffusion of walkers in the micro-CT image

The unit distance diffused by the walkers at each time step is chosen as a function of the resolution of the image: $s = 0.2L_R$ where $L_R$ is the resolution of the image with $s$ substituted in equation (3.17) to determine the time step, $\Delta t$. This will ensure that walkers take significant number of steps before encountering a grain surface. Each walker can either diffuse within its respective pore voxel or into any of the neighbouring pore voxels. A walker in a pore voxel which is not at the boundary of the image has 26 other voxels surrounding it, as shown in Figure 4-2. These surrounding voxels may include both grain and pore voxels. A walker in pore voxel X shown in Figure 4-2 can diffuse into any of the neighbouring pore voxels depending on its respective x, y and z-coordinates. When a walker diffuses out of its voxel, the new voxel it enters is determined based on its x, y and z-coordinates as shown in Appendix A-2.
This new voxel is checked whether it is a pore voxel or a grain voxel. If it is a pore voxel, the walker diffuses into that voxel, and if it is a grain voxel, the killing probability of the walker is calculated from equation (3.21) to determine if the walker survives or not. If the walker survives, it is returned to its previous voxel and position. The fraction of walkers alive at a given time interval $P(t)$ is then recorded against their respective times. This is the normalized magnetization decay due to surface relaxation alone. The relevant experimental and fluid parameters are substituted along with $P(t)$ into equation (3.27) to generate the magnetization decay due to all relaxation mechanisms. When a walker in any pore voxel diffuses out of the entire image, a new walker is placed in a randomly selected pore voxel on the opposite face of the image. This will lead to a conservation of the total number of walkers in the image at any given time.

### 4.4 Calculation of grain surface areas

Magnetization decay is highly influenced by the surface area available to relax the protons (walkers). Magnetization will decay more rapidly if we have a high surface area to relax a given volume of fluid than a small area to relax the same volume of fluid. Hence, it is necessary to calculate the total grain surface area in a micro-CT image. This will assist in providing suitable explanation for differences in the simulation results of an array of micro-CT images.
A voxel has six surfaces each with an area of \( L_R^2 \) the adjoining six voxels to each pore voxels are checked if they are grain voxels. All faces of the grain voxels adjacent to pore voxels are summed and multiplied by the surface area of each side of the voxel as shown in equation (4.1).

\[
W_T = N_G L_R^2
\]

where \( W_T \) is the total grain surface area, \( N_G \) is the total number of the faces of grain voxels adjacent to pore voxels and \( L_R \) is the resolution of the image.

### 4.5 Validation of the simulation algorithm

The algorithm for the simulation of magnetization decay in micro-CT images was validated by comparing the magnetization decay of a cubic pore with its equivalent discretized image. For this cubic pore with dimension \( d \), we assign walkers randomly within the pore, a walker encounters a solid surface when any of its \( x \), \( y \) or \( z \) coordinate is negative or greater than the dimension of the cube. Simultaneously, we discretize the pore space into voxels with the surfaces as the grain voxels. For a cubic pore of length 48µm, we can discretize the pore into \( 50 \times 50 \times 50 \) voxels. The pore voxels are actually \( 48 \times 48 \times 48 \) voxels; the remaining voxels are the boundary grain voxels. The resolution of this discretized image is 1µm, so that it is of the same pore dimension as the cubic pore.

The magnetization decay of this cubic pore and its equivalent discretized image was simulated by using fluid with a diffusion coefficient of \( 2.0 \times 10^{-9} \text{m}^2/\text{s} \), pore surface relaxivity of \( 15 \times 10^{-6} \text{m/s} \), time step of 3.3µs and 100,000 walkers as shown in Figure 4-3. From this figure, it is shown that the magnetization decay of the cubic pore is consistent with that of its equivalent discretized image thereby validating the algorithm for the simulation of magnetization decay in 3D images.
Figure 4-3: Comparison of the magnetization decay of a cubic pore with its equivalent discretized image.

### 4.6 Simulation Results

Poorly consolidated sandstone, S2 was used to investigate the effect of sample size and number of walkers on magnetization decay. This sandstone has a porosity of 24.6%, resolution of 5µm and a voxel size of 300³. The magnetization decays of three voxel sizes, 100³, 200³ and 300³ shown in Figure 4-4 were simulated.

![Micro-CT images](image)

Figure 4-4: (a) Micro-CT image of sandstone S2 with a voxel size of 100³ (b) voxel size 200³ and (c) voxel size 300³.
The $100^3$, $200^3$ voxel images were cut from the central subsections of the original image of voxel size $300^3$. From the comparisons of the simulated magnetization decays shown in Figure 4-5, it can be observed that the magnetization of the $100^3$ and $300^3$ images decays faster than that of the $200^3$ image. This is due to slightly microstructural differences in these images; however the decays of the $100^3$ and $300^3$ images are consistent with each other.

Figure 4-5: (a) The magnetization decays of $100^3$, $200^3$ and $300^3$ voxel images, S2_100, S2_200 and S2_300 respectively and (b) their corresponding T2 distributions.
The $T_2$ distribution of the $100^3$ voxel image is narrower than those of the other images. This is as a result of the small size of the image thereby preventing it from having a wide variation of pore sizes. The largest image that can sample a wider range of pore size has the broadest $T_2$ distribution. The algorithm for the inversion of $T_2$ distributions from magnetization decays is described in Appendix A-3. The effect of the number of walkers on magnetization decay was also investigated on the $300^3$ voxel image.

![Graph showing magnetization decay comparison between 0.5 million and 2 million walkers.](image)

Figure 4-6: Comparison of the magnetization decay of the $300^3$ voxel image of S2 using 0.5 million and 2 million walkers.

The magnetization decay obtained using 0.5 million walkers is consistent with that obtained using 2 million walkers as shown in Figure 4-6; thus the number of walkers does not really have a significant effect on the magnetization decay. However, sufficient walkers must be used so as to ensure that the walkers diffuse through the entire pore space.
5. Simulation of NMR response of single-phase fluids in networks

The random walk method is extended to simulate magnetization decay in networks. This is of significant importance because it will enable a suitable comparison with the magnetization decay of the micro-CT image from which the network was extracted. It also allows the simulation of NMR response for multiphase fluid distributions – see chapter 6. Magnetization decay has been used to validate the reconstructed microstructure of Fontainebleau sandstone by comparing the simulation results of this reconstructed microstructure with that of a micro-CT image of similar porosity (Øren et al., 2002). Magnetization decay is primarily influenced by the surface areas available to relax the proton spins, the volume of the fluid and surface relaxivity of the porous medium. However, just because two pores have the same surface area, surface relaxivity and volume does not necessarily mean that they will have the same magnetization decay. They will have the same magnetization decay if they have the same relative paths available for the protons to diffuse through, which are similar to the paths available for fluid flow. If a network is a good representation of the micro-CT image from which it was extracted, then the two magnetization decays and T<sub>2</sub> distributions must be similar.

5.1 Geometry of network elements

The volume \( V \), inscribed radius \( r \) and shape factor, \( G \) of each network element (pore or throat) was used to determine its length \( L \). From the equation relating the cross-sectional area \( A \), with the shape factor \( G \) and inscribed radius \( r \) of a pore (Mason and Morrow, 1991):

\[
A = \frac{r^2}{4G}
\]

and the volume given by:

\[
V = AL
\]
For any network element having a shape factor between 0 and $\sqrt{3}/36$ (shape factor of an equilateral triangle), we determine the three half angles $\beta_1, \beta_2, \beta_3$ of the triangular cross-section of that element. For a given shape factor, the corner half angles $\beta$ can take a range of values (Patzek and Silin, 2001) where $\beta_1 < \beta_2 < \beta_3$; first $\beta_2$ is chosen randomly within the allowed range:

$$\beta_{2,\text{min}} = \tan^{-1} \left( \frac{2}{\sqrt{3}} \cos \left[ \frac{\cos^{-1} \left( -12 \sqrt{3} G / 3 \right)}{3} + \frac{4\pi}{3} \right] \right)$$

(5.3)

and

$$\beta_{2,\text{max}} = \tan^{-1} \left( \frac{2}{\sqrt{3}} \cos \left[ \frac{\cos^{-1} \left( -12 \sqrt{3} G / 3 \right)}{3} \right] \right)$$

(5.4)

with $\beta_1$ given by:

$$\beta_1 = \frac{-\beta_2}{2} + \frac{1}{2} \sin \left( \tan^{-1} \left( \frac{4G}{\tan \beta_2 - 4G \sin \beta_2} \right) \right)$$

(5.5)

and $\beta_3$ determined from:

$$\beta_3 = \pi / 2 - \beta_1 - \beta_2$$

(5.6)

For each network element with the shape factor of a triangle, we determine its three geometrical properties, these are the half angles $\beta_1, \beta_2, \beta_3$, the height $H$ and the base length of the triangular cross section. For a network element having the shape factor of a square, we divide its volume by its cross sectional area using equations (5.1) and (5.2) in order to determine its length.

### 5.2 Initialization of walkers in networks

We define a walker density, this is the number of walkers to be assigned to a given volume of the element. This will ensure a uniform distribution of walkers in all the network elements at initial time, $t = 0$. A walker is assigned two data sets, the first is its positional data, which includes the element type (throat or pore) that the walker is embedded in, the index number (which differentiates each network element), and the x, y and z-coordinate of the walker.
All cylindrical elements in the network are replaced with square shaped elements. This will reduce the complexity of the simulation procedure without having any impact on the magnetization decay. This is due to the fact that circular shaped elements constitute only a small proportion of the entire network elements. For triangularly shaped network elements, we place the walkers within the two rectangular sections shown in Figure 5-1 by generating their coordinates (x, y, z) randomly.

![Figure 5-1: The geometry of a typical triangular element in a network.](image)

When the x-coordinate of a walker is less than $x_1$, the walker is in rectangular section 1, the arctangent of $(y/x)$ is then determined, if it is less than $2\beta_1$, the walker is placed in that location (i.e. its x, y and z values are retained) if not, we determine another random location (x, y, z) for the walker until we get an arctangent of $(y/x)$ that is less than the angle $2\beta_1$.

Similarly if the x-coordinate of the walker is greater than $x_1$, that means that the walker is now in rectangular section 2, we determine the arctangent of $(y/(B_3 - x))$ in this case, if it is greater than the angle $2\beta_2$, that means that the random walker is outside the triangle and as such another random location is determined for the walker. This approach enables the walkers to be uniformly distributed within the triangular cross section. In all these cases the z-coordinate is determined randomly based on the length of the network element.
To place walkers randomly within a square cross section, we place them randomly in the x, y and z-axis where there limits are the dimension of the square cross section and the length of the network element determined in the geometry section.

### 5.3 Diffusion of walkers in networks

It is assumed that a pore with a coordination number (number of throats connected to the pore) $n$, has half of the throats connected to the pore at $z = 0$ and the other half connected to the opposite face at $z = L$ as shown in Figure 5-2. A walker in this pore will diffuse into any of the connected throats (pore-to-throat diffusion), if the $z$-coordinate of the walker is negative or greater than the length of the pore; the walker then diffuses into a randomly selected throat connected to that pore. The $z$-coordinate of the walker in this new throat is determined from its previous value to ensure continuity along the diffusion paths. The shape factor of this new throat is then checked to determine its cross section since it will influence how the walker will be placed randomly in its XY plane.

![Figure 5-2](image)

Figure 5-2: (a) Throats are connected to pores at different locations within the pore section (b) in the simulation algorithm. It is assumed that half of the throats connected to a pore at one end, while the remaining throats are connected at the other end.

The positional data of this walker in a new throat now becomes: throat index, x, y coordinates (determined randomly) and z-coordinate (determined from its previous value).
This pore-to-throat diffusion of a walker is also valid for throat-to-pore diffusion except that a throat is now connected to only one pore each at its opposite ends as shown in Figure 5-3.

![Figure 5-3](image)

Figure 5-3: A triangular shaped throat connected to the two ends of triangular shaped pores.

### 5.4 Relaxation of walkers in networks

For all the network elements there are 3 sides available for relaxing the walkers in a triangular element as shown in Figure 5-4, and 4 sides for a square element. A walker encounters a solid surface when any of the following conditions are satisfied.

![Figure 5-4](image)

Figure 5-4: The three faces available for relaxing walkers in triangular elements.
Face 1
A walker hits face 1 when its x-coordinate falls within the interval $x_1 < x < B_3$, its y-coordinate within the interval $0 < y < H$ and the tangent of $(y/(B_3 - x))$ is greater than the angle $2\beta_2$. A record of the number of walkers that decay on this face is kept as $D_1$.

Face 2
A walker hits face 2 when its x-coordinate falls within the interval $0 < x < x_1$, its y-coordinate fall within the interval $0 < y < H$ and the tangent of $y/x$ is greater than the angle $2\beta_1$. A record of the number of walkers that decay on this face is kept as $D_2$.

Face 3
Since face 3 has the largest length we expect the majority of the walkers to die on this face. A walker hits face 3 when its y-coordinate is negative. A record of the number of walkers that decay on this face is kept as $D_3$.

Square Shape:
A walker will hit any of the four sides of the square cross-section when any of the x or y-coordinate of the walker is negative or greater than the dimension of the cross section. We also keep a record of the number of walkers $D_5$ that die on any of the surfaces of this square cross-section.

Relaxation:
When a walker comes in contact with a solid surface, a random number is generated to determine if the killing probability is honored or not. If the walker survives, it is returned to its previous position. The fraction of walkers alive at selected time intervals is then recorded. The bulk relaxation component is then applied to determine the magnetization decay due to surface and bulk relaxation mechanisms. A flow chart showing the algorithm for the simulation of NMR response of single-phase fluid in a network is described in Appendix A-4.
5.5 Validation of the simulation algorithm

To validate the simulation algorithm, the surface area of each of the sides of the triangular cross section is determined. For each triangular element, the smallest side is $B_1$, the longest side is $B_3$, with $B_2$ as the middle value as shown in Figure 5-4. Their respective surface areas, $A_1$, $A_2$ and $A_3$ are determined from:

\[
A_1 = B_1 L \tag{5.7}
\]
\[
A_2 = B_2 L \tag{5.8}
\]
\[
A_3 = B_3 L \tag{5.9}
\]

where $L$ is the length of the network element determined from equations (5.1) and (5.2). For the square cross section we also determine the total surface area of that particular element.

\[
A_s = 4BL \tag{5.10}
\]

where $B$ is the dimension of the square cross section. The areas of each side of all the triangular elements are summed as:

\[
A_{T1} = \sum_{i=1}^{n} A_{1i} \tag{5.11}
\]
\[
A_{T2} = \sum_{i=1}^{n} A_{2i} \tag{5.12}
\]
\[
A_{T3} = \sum_{i=1}^{n} A_{3i} \tag{5.13}
\]

where $A_{T1}$, $A_{T2}$, $A_{T3}$, are the total surface areas of sides $B_1$, $B_2$ and $B_3$, respectively while $n$ is the number of triangularly shaped network elements. Similarly for square shaped elements, the total surface area $A_{TS}$, is given as:

\[
A_{TS} = \sum_{i=1}^{m} A_{si} \tag{5.14}
\]

where $m$ is the number of square shaped network elements. These total surface areas are then expressed as fractions.
The fraction of walkers $F_{A1}$, $F_{A2}$ and $F_{A3}$, that decays on sides $B_1$, $B_2$ and $B_3$, respectively are determined as:

$$F_{A1} = \frac{A_{T1}}{A_{T1} + A_{T2} + A_{T3} + A_{TS}}$$

$$F_{A2} = \frac{A_{T2}}{A_{T1} + A_{T2} + A_{T3} + A_{TS}}$$

$$F_{A3} = \frac{A_{T3}}{A_{T1} + A_{T2} + A_{T3} + A_{TS}}$$

$$F_{AS} = \frac{A_{TS}}{A_{T1} + A_{T2} + A_{T3} + A_{TS}}$$

The fraction of walkers $F_{D1}$, $F_{D2}$ and $F_{D3}$, that decays on sides $B_1$, $B_2$ and $B_3$, respectively are determined as:

$$F_{D1} = \frac{D_1}{D_1 + D_2 + D_3 + D_S}$$

$$F_{D2} = \frac{D_2}{D_1 + D_2 + D_3 + D_S}$$

$$F_{D3} = \frac{D_3}{D_1 + D_2 + D_3 + D_S}$$

$$F_{DS} = \frac{D_S}{D_1 + D_2 + D_3 + D_S}$$

It is expected that $F_{A1} \approx F_{D1}$, $F_{A2} \approx F_{D2}$, $F_{A3} \approx F_{D3}$ and $F_{AS} \approx F_{DS}$ because the decay of walkers depends to a large extent on the surface areas available to relax them. Thus, higher surface areas are expected to relax a higher number of walkers and vice versa. This comparison also helps to ascertain if the walkers fully diffuse through the network and encounter the entire surface area.
6. Simulation of NMR response of two-phase fluids in networks

Comparison of the magnetization decay in a network with that of the micro-CT image from which the network was extracted, helps to check if the network is representative of the image. Such successful comparisons are the basis for the extension of the algorithm to model magnetization decay of two-phase fluid in networks. For single-phase simulations, we only have to deal with the contact of the diffusing protons (walkers) with the grain surface. On the other hand for two-phase simulations we have to deal with contacts with solid surfaces and fluid interfaces. Unlike single-phase flow where the fluid completely saturates the network, for two-phase situations, the saturation and configuration of each fluid phase in each element are required. From predictive pore scale modelling, the fluid saturations and configurations in each element can readily be determined (Valvatne and Blunt, 2004).

6.1 Initialization of walkers in the fluid phases

At any given water saturation during drainage, some elements would have been invaded by oil, while the others are uninvaded.

![Diagram](image)

Figure 6-1: (a) The curved areas occupied by water in corners are replaced by (b) equivalent triangles. (c) Uninvaded element.
Invaded polygonal elements will have two phases as shown in Figure 6-1. Water retained in corner \( i \) of a polygonal element will have area \( A_i \) given by:

\[
A_i = R^2 \left[ \frac{\cos \theta_i \cos(\theta_i + \beta_i)}{\sin \beta_i} + \theta_i + \beta_i - \frac{\pi}{2} \right]
\] (6.1)

In order to reduce the complexity of taking into consideration the curved fluid interface at each corner during the diffusion of walkers both in the oil and water phase, the water in these corners are assumed to have a triangular shape as shown in Figure 6-1b while preserving the corner areas in equation (6.1). We assign specified number of walkers, \( N_w \) in the water phase and \( N_o \) in the oil phase. We refer to walkers in the water phase as water walkers and in the oil phase oil walkers.

For an uninvaded element, we assign water walkers based on the method described for the initialization of walkers for a single-phase fluid in the previous section. In an invaded element, we assign oil walkers to the polygonal section occupied by the oil phase, while water walkers are assigned to the water in the corners of the element. Similarly at any given water saturation during imbibition, uninvaded triangular shaped elements will have the fluid configuration shown in Figure 6-1a while invaded triangular shaped elements can have the fluid configuration shown in Figure 6-1c or have oil layers in corners as shown in Figure 6-2a.

![Figure 6-2](image-url): (a) The oil layers formed in corners are replaced by (b) equivalent rectangles.
The oil layers formed in corners of polygonal elements are represented by polygonal sections. Oil walkers are assigned to the oil layers and water walkers are assigned to the sections occupied by water.

6.2 Diffusion of walkers in the network

Since water and oil have different diffusion coefficients, their respective walkers diffuse at different speeds. At each time step $\Delta t$, the oil walkers diffuse from their initial position, $[x_o(t), y_o(t), z_o(t)]$ to a new position, $[x_o(t + \Delta t), y_o(t + \Delta t), z_o(t + \Delta t)]$, covering a distance of $\varepsilon_o$ defined by:

$$\varepsilon_o = \sqrt{6D_o \Delta t} \quad (6.2)$$

The new position of the oil walkers after each time step is given by:

$$x_o(t + \Delta t) = x_o(t) + \varepsilon_o \sin \phi \cos \theta \quad (6.3)$$
$$y_o(t + \Delta t) = y_o(t) + \varepsilon_o \sin \phi \sin \theta \quad (6.4)$$
$$z_o(t + \Delta t) = z_o(t) + \varepsilon_o \cos \phi \quad (6.5)$$

Similarly the water walkers diffuse from their initial position $[x_w(t), y_w(t), z_w(t)]$ to a new position $[x_w(t + \Delta t), y_w(t + \Delta t), z_w(t + \Delta t)]$, covering a distance of $\varepsilon_w$ defined by:

$$\varepsilon_w = \sqrt{6D_w \Delta t} \quad (6.6)$$

The new position of the water walkers after each time step is given by:

$$x_w(t + \Delta t) = x_w(t) + \varepsilon_w \sin \phi \cos \theta \quad (6.7)$$
$$y_w(t + \Delta t) = y_w(t) + \varepsilon_w \sin \phi \sin \theta \quad (6.8)$$
$$z_w(t + \Delta t) = z_w(t) + \varepsilon_w \cos \phi \quad (6.9)$$
$D_o$ and $D_w$ are the diffusion coefficients of the oil and water phase respectively, the angle $\theta$ is randomly selected in the range $\left(0 \leq \theta \leq 2\pi\right)$ and $\phi$ is randomly selected in the range $\left(0 \leq \phi \leq \pi\right)$. If an oil walker encounters a solid surface, it is killed with a finite killing probability, $\delta_o$ defined by:

$$\delta_o = \frac{2\rho_o \varepsilon_o}{3D_o} \tag{6.10}$$

Similarly when a water walker encounters a solid surface, it is killed with a finite killing probability, $\delta_w$ also defined by:

$$\delta_w = \frac{2\rho_w \varepsilon_w}{3D_w} \tag{6.11}$$

where $\rho_o$ and $\rho_w$ are the surface relaxivities of the porous medium to oil and water and oil respectively. The relaxivity of a given surface to oil is much less than that of water, the ratio $\rho_o / \rho_w$ is often in the range 0.1 to 0.4 (Looyestijn and Hofman, 2005). If any walker survives upon contact with a solid surface, it simply bounces off the surface and returns to its previous position and time is advanced by the unit time step $\Delta t$. When a walker hits a fluid interface, we place the walker randomly in its respective phase within the element it is embedded in, because of negligible relaxivity at the fluid interface (Toumelin et al., 2003). When $z_o(t + \Delta t)$ or $z_w(t + \Delta t)$ of a walker in a pore is negative or greater than the length of its element, the walker diffuses into one of the connected throats with the same fluid phase as that of the walker.

If the neighbouring element does not contain the walker’s phase, then the walker has encountered a fluid interface and it is put back into a random position within the element. A similar thing occurs for diffusion of walkers from throats to pores. At each time step, a record of the fraction of the walkers alive in each fluid phase is kept.

$$P_o(t) = \frac{N_o(t)}{N_o} \tag{6.12}$$
\[ P_w(t) = \frac{N_{sw}}{N_w} \tag{6.13} \]

\( P_o(t) \) and \( P_w(t) \) are the fraction of walkers that are alive in oil and water phase respectively while \( N_{or} \) and \( N_{sw} \) are the actual number of walkers alive in the water and oil phase respectively. Equations (6.12) and (6.13) are the normalized magnetization decay due to surface relaxation in the oil and water phase respectively. The total magnetization decay as a result of both surface and bulk relaxations in each fluid phase is obtained by incorporating into equations (6.12) and (6.13) the bulk relaxation component.

\[ M_o(t) = P_o(t) \exp \left( -\frac{t}{T_{2bo}} \right) \tag{6.14} \]
\[ M_w(t) = P_w(t) \exp \left( -\frac{t}{T_{2bw}} \right) \tag{6.15} \]

\( M_o(t) \) and \( M_w(t) \) are the total magnetizations at time \( t \) in oil and water phase respectively while \( T_{2bo} \) and \( T_{2bw} \) are the bulk relaxation time of oil and water respectively. The combined magnetization \( M(t) \) of the two phases is given by:

\[ M(t) = \frac{S_o M_w(t) + H_o S_o M_o(t)}{S_w + H_o S_o} \tag{6.16} \]

where \( S_o \) and \( S_w \) are the oil and water saturations respectively, \( H_o \) in equation (6.16) is the hydrogen index of the oil-phase (Toumelin et al., 2007). The hydrogen index of a fluid is a measure of its hydrogen content per unit volume. Hydrogen index of oil is dependent on its specific gravity and is usually determined from;

\[ H_o = 1.26 \times \rho_o \tag{6.17} \]

where \( \rho_o \) is the specific gravity of the oil (Smolen, 1996).
7.

Single-phase simulation results for sand packs

In this chapter, we compare the simulated NMR response on sand packs with experimental measurements. The experiments were performed in the Petrophysics Laboratory at Imperial College by my colleagues, Dr Stefan Iglauer, Saif AlSayari and Saleh Al-Mansoori.

7.1 Sand preparation

Quartz sands, LV60 (Leavenseat sand, WBB Minerals, UK) and Ottawa F42 (unground silica, US Silica Company) were used in this study. The grain size distributions of the sands were determined by sieving them for 80 minutes using British standard meshes on an electric shaker. The mass fraction of grains that passed through each sieve size is plotted against their respective sieve size as shown in Figure 7-1.

![Figure 7-1: Grain size distributions of the F42 and LV60 sand packs](image)

The sands were then prepared for the NMR experiments by carefully pouring into a 10 cm length of a thermo-plastic heat shrink sleeve of diameter 3.81 cm with fitted plastic end caps with one piece of circular filter paper to ensure a tight fit. The sleeve was filled with sand to about two thirds of its length, the sample was then tapped and vibrated using an electric vibrator to ensure compaction, the sleeve was filled to the top and the compaction process is repeated.
The sand pack sample is then placed in an oven at 80°C for 20 minutes. It is allowed to cool and placed in an oven at 100°C to seal the end caps after which the sample is weighed. Two samples each of LV60 and F42 sand packs were made for the NMR experiments to ensure good reproducibility of our packing procedures and the measurements were repeated thrice.

7.2 Sand properties

The porosity of F42 sand pack is 35.4% ± 1.3% while that of LV60 is 37.0% ± 0.2%. Formation factors were determined from electrical resistivity measurements. The experimental formation factor is 4.8 and 5.2 for the LV60 and F42 sand packs respectively. Permeabilities of the sand packs were measured on similar but longer columns of 2 cm diameter and 1m length; the values are 42.0D ± 4.0 D for F42 and 32.2D ± 0.3D for LV60.

7.3 NMR measurement

As mentioned previously, sand packs 3.81 cm in diameter and 10 cm in length saturated in brine were used for NMR measurement. The brine was a mixture of de-ionized water, \((5\text{wt}\% \text{ NaCl and 1 wt}\% \text{ KCl solution})\). Potassium Chloride (KCl) was used to prevent the sand from swelling, while Sodium Chloride (NaCl) was added to increase the ionic strength of the water to levels found in oil reservoirs. The density of the brine was measured to be 1035 kg/m³. NMR relaxation measurements were performed using a MARAN2 bench top spectrometer (Resonance Instruments) at a temperature of 308K operating at 2 MHz. The Carr-Purcell-Meiboom-Gill (CPMG) sequence was used for transverse relaxation measurements \((T_2\) -measurements) with an inter-echo spacing of 200µs. The short inter-echo time was selected to minimize relaxation due to diffusion in internal field gradients. A single data point was acquired at the center of each echo, with 32,000 data points being collected. The \(T_2\) relaxation time distributions were obtained from the magnetization decays by using the curvature-smoothing regularization method (Chen et al., 1999).
7.4 Micro-CT imaging

In order to ensure the consistency of our simulation results, six small sand pack samples, three for each of sand pack type, F42A, F42B and F42C for the F42 sand pack and LV60A, LV60B and LV60C for LV60 sand pack were made for micro-CT imaging as shown in Figure 7-2. The samples are 0.65 cm in diameter and 4 cm in length. They were packed in a similar manner as the plugs used in the experiments described above; analysis of the resultant images (see below) confirms that they have similar porosity as the plugs used in the experiments. The micro-CT imaging was performed on a commercial XMT unit (Phoenix—X-ray Systems and Services GmbH). Scanned images of 750×750×450 voxels, with resolutions ranging between 8 µm and 10 µm were collected for each sample with the images cropped digitally to remove the edge artifacts.

![3D Micro-CT sections of (a) LV60A, (b) LV60B, (c) LV60C, (d) F42A, (e) F42B and (f) F42C.](image)

Figure 7-2: 3D micro-CT sections of (a) LV60A, (b) LV60B, (c) LV60C, (d) F42A, (e) F42B and (f) F42C.
7.5 Experimental results

The experimental results shown in Figures 7-3 and 7-4 demonstrate reproducibility between different packs of the same sand. The magnetization of LV60 decays faster than F42 and hence the mean transverse relaxation time, $T_2$, for F42 is higher than that of LV60.

(a)

![Normalized Amplitude vs. Time](image1)

(b)

![Frequency vs. T2](image2)

Figure 7-3: (a) The experimental magnetization decay of two samples (LV60X and LV60Y) of the LV60 sand packs. (b) The inverted $T_2$ distribution of the magnetization decays in (a).
The chemical compositions of the sands are similar; the difference in their magnetization decays arises from their different pore size distributions: the faster decay of the LV60 sand implies smaller pores – this is consistent with the smaller grain size distribution shown in Figure 7-1.

Figure 7-4: (a) The experimental magnetization decay of two samples (F42X and F42Y) of F42 sand packs. (b) The inverted T₂ distributions of the magnetization decays in (a).
In the $T_2$ distributions, frequency is plotted against $T_2$ values. The differences between the magnetization decays of LV60 and F42 sand packs are as a result of their grain shapes and sizes which are responsible for their different pore size distributions. The micro-CT images shown in Figure 7-2 indicate that the grains of the F42 sands are larger, more spherical and have smooth surfaces than those of LV60. The grains of the LV60 sand pack on the other hand, have rough surfaces with a wider variation of sizes, as shown by the grain size distributions in Figure 7-1.

### 7.6 Simulation results

NMR Simulations were carried out on the six micro-CT images, F42A, F42B and F42C for the F42 sand pack and LV60A, LV60B and LV60C for LV60. Simulations were also performed on networks extracted from these images. The networks were extracted from the micro-CT images by using a maximal ball algorithm, (Silin et al., 2003; Silin and Patzek, 2006; Al-Kharusi and Blunt, 2007; Dong, 2007). Figure 7-5 shows example images and networks for the two sands. The micro-CT images and extracted networks cover a rock volume of $3^3$ mm$^3$. Table 7-1 shows the resolution, voxel size, porosity, total grain surface area per unit volume of each micro-CT image.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resolution (µm)</th>
<th>Voxel Size</th>
<th>Porosity (%)</th>
<th>Surface Area (m$^2$/m$^3$)</th>
<th>Pores</th>
<th>Throats</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>F42A</td>
<td>9.996</td>
<td>300$^1$</td>
<td>33.0</td>
<td>43,770</td>
<td>1,246</td>
<td>2,856</td>
<td>4.4</td>
</tr>
<tr>
<td>F42B</td>
<td>10.002</td>
<td>300$^1$</td>
<td>33.3</td>
<td>44,930</td>
<td>1,323</td>
<td>3,262</td>
<td>4.8</td>
</tr>
<tr>
<td>F42C</td>
<td>10.002</td>
<td>300$^1$</td>
<td>33.1</td>
<td>45,760</td>
<td>1,434</td>
<td>3,877</td>
<td>5.2</td>
</tr>
<tr>
<td>LV60A</td>
<td>10.002</td>
<td>300$^1$</td>
<td>37.7</td>
<td>57,670</td>
<td>3,135</td>
<td>7,818</td>
<td>4.9</td>
</tr>
<tr>
<td>LV60B</td>
<td>8.851</td>
<td>338$^1$</td>
<td>36.8</td>
<td>61,090</td>
<td>3,502</td>
<td>9,044</td>
<td>5.0</td>
</tr>
<tr>
<td>LV60C</td>
<td>10.002</td>
<td>300$^1$</td>
<td>37.2</td>
<td>61,590</td>
<td>3,582</td>
<td>9,001</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 7-1: Micro-CT images and extracted networks’ properties
Table 7-1 also shows the number of network elements (pores and throats) and coordination number of the networks extracted from each micro-CT image. The porosity of the packs inferred from the images is similar to that obtained by direct measurement on larger packs, although we tend to under-estimate the porosity of the F42 sand (33% from the images as opposed to 35% measured directly.)

Figure 7-5: (a) Sections of the micro-CT image of LV60A sand pack and (b) F42A sand pack. The resolution of both images is 10µm, *(the dark areas are the pore spaces and the white represent grains)*. (c) Equivalent network extracted from LV60A. (d) Network extracted from F42A.
7.6.1 Simulation Parameters

The diffusion coefficient and the bulk relaxation time of brine used in the simulation were determined from the correlations (Vinegar, 1995):

\[ D_{0(\text{brine})} = \left( \frac{2T}{298(\eta)} \right)10^{-12} \]  \hspace{1cm} (7.1)

and

\[ T_{2B(\text{brine})} = \left( \frac{3T}{298(\eta)} \right)10^{-3} \]  \hspace{1cm} (7.2)

where \( D_{0(\text{brine})} \) is the diffusion coefficient of the brine in \( \text{m}^2/\text{s} \), \( T \) is the temperature of the brine in K, \( \eta \) is the viscosity in Pa.s and \( T_{2B(\text{brine})} \) is the bulk relaxivity of brine in seconds. Since the experiment was performed at 308K, this corresponds to a diffusion coefficient of \( 2.07 \times 10^{-9} \text{m}^2/\text{s} \) and bulk relaxivity of 3.1 seconds using the experimental brine viscosity of 0.001 Pa.s. Relaxation due to diffusion in magnetic gradients is neglected in the simulations because of the small inter echo spacing used in the NMR experiments, hence only surface and bulk relaxations were accounted for.

7.6.2 Surface Relaxivity

The surface relaxivity (41×10^{-6} m/s) used in our simulations was obtained by adjusting the value until a match was obtained with the magnetization decay of the experimental data. The same surface relaxivity was used to match the experimental data for the two sand packs since they are made up of the same mineral (quartz) and they have similar chemical composition. The relatively high value of surface relaxivity used, compared to literature values in the range 9 to 46 µm/s for sandstones (Roberts et al., 1995) and 2.89 to 3.06 µm/s for silica sands (Hinedi et al., 1997) is due to two reasons. First, the sand packs used in this work has minute proportions of iron oxide within the range 0.02% to 0.06% along with some other paramagnetic substances. Second, and more significantly, the overall surface decay is given by the apparent surface area multiplied by the surface relaxivity. In our work the surface area is determined at the resolution of the micro-CT image, around 10 µm, whereas in other work (Hinedi et al., 1997) this is determined using nitrogen absorption method, which probes the surface at a much higher resolution, resulting in a larger measured surface area per unit volume. Hence to obtain the same magnetization, a lower apparent surface relaxivity was obtained.
7.6.3 Magnetization Spectrum

F42 Sand Packs

The simulated magnetization decays and $T_2$ distributions of the F42 samples (F42A, F42B and F42C) are compared with the experimental data of F42Y as shown in Figures 7-6, 7-7 and 7-8.

Figure 7-6: (a) Comparison of the experimental magnetization decay of F42Y with the micro-CT image and extracted network for F42A. (b) Comparison of the inverted $T_2$ distributions from the magnetization decays in (a).
Figure 7-7: (a) Comparison of the experimental magnetization decay of F42Y with the micro-CT image and extracted network for F42B. (b) Comparison of the inverted $T_2$ distributions from the magnetization decays in (a).
Figure 7-8: (a) Comparison of the experimental magnetization decay of F42Y with the micro-CT image and extracted network for F42C. (b) Comparison of the inverted T2 distributions from the magnetization decays in (a).

In all cases there is good agreement between the experimental measurement and the simulations on the micro-CT image and the network. However in the F42C sample, the network results tend to give a more rapid decay, indicating a lower estimated average pore size. This is due to the more constricted diffusion in slit-like triangular elements that allows a low mean-free-path before encountering the grain.
LV60 Sand Packs

The simulated magnetization decays and $T_2$ distributions of the LV60 samples, (LV60A, LV60B and LV60C) are compared with the experimental data from LV60Y as shown in Figures 7-9, 7-10, and 7-11.

Figure 7-9: (a) Comparison of the experimental magnetization decay of LV60Y with the micro-CT image and extracted network for LV60A. (b) Comparison of the inverted $T_2$ distributions from the magnetization decays in (a).
Figure 7-10: (a) Comparison of the experimental magnetization decay of LV60Y with the micro-CT image and extracted network for LV60B. (b) Comparison of the inverted $T_2$ distributions from the magnetization decays in (a).
Figure 7-11: (a) Comparison of the experimental magnetization decay of LV60Y with the micro-CT image and extracted network for LV60C. (b) Comparison of the inverted $T_2$ distributions from the magnetization decays in (a).
The magnetization of the networks representing LV60B and LV60C decay faster than the network from LV60A; this is as a result of an increase in the number of network elements extracted from their respective micro-CT images. These results again suggest that we under-estimate the mean-free-path of a random walker in the networks. The main peak is narrower for all the networks than the experiment and micro-CT images, implying that some features of full ranges of pore sizes and shape are lost in the extraction algorithm.

### 7.6.4 Comparisons of other single-phase properties

Permeabilities and formation factors of the networks (Bakke and Øren, 1997; Øren and Bakke, 2003) were computed and compared with those of the micro-CT images (Øren et al., 2002; Knackstedt et al., 2004) and experimental values. We also computed the mean transverse relaxation times $T_{2\text{lm}}$ for the micro-CT images, networks and experimental data using equation (3.16). Table 7-2 shows the comparisons of experimental, image and network estimates of mean $T_2$, permeability and formation factor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $T_2$ (ms)</th>
<th>Permeability (D)$^*$</th>
<th>Formation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Micro-CT</td>
<td>Network</td>
</tr>
<tr>
<td>F42A</td>
<td>668</td>
<td>677</td>
<td>756</td>
</tr>
<tr>
<td>F42B</td>
<td>668</td>
<td>654</td>
<td>727</td>
</tr>
<tr>
<td>F42C</td>
<td>668</td>
<td>647</td>
<td>694</td>
</tr>
<tr>
<td>LV60A</td>
<td>496</td>
<td>512</td>
<td>565</td>
</tr>
<tr>
<td>LV60B</td>
<td>496</td>
<td>488</td>
<td>543</td>
</tr>
<tr>
<td>LV60C</td>
<td>496</td>
<td>471</td>
<td>530</td>
</tr>
</tbody>
</table>

$^*$ $1\text{D} = 9.86923 \times 10^{-13}$ m$^2$

Table 7-2: Comparison of experimental data with simulation results
The LV60 sand packs have a much higher surface area and a smaller grain size distribution than the F42 sand packs, leading to more pores and throats per unit volume, a faster magnetization decay (lower $T_2$) and lower permeability. The predictions of permeability are good, although the permeability of the F42 pack is slightly over-estimated, while that of the LV60 sand is under-estimated.

### 7.6.5 Pore size distributions

If bulk relaxation and relaxation due to magnetic gradients are negligible and there is no diffusion between elements, the pore size ($V/S$) distribution can be estimated from equation (3.14).

$$\frac{V}{S} = \rho T_2$$  \hspace{1cm} (7.3)

The experimental pore size distribution of the F42Y sand pack using equation (7.3) is compared with the distribution of inscribed radius for the pores and throats in F42A network in Figure 7-12.

![Figure 7-12: Comparison of inscribed radius distribution of network elements of F42A with the pore size distribution of F42 sand pack inferred from the NMR response.](image-url)
The inscribed radius distribution of the network elements is wider than the experimental pore size distribution obtained from the $T_2$ distribution of the F42 sand pack. This is because the pore size distribution from $T_2$ distribution can combine several throats to a given pore and see them as a single pore; it can even combine several pores together and see them as a single pore, while in the network, the elements are clearly distinguished from each other. However, the range of the pore size distribution obtained from the $T_2$ distribution lies within the range of the inscribed radius distribution of the pores.

The maximum distance that a walker will diffuse before bulk relaxation is significant is approximately $\sqrt{6DT_B} \approx 200 \mu$m for our experiments. This is of order a typical pore-to-pore distance and hence some protons will sample more than one network element before decaying. The $T_2$ distribution gives an indication of pore size distribution but it is not a direct and accurate way to find it.
8.

Single-phase simulation results for sandstones

Having obtained consistencies in the comparisons of the simulation results from networks and micro-CT images for sand packs, we also compared the results from a poorly consolidated sandstone (S) and consolidated sandstones (Fontainebleau, Berea and Bentheimer). One advantage of these comparisons is that we can determine how consistent are the extracted networks with the micro-CT image or reconstructed microstructures from which they were extracted. These comparisons can serve as a validation for pore-network models and the methods used to generate networks.

8.1 Fontainebleau sandstone

Øren et. al., (2002) reconstructed the three dimensional (3D) microstructure of Fontainebleau sandstone samples of different porosities by a process-based reconstruction method. The process-based reconstruction method consists of simulating the results of the main rock-forming processes; sedimentation, compaction and diagenesis. The reconstructions were performed in a discrete manner on a cubic grid of size 300³ voxels with porosities ranging from 0.03 to 0.3. Magnetization decay was used to validate these reconstructed microstructures by comparing their decays with those of micro-CT images of similar porosity. The comparisons in Figure 8-1 show that the reconstructions faithfully reproduce the angular and irregular pore shapes observed in the true microstructure. NMR simulations were performed on a reconstructed microstructure of Fontainebleau sandstone of porosity 13.6% and a network extracted from the microstructure using a dilation method (Øren and Bakke, 2002, 2003). Simulations were also performed on a network extracted using a maximal ball algorithm (Dong, 2007). The microstructure has a resolution of 7.5µm with a cubic grid size of 300³ voxels. The number elements in the networks extracted using the two network extraction methods are shown in Table 8-1.
Figure 8-1: The pore spaces in a $128^3$ voxels sub region of a reconstructed Fontainebleau sandstone (right) of porosity 0.18 and a micro-CT image of an actual Fontainebleau sandstone (left) with similar porosity. The resolution of both images is $5.7\,\mu m$ (Øren et. al., 2002).

<table>
<thead>
<tr>
<th>Network</th>
<th>Dilation Method</th>
<th>Maximal Ball</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pores</td>
<td>4,997</td>
<td>3,101</td>
</tr>
<tr>
<td>Throats</td>
<td>8,192</td>
<td>6,112</td>
</tr>
<tr>
<td>Coordination number</td>
<td>3.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 8-1: Comparison of the number of elements and average coordination number in each network extracted using the dilation method (Øren and Bakke, 2002, 2003) and the maximal ball algorithm (Dong, 2007).

<table>
<thead>
<tr>
<th>Rock and fluid properties used in the simulations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient (m$^2$/s)</td>
</tr>
<tr>
<td>Bulk relaxivity (s)</td>
</tr>
<tr>
<td>Surface relaxivity (m/s)</td>
</tr>
<tr>
<td>Number of walkers</td>
</tr>
</tbody>
</table>
The diffusion coefficient and bulk relaxivity used in the simulations shown in Table 8-2 are typical values for brine; these are the same values used for the NMR simulations in the sand packs. The surface relaxivity value used is a typical value for Fontainebleau sandstone (Hurlimann et al., 1994).

Figure 8-2: (a) Comparison of the magnetization decay of the reconstructed microstructure of Fontainebleau sandstone, the network extracted using a dilation method (Oren and Bakke; 2002, 2003) and the network extracted using a maximal ball algorithm (Dong, 2007). (b) Comparison of the inverted $T_2$ distributions of the magnetization decays in (a).
The magnetization decay of the network extracted using the dilation method is very similar to that of the reconstructed microstructure, as shown in Figure 8-2 indicating, that this network is an ideal representation of the microstructure. On the other hand, the magnetization of the network extracted using the maximal ball algorithm decays faster than the reconstructed microstructure. This is because the maximal ball algorithm seems to slightly over estimate the grain surface area in the networks. The total grain surface area of the reconstructed microstructure is $1.55 \times 10^{-4}$m$^2$. The total surface areas of the networks calculated using equations (5.11 – 5.14) are $1.55 \times 10^{-4}$m$^2$ and $1.74 \times 10^{-4}$m$^2$ for the networks extracted using the dilation method and maximal ball respectively.

The total grain surface area in the microstructure is expected to be higher than the networks because the rough surfaces of the pores in the microstructures are replaced by smooth geometrical shapes in the networks. The mean transverse relaxation times, $T_{2lm}$ is 570ms for the microstructure and network extracted using the dilation method while a value of 493ms was obtained for the maximal ball network. In order to further validate the results of the magnetization decay obtained in the network, we compared the ratios of the respective areas of the sides of triangular and square shaped elements in the network as given in equations (5.15 – 5.18) with the ratio of walkers that decay on their respective sides given in equations (5.19 – 5.22) as shown in Table 8-3.

The comparisons in Table 8-3 show that the walkers decay on each side of the triangular elements based on their respective ratios as expected. The minor differences observed are as a result of the random nature of the walkers’ diffusion. The difference for the square shaped elements is quite significant, because of the small fraction of network elements that are made of square shaped sections. Hence, the number of walkers that decay on these square shaped sections depends on how accessible the walkers are; to these elements since they may be scattered across the network or may be clustered around a particular region. The maximal ball method over-estimates the surface area due to the creation of spurious connections between pores. This leads to the creation of slit-like elements in which walkers decay rapidly.
Table 8-3: Comparison of the fractional surface area of the smallest sides (Sides 1), middle sides (Sides 2), longest sides (Sides 3) of all the triangular elements and square sides (Sq. sides) in the network with the fraction of walkers that decay on these respective sides for the network extracted from dilation method. (b) Comparisons of the maximal ball network.

8.2 Poorly consolidated sandstone (S)

NMR simulations were also performed on the micro-CT image and extracted network of a poorly consolidated sandstone, S. The porosity of the micro-CT image is 16.9% while its resolution is 9.1µm; as shown in Figure 8-3. The micro-CT image data were converted into binary format where 0 and 1 represent the pore and grain voxels respectively. A central cubic section of voxel size 300^3 cropped from the micro-CT image was used for the simulations. The maximal ball algorithm was used to extract a network of 3,127 pores and 7,508 throats with an average coordination number of 4.7. A surface relaxivity of 15µm/s was used in the simulations; the fluid properties used are shown in Table 8-2.
Figure 8-3: (a) 3-D image of sandstone S and (b) network extracted from the image using the maximal ball algorithm.

Figure 8-4: (a) Magnetization decays of the micro-CT image and extracted network of Sandstone S. (b) The inverted T2 distributions from the magnetization decays in (a).
The decays shown in Figure 8-4 indicate that the magnetization in the network decays slightly faster than the micro-CT image. The same trend was observed in the comparisons of the magnetization decays of the networks extracted from the reconstructed microstructure of Fontainebleau sandstone shown in Figure 8-2a. However, the inverted $T_2$ distributions shown in Figure 8-4(b) indicate that the two distributions are similar having almost the same $T_2$ value at their peaks.

8.3 Berea sandstone

Magnetization decay was simulated on Berea sandstone of porosity 19.6%. The simulations were carried out on a cubic grid size of $300^3$ voxels cropped from the micro-CT image shown in Figure 8-5(a); the resolution of the image is $5.345\mu$m. The maximal ball algorithm was used to extract a network of 3,212 pores and 5,669 throats with an average coordination number of 3.4 from the cubic grid. The simulation results were compared with that from a network of 12,349 pores and 26,146 throats extracted from reconstructed Berea sandstone (Lerdahl et al., 2000) using the dilation method (Øren and Bakke, 2002, 2003). A surface relaxivity of $15\mu$m/s was used in the simulations; the fluid properties used are shown in Table 8-2. A summary of the micro-CT and extracted networks properties for Sandstone S and Berea sandstone is shown in Table 8-4. Permeability and formation factors are calculated in the networks and micro-CT images of sandstone S and Berea sandstones are shown in Table 8-5.

![Figure 8-5: (a) 3D micro-CT image of the Berea sandstone. (b) Network extracted from the micro-CT image in (a) using the maximal ball method. (c) Network extracted from a reconstructed microstructure of Berea sandstone (Lerdahl et al., 2000).](image-url)
Figure 8-6: (a) Comparison of the magnetization decays of the micro-CT image of Berea sandstone, the network extracted using a dilation method (Øren and Bakke; 2002, 2003) from reconstructed Berea sandstone (Lerdahl et al., 2000) and a network extracted from the micro-CT image using a maximal ball algorithm (Dong, 2007). (b) Comparison of the inverted T2 distributions of the magnetization decays in 7(a).
Table 8-4: Micro-CT and extracted networks properties for sandstone S and Berea sandstone, the microstructure properties of Berea PBM network are unavailable.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resolution (µm)</th>
<th>Voxel Size</th>
<th>Porosity (%)</th>
<th>Surface Area (m²/m³)</th>
<th>Pores</th>
<th>Throats</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandstone S</td>
<td>9.1</td>
<td>300³</td>
<td>16.9</td>
<td>115,240</td>
<td>3,127</td>
<td>7,508</td>
<td>4.7</td>
</tr>
<tr>
<td>Berea (MB)</td>
<td>5.345</td>
<td>300³</td>
<td>19.6</td>
<td>118,960</td>
<td>3,212</td>
<td>5,669</td>
<td>3.4</td>
</tr>
<tr>
<td>Berea (PBM)</td>
<td>-----</td>
<td>-----</td>
<td>18.3</td>
<td>12,349</td>
<td>26,146</td>
<td>21,920</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 8-5: Comparison of mean transverse relaxation time $T_2$, permeability and formation factor of micro-CT images and extracted networks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $T_2$ (ms)</th>
<th>Permeability (mD)</th>
<th>Formation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Micro CT</td>
<td>Network</td>
<td>Micro CT</td>
</tr>
<tr>
<td>Sandstone S</td>
<td>570</td>
<td>543</td>
<td>224</td>
</tr>
<tr>
<td>Berea (MB)</td>
<td>584</td>
<td>519</td>
<td>1286</td>
</tr>
<tr>
<td>Berea (PBM)</td>
<td>---</td>
<td>572</td>
<td>---</td>
</tr>
</tbody>
</table>

The magnetization of both networks decay faster than the micro-CT image as shown in Figure 8-6(a). The PBM network was extracted from a reconstructed microstructure of Berea sandstone and not from the micro-CT image shown in Figure 8-5. Also the PBM network was extracted from a microstructure of porosity 18.3% which is slightly lower than the porosity of 19.6% in both the micro-CT image and the network extracted using the maximal ball method. These could result in the differences observed in their respective magnetization decays since lower porosity images and networks decay faster than higher porosities.
However, the magnetization decay of the PBM network is much closer to that of the micro-CT image than the decay of the network extracted using the maximal ball algorithm. The $T_2$ distributions shown in Figure 8-6(b) indicate that the distribution of the PBM network and the micro-CT image are somewhat similar inferring similar pore size distributions. However, the distribution of the maximal ball network is narrower with a higher peak.

### 8.4 Bentheimer sandstone

In order to further validate the method used in simulating NMR response in networks, simulations results were compared with experimental data for Bentheimer sandstone performed by colleagues at the Department of Physics and Technology, University of Bergen. Unlike previous analysis where networks were extracted from either a micro-CT image or a reconstructed microstructure, we used the network extracted from a reconstructed microstructure of Berea sandstone (PBM Network) as already discussed in section 8.3. The properties (pore and throat size distribution) of this network were tuned to match the mercury injection capillary pressure data of Bentheimer sandstone as shown in Figure 8-7, an approach fully described in Valvatne (2003). The resulting network was then used for the simulation of NMR response which was compared with experimental values. The Bentheimer sandstone used in these comparisons have porosities and permeabilities in the range $23\% \pm 4\%$ and $1,410\text{mD} \pm 28\text{mD}$ respectively.

#### 8.4.1 NMR measurements

Bentheimer sandstone plugs of diameter $3.73\text{cm}$ and length $6.01\text{cm}$ were used for the NMR measurements. The plugs were saturated in brine of viscosity $1.09 \times 10^{-3} \text{Pas}$ and density $1005 \text{kg/m}^3$. NMR relaxation measurements were performed using a MARAN2 bench top spectrometer (Resonance Instruments) at a temperature of 308K operating at 2 MHz. The Carr-Purcell-Meiboom-Gill (CPMG) sequence was used for transverse relaxation measurements ($T_2$-measurements) with an inter-echo spacing of $400\mu\text{s}$.
A single data point was acquired at the centre of each echo, with 8,000 data points in total collected. The magnetization decay curve was inverted into $T_2$ distribution using Win DXP software (Resonance Instruments).

![Figure 8-7: Comparison of the experimental capillary pressure data of the Bentheimer sandstone with simulation results from a tuned Berea network and the original Berea network.](image)

8.4.2 Simulation parameters

The diffusion coefficient and the bulk relaxation time of brine used in the simulation were determined from the correlations given in equations (7.1) and (7.2). By substituting the temperature at which the experiment was performed (308K) and the viscosity of the brine ($1.09 \times 10^{-3}$ Pas), a diffusion coefficient of $1.9 \times 10^{-9}$ m$^2$/s and bulk relaxivity of 2.84 seconds were obtained and used in the simulations. The surface relaxivity used in the simulation is $9.3 \mu$m/s which is typical for Bentheimer sandstones (Liaw et. al, 1996).

8.4.3 Simulation results

The simulated magnetization decay is consistent with experimental values at early times as shown in Figure 8-8a; however at late times the simulated magnetization decays faster than the experimental values. These differences could be as a result of the network not being able to fully capture accurately the topology of this Bentheimer sandstone.
Figure 8-8: (a) Comparison of magnetization decays of the experimental data of Bentheimer sandstone with simulation results of the tuned network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).

The inverted $T_2$ distributions shown in Figure 8-8b are similar; their mean values are 677ms and 604ms for the experiment and simulation respectively. The computed permeability of the network is 950mD compared with experimental values in the range 1,410mD ± 28mD.
These results validate the algorithm used for the simulation of magnetization decay in networks. Unlike in the analysis of the sand packs where surface relaxivity was used to match experimental data of the magnetization decay, we used the typical surface relaxivity of Bentheimer sandstone and consistent results were obtained. The accuracy of the simulation results using this network NMR algorithm could be improved considerably if the actual surface relaxivity of the porous medium is known and an appropriate network extracted from either a micro-CT image or a reconstructed microstructure.
9. Single-phase simulation results for carbonates

The methods used in simulating NMR response in the previous sections are applied to carbonates. Carbonates often have bimodal pore size distributions (micro-pores and macro-pores), with micro pores having sizes in sub-micron range. Micro-CT scans with resolutions of a few microns cannot capture the features of these micro pores. In order to overcome this limitation, multiple point statistics have been used to reconstruct 3D images of carbonates from 2D thin section images (Okabe and Blunt, 2004; Okabe and Blunt, 2005). The challenge in pore scale modelling of carbonates lies in extracting a suitable network that is topologically identical to the parent sample. However, predictions of transport properties such as permeability, formation factor, relative permeability and capillary pressures have been made on networks extracted from the reconstructed 3D images of carbonates using a maximal ball algorithm (Al-Kharusi and Blunt, 2007). An alternative to generating networks without an underlying microstructure is by tuning the properties of a known network to generate simulated capillary pressures that matches the measured data, (Valvatne, 2003; Valvatne and Blunt, 2004) as described in the previous section.

9.1 Heterogeneous carbonate C

Carbonate C is a typical calcrete or lithified paleosol, enclosing carbonate clastic detritus. Analysis of its thin-section images suggests it probably developed as a weathering rind of limestones during exposure (uplift or sea-level drop). The porosity of its micro-CT image shown in Figure 9-1a is 14.8% while its resolution is 5.345µm. This carbonate has highly heterogeneous pore structure with poorly connected pores as shown in Figure 9-1. NMR simulations were performed on the micro-CT image and extracted network.
Figure 9-1: (a) 3D micro-CT image of carbonate C (the dark areas are the pore spaces and the white represent grains). (b) Network extracted from the image in (a) using the maximal ball method.

A central cubic section of voxel size $300^3$ cropped from the micro-CT image shown in Figure 9-1(b) was used for the simulations. The maximal ball algorithm was used to extract a network of 3,574 pores and 4,198 throats with an average coordination number of 2.3. This relatively low coordination number is as a result of a large number of poorly connected pores as shown in Figure 9.1.

Figure 9-2a: Comparison of the magnetization decays of the micro-CT image of carbonate C and the extracted network.
A surface relaxivity of 5µm/s which is in the range of typical values for carbonates (Chang et al., 1997; Ramakrishnan et al., 1998) was used in the simulations; the fluid properties used are shown in Table 8-2. Comparisons were made between the NMR responses of the extracted network with that of the micro-CT image as shown in Figure 9-2a. Other properties such as permeability and formation factor were also computed in the micro-CT image and extracted network and are shown in Table 9.1.

![Carbonate C](image)

Figure 9-2b: Comparison of the inverted T2 distribution of the magnetization decays for carbonate C shown in Figure 9-2a.

The magnetization of the network decays faster than that of the micro-CT image as shown in Figure 9-2a. The total grain surface area of the micro-CT image is 7.47×10^{-5} m^2 while that of the extracted network is 6.83×10^{-5} m^2. Although the image has a slightly higher surface area, the magnetization of the network decays faster than the image. This result shows that network did not fully capture the geometries and topology of the micro-CT image. There is also a significant difference in their respective T2 distributions shown in Figure 9-2b. An alternative method of generating networks from capillary pressure measurements will be used for other carbonates later to be discussed in this work.
Table 9-1: Comparison of mean transverse relaxation time T2, permeability and formation factor of micro-CT image and extracted network of carbonate C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean T2 (ms)</th>
<th>Permeability (mD)</th>
<th>Formation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-CT</td>
<td>Network</td>
<td>Micro-CT Network</td>
<td>Micro-CT Network</td>
</tr>
<tr>
<td>Carbonate C</td>
<td>1235</td>
<td>874</td>
<td>72</td>
</tr>
</tbody>
</table>

9.2 Edward limestone

NMR and mercury injection capillary pressure measurements were performed on two cores MB03 and MB11 of Edward limestone by Martin Fernø, Haldis Riskedal of the Department of Physics and Technology, University of Bergen, Norway. The MB03 cores have porosities and permeabilities in the range 19.2% ± 0.2% and 5.3 mD ± 0.2 mD respectively while they are 18% ± 0.2% and 5.6 mD ± 0.2 mD for the MB11 cores. Core plugs of diameter 3.81 cm and length 6.0 cm were used for the NMR measurements. The plugs were saturated in brine of viscosity $1.09 \times 10^{-3}$ Pas and density 1005 kg/m$^3$. The NMR measurements were performed using a MARAN2 bench top spectrometer (Resonance Instruments) at a temperature of 308K operating at 2 MHz.

The Carr-Purcell-Meiboom-Gill (CPMG) sequence was used for transverse relaxation measurements ($T_2$-measurements) with an inter-echo spacing of 400µs. A single data point was acquired at the centre of each echo, with 8,000 data points being collected. The resulting magnetization decay curves were inverted into $T_2$ distribution using WinDXP software (Resonance Instruments). The properties of a Berea network (Lerdahl et al., 2000) were tuned to match the mercury injection capillary pressure data of the plugs as shown in Figures 9-3 and 9-5. This network has 12,349 pores and 26,146 throats with an average coordination number of 4.2. The resulting tuned networks were then used for the simulation of NMR response which were compared with experimental measurements.
Figure 9.3: Comparison of the measured capillary pressure curve of MB03 with simulation results and the original Berea network. Berea network elements’ properties were tuned to give a capillary pressure curve that matches the measured data.

The diffusion coefficient and the bulk relaxation time of brine used in the NMR simulation were determined from the correlations given in equations (7.1) and (7.2). By substituting the temperature at which the experiment was performed (308K) and the viscosity of the brine ($1.09 \times 10^{-3}$ Pas), a diffusion coefficient of $1.9 \times 10^{-9}$ m$^2$/s and bulk relaxivity of 2.84 seconds were obtained and used in the simulations.

The surface relaxivity used was selected to match the experimental data; surface relaxivity values of $3 \mu$m/s and $4.5 \mu$m/s were used for MB03 and MB11 simulations respectively. These values are within the range for carbonates, usually between $1 \mu$m/s and $10 \mu$m/s (Chang et al., 1997; Ramakrishnan et al., 1998).
Figure 9-4: (a) Comparison of the measured magnetization decay from MB03 with simulation results from the tuned network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 9-5: Comparison of the measured capillary pressure curve of MB11 with simulation results of the tuned network.

Figure 9-6a: Comparison of the measured magnetization decay for MB11 with simulation results from the tuned network.
Figure 9-6b: Comparison of the inverted T2 distributions of the magnetization decays of MB11 shown in Figure 9-6a.

Despite the fact that the surface relaxivity values were selected to match experimental data, the magnetization decays faster in the network than the experimental data at late times as shown in Figures 9-4a and 9-6a. This is as a result of the topological differences that do exist between the networks and the cores. Similar trends were observed in their T2 distributions shown in Figures 9-4b and 9-6b, although the T2 distributions of the networks seem to be wider than the experimental data. Both samples appear to have a bimodal pore size distribution which is hard for a modified sandstone network to capture.

9.3 Homogeneous carbonates

NMR and mercury injection capillary pressure measurements were also performed by my colleague, Saif AlSayari at the Reslab Laboratory in Abu Dhabi on two homogeneous carbonate reservoir core samples (C22 and C32) from a producing field in the Middle East. The C22 cores have porosities and permeabilities in the range 27.5% ± 0.2% and 6.6 mD ± 0.2 mD respectively while they are 29.6% ± 0.2% and 7.7 mD ± 0.2 mD for the C32 cores. Core plugs of diameter 3.81 cm and length 6.1 cm were used for the NMR measurements.
The plugs were saturated in brine of viscosity $1.04 \times 10^{-3}$ Pas and density 1035 kg/m$^3$. Just as in Edward limestone, properties of the Berea network were tuned to match the mercury injection capillary pressure data as shown in Figures 9-7 and 9-9. The diffusion coefficient and the bulk relaxation time of brine used in the NMR simulation were also determined from the correlations given in equations (7.1) and (7.2).

Figure 9-7: Comparison of the measured capillary pressure curve for carbonate C22 with simulation results from the tuned network.

Figure 9-8a: Comparison of the measured magnetization decay of carbonate C22 with simulation results from the tuned network.
The surface relaxivity used was also selected to match the experimental data, surface relaxivity values of 2.8µm/s and 2.1µm/s were used for C22 and C32 plugs respectively.

Figure 9-8b: Comparison of the inverted T₂ distributions of the magnetization decays of carbonate C22 shown in Figure 9-8a.

Figure 9-9: Comparison of the measured capillary pressure curve for carbonate C32 with simulation results from the tuned network.
Figure 9-10: (a) Comparison of the measured magnetization for carbonate C32 with simulation results from the tuned network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).

The magnetization decays of the networks and experimental data of these two carbonates are consistent with each other as shown in Figures 9-8a and 9-10a. The differences in their $T_2$ distributions shown in Figures 9-8b and 9-10b are also as a result of the topological difference between the network and these carbonate cores.
Since the original network was extracted from a Berea sandstone microstructure, tuning this network to match the capillary pressure data of another core would result in slight differences with comparison to experimental data. In the Bentheimer sandstone, the magnetization decay and T₂ distributions of the simulation is consistent to a large extent with experimental values, however slight differences are observed in the comparison of the simulation results of carbonates with their respective experimental values. This is because the network was extracted from a sandstone which is expected to be topologically different to carbonates. However, in this case the agreement with experiment is still satisfactory. Note that the inferred pore size distribution from the T₂ distribution is much wider than seen for sandstones, consistent with a wider range of pore sizes in the network. To confirm this, Figure 9-11 compares the pore size distributions of the original Berea network and the networks tuned to match the capillary pressure data. To obtain this match, the average pore size is lower, while the distributions are broader.

![Figure 9-11: Comparison of the pore size distributions estimated from the T₂ distributions for carbonates C22 and C32 with the original Berea network.](image)

Figure 9-11: Comparison of the pore size distributions estimated from the T₂ distributions for carbonates C22 and C32 with the original Berea network.
10. Two-phase simulation results

Two-phase NMR simulations were performed on the networks obtained from the different porous media already discussed in previous chapters. The simulations were carried out for both drainage and waterflooding. During drainage, NMR response was simulated at regular water saturation intervals. For waterflooding, the simulations were performed at a fixed water saturation with different wettabilities. The surface relaxivities to oil was chosen as a function of the surface relaxivity to water that was used in all the previous single-phase simulations. A surface relaxivity ratio, \( \rho_o / \rho_w \) of 0.33 was used in all the simulations, where \( \rho_o \) and \( \rho_w \) are the surface relaxivities of the porous medium to oil and water and oil respectively. A light oil with viscosity 0.002 Pa.s and brine with viscosity 0.001 Pa.s were used. The diffusion coefficient and bulk relaxivity of the light oil are \( 0.67 \times 10^{-9} \) m\(^2\)/s and 0.62s while they are \( 2.07 \times 10^{-9} \) m\(^2\)/s and 3.1s for the brine. These values were obtained by substituting the brine and light oil viscosities and a temperature of 313K in equations (A.1.2 – A.1.5). Note that the oil diffusion coefficient and bulk relaxivity are small indicating that it will be significant at high oil saturations. The typical distance diffused by oil protons before bulk relaxation is \( \sqrt{6 D_o T_{Bo}} \approx 50 \) µm (\( D_o \) and \( T_{Bo} \) are the diffusion coefficient and bulk relaxivity of oil) as opposed to 200 µm for the brine.

10.1 Sand packs

Simulations were performed on six networks F42A, F42B, F42C, LV60A, LV60B and LV60C extracted from the two sand packs discussed in previous chapters. Surface relaxivity to oil used was \( 14 \times 10^{-6} \) m/s while that of water was \( 41 \times 10^{-6} \) m/s. For the drainage NMR simulations, the drainage process in the two-phase simulator (Valvatne and Blunt, 2004) was terminated at the desired water saturation. For the waterflooding NMR simulations, the waterflooding process in the two-phase simulator is terminated at the chosen fixed water saturation. For that given saturation, intrinsic contact angles in the range 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) were chosen for the simulation.
Actual angles in waterflooding are larger; the effective advancing angles during waterflooding are around 30°-40°, 90°-120° and 160°-170° (Valvatne and Blunt, 2004). The simulation results will help to highlight the significance of wettability in NMR simulations on networks.

**F42 Networks**

![Comparison of two-phase drainage magnetization decays at different water saturations for the F42A sand pack network. (b) The inverted T_2 distributions from the magnetization decays in (a).](image-url)

Figure 10-1: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the F42A sand pack network. (b) The inverted T_2 distributions from the magnetization decays in (a).
Figure 10-2: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.5$) for the F42A sand pack network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-3: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the F42B sand pack network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-4: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.5$) for the F42B sand pack network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-5: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the F42C sand pack network. (b) The inverted T$_2$ distributions from the magnetization decays in (a).
Figure 10-6: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.5$) for the F42C sand pack network. (b) The inverted T2 distributions from the magnetization decays in (a).
LV60 Networks

(a)

(b)

Figure 10-7: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the LV60A sand pack network. (b) The inverted T₂ distributions from the magnetization decays in (a).
Figure 10-8: (a) Comparison of two-phase waterflooding magnetization decays at contact angles $30^\circ$-$40^\circ$ (moderately water-wet), $70^\circ$-$80^\circ$ (intermediate-wet) and $110^\circ$-$120^\circ$ (oil-wet) at an intermediate water saturation ($S_w = 0.4$) for the LV60A sand pack network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-9: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the LV60B sand pack network. (b) The inverted T_2 distributions from the magnetization decays in (a).
Figure 10-10: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation (S_w = 0.4) for the LV60B sand pack network. (b) The inverted T2 distributions from the magnetization decays in (a).
Figure 10-11: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the LV60C sand pack network. (b) The inverted T$_2$ distributions from the magnetization decays in (a).
Figure 10-12: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation (S_w = 0.4) for the LV60C sand pack network. (b) The inverted T2 distributions from the magnetization decays in (a).
From Figures 10-1 to 10-12, it is observed that the magnetization decays and the inverted T2 distributions are similar for each sand pack type. This again validates the consistencies of the simulation results. The magnetization decays of F42 networks shown in Figures 10-1 to 10-6, at different saturation are distinct, this is also evident in their inverted T2 distributions, while for LV60 networks they are somewhat similar, during drainage likewise their T2 distributions. From all the magnetization decays, it is observed that as the oil saturation increases, magnetization decays faster and this results in a narrower T2 distribution centred at a lower value. This is as a result of the fact that, at higher oil saturations, magnetization decays predominantly as a result of bulk relaxation of the oil. Figure 10-13 shows the impact of surface and bulk relaxation of each phase using the F42A network at water saturation, $S_w = 0.5$ during drainage.

![Diagram showing magnetization decays due to bulk and surface relaxations](image)

Figure 10-13: (a) Comparison of the magnetization decays due to bulk and surface relaxations of oil and water phases in the F42A network at a water saturation of 0.5.

From Figure 10-13, magnetization decay due to bulk relaxation of oil is dominant, especially at higher oil saturations, while surface relaxation of water will be significant at high water saturations. The bulk relaxation of water and surface relaxation of oil are not significant, simply because the bulk relaxation time of water is higher than that of oil at high oil saturation and the surface relaxivity to oil is much lower than that of water.
The effect of saturation in the LV60 networks is less significant, LV60 has smaller pores, a greater surface area and surface relaxation plays a more significant role.

10.2 Fontainebleau Network

Figure 10-14: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the Fontainebleau network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-15: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.4$) for the Fontainebleau network. (b) The inverted T$_2$ distributions from the magnetization decays in (a).
10.3 Poorly consolidated sandstone network (S)

Figure 10-16: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the poorly consolidated sandstone (S) network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-17: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.4$) for the poorly consolidated sandstone (S) network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
10.4 Berea PBM Network

Figure 10-18: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the network obtained from reconstructed microstructure of Berea sandstone, Berea PBM. (b) The inverted T2 distributions from the magnetization decays in (a).
Figure 10-19: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.4$) for the Berea PBM network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
10.5 Berea MB Network

Figure 10-20: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the network extracted using the maximal ball algorithm from the micro-CT image of a Berea sandstone. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
Figure 10-21: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.4$) for the Berea MB network. (b) The inverted T$_2$ distributions from the magnetization decays in (a).
10.6 Bentheimer network

Figure 10-22: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the network obtained by tuning the Berea PBM network to match the experimental capillary pressure data of Bentheimer sandstone. (b) The inverted T2 distributions from the magnetization decays in (a).
Figure 10-23: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation ($S_w = 0.4$) for the Bentheimer network. (b) The inverted $T_2$ distributions from the magnetization decays in (a).
10.7 Carbonate (C) network

Figure 10-24: (a) Comparison of two-phase drainage magnetization decays at different water saturations for the network extracted from the micro-CT image of the carbonate C, using the maximal ball algorithm. (b) The inverted T2 distributions from the magnetization decays in (a).
Figure 10-25: (a) Comparison of two-phase waterflooding magnetization decays at contact angles 30°-40° (moderately water-wet), 70°-80° (intermediate-wet) and 110°-120° (oil-wet) at an intermediate water saturation (S_w = 0.4) for the carbonate C network. (b) The inverted T2 distributions from the magnetization decays in (a).
The imbibition results are surprising, for a water-wet sample, the magnetization decay is slightly faster during imbibition than drainage at the same saturation. In drainage, oil remains connected in the largest pores; whereas in imbibition, oil can be trapped surrounded by water. At the same water saturation, the capillary pressure is lower and more water resides in corners during imbibition. The magnetization decay from water in the corners and bulk oil is rapid – the greater fraction of water in corners and the poorer connectivity of the oil, preventing walkers moving between pores before reaching a surface, leads to a slightly more rapid decay in imbibition.

There is a dramatic change in behaviour as the system becomes intermediate to oil wet. The magnetization decay is now much slower than for a water-wet system or during drainage. In these cases during waterflooding, layers of oil can be formed sandwiched in the corners of pore between water in the corners and water in the centre of the pore space as shown in Figure 10-26.

Figure 10-26: During waterflooding oil layers are sandwiched between water in corners and water at the centre of the pore (Valvatne and Blunt, 2004).

These layers allow the magnetization to decay very rapidly in the oil, since the layers are thin and they cover a large fraction of the grain area. In contrast, water in the centre of the pores has a very small area in contact with the surface. This combined with a long bulk relaxation time means that the magnetization in much of the water phase decays slowly as evident in Figures 10-1 to 10-12.
These results demonstrate that the magnetization decay is affected by pore size distribution, water saturation and wettability. Unfortunately, while it is possible to explain trends in the results, it is not possible to disentangle these individual effects uniquely. However, the delayed relaxation during waterflooding compared to drainage is a clear indication of oil-wet conditions – we do require experimental verification of this prediction, however.

For the consolidated media studied we observed similar trends to those observed in the sand packs. For media with small pore sizes, we see little change in magnetization decay during drainage as saturation changes, since the effects of surface relaxation are more significant and are confused with the similarly bulk relaxation of oil. This indicates that NMR response may not be a sensitive gauge of saturation in drainage. In contrast, all the samples display a dramatic decrease in decay rate for oil-wet conditions. Again, this suggests that a simple and clear-cut way to identify oil-wet media - $T_2$ values larger in media with small pore sizes indicates the suppression of surface relaxation of water due to the presence of oil layers.

### 10.8 Comparison with experimental results

NMR is suitable for the characterization of wettability in porous media; this is because NMR relaxation rates are sensitive to the interactions between protons in fluids and the surrounding pore walls (Howard, 1994). Wettabilities determined from NMR measurements have been successfully compared with other standard laboratory wettability indices (Hsu et al., 1992; Howard, 1998). For light hydrocarbons characterized by slow relaxation times, the separation between water and hydrocarbon is distinct (Howard, 1998). For the two phases in a rock, the relaxation time distributions are affected by the distribution and thickness of the wetting phase on the pore surfaces (Howard, 1998). Hsu et al., (1992) used NMR relaxation methods to characterize the wettability of water-wet and oil-wet carbonate cores. They observed that water-wet cores gave the shortest relaxation rates – this is as a result of the dominant surface relaxation of water.
Their experimental measurements also show the relaxation rates in oil-wet cores were longer because bulk relaxation of the oil is dominant. Freedman et al., (2003) used NMR relaxation methods to determine wettability, saturation and oil viscosity in rocks partially saturated with oil and brine. In mixed-wet samples; they observed a shortening in the relaxation times of the oil distribution compared to the oil bulk distribution which provides a clear evidence of surface relaxation of the oil. In oil-wet samples, the brine molecules do not contact the pore surfaces and therefore experience reduced relaxation. As a result, the brine $T_2$ values were shifted towards higher values approaching its bulk value.

In order to investigate the effect of wettability on NMR response and to validate the algorithm used for the simulation of NMR response of two-phase fluid in networks, simulation results were qualitatively compared with experimental data. The experimental data used for this comparison was taken from Al-Marooqi et al. (2003) where they performed NMR measurements on sandstone samples from a North Sea reservoir. The measurements were performed at different saturations (residual saturations and some intermediate saturations) with wettability states ranging from mixed-wet to oil-wet. Wettability changes were induced in the rocks by aging with dead crude oil. The rocks were saturated with brine and a mixture of light paraffin oils (density: 764 kg/m$^3$ and viscosity: $1.13\times10^{-3}$ Pa.s).

The network extracted from the reconstructed microstructure of Berea sandstone (Berea PBM) was used for the simulations. The diffusion coefficient and bulk relaxivity of brine used in the simulations are the same as in the previous simulations (i.e. $2.07\times10^{-9}$ m$^2$/s and 3.1 seconds respectively). For the paraffin oil, its viscosity was substituted in equations (A.1.2) and (A.1.4) along with the temperature at which the NMR experiment was performed (307K) to obtain a diffusion coefficient of $1.2\times10^{-9}$ m$^2$/s and bulk relaxivity of 1.1 seconds which were used in the simulations. Contact angles in the range 70° -80° and 110° -120° were used in the simulations for the mixed-wet and oil-wet conditions respectively. For the mixed-wet condition, experiments were performed at water saturations, (0.27, 0.39, 0.76 and 1.0), similar water saturations (0.29, 0.40, 0.76 and 1.0) were used for the simulations for this wettability state.
Figures 10-27 and 10-29 show the experimental results for the different water saturations for the mixed-wet condition while Figures 10-28 and 10-30 show the corresponding simulation results using contact angles in the range 70° - 80°. Similar trends were observed in the comparison of the experimental and simulation results in Figures 10-27 and 10-28 respectively, the presence of oil at a high saturation caused a shift in the T₂ distribution towards higher values. This is because the relaxation rate in the oil phase is lower thereby resulting in a slower magnetization decay compared to the fully saturated (Sₙₐₚ = 1.0) result as shown in Figure 10-31. Comparing these results with those of the previous section where an increase in oil saturation leads to faster magnetization decay; this is because a much more viscous oil was used with a shorter bulk relaxation time of 0.62s. Thus, magnetization decays faster in high viscosity oils.

**Mixed-wet results**

![Figure 10-27: Experimental T₂ distributions of a mixed-wet North Sea sandstone at water saturations (Sₙₐₚ = 1.0 and 0.27)](image)

![Figure 10-28: Simulated T₂ distributions of Berea PBM network at contact angles in the range 70° – 80° (mixed-wet) and saturations (Sₙₐₚ = 1.0 and 0.29)](image)

![Figure 10-29: Experimental T₂ distributions of a mixed-wet North Sea sandstone at water saturations (Sₙₐₚ = 0.39 and 0.76)](image)

![Figure 10-30: Simulated T₂ distributions of Berea PBM network at contact angles in the range 70° – 80° (mixed-wet) and saturations (Sₙₐₚ = 0.40 and 0.76)](image)
Similar trends were also observed in the comparison of the simulation results with experimental data for the intermediate saturations as shown in Figures 10-29 and 10-30. As the oil saturation increases, the $T_2$ distribution becomes narrower which approaches the bulk relaxation value. It is also observed that the bulk relaxivity of the paraffin oil used in this simulation, (1.1s) is consistent with the value obtained in the experimental measurements shown in Figures 10-27 and 10-29 thereby validating the correlation used for the estimation of this property.

![Figure 10-31: Simulated magnetization decays of the Berea PBM network at mixed-wet condition for different water saturations.](image1)

![Figure 10-32: Simulated magnetization decays of the Berea PBM network at oil-wet condition for different water saturations.](image2)

**Oil-wet results**

![Figure 10-33: Experimental $T_2$ distributions of an oil-wet North Sea sandstone at water saturations ($S_w = 1.0$ and 0.38)](image3)

![Figure 10-34: Simulated $T_2$ distributions of Berea PBM network at contact angles in the range $110^\circ - 120^\circ$ (oil-wet) and saturations ($S_w = 1.0$ and 0.38)](image4)
For the oil-wet conditions, experiments were performed at water saturations, (0.38, 0.40, 0.85 and 1.0), the same water saturations were used for the simulations. Figures 10-33 and 10-35 show the experimental results for the different water saturations while Figures 10-34 and 10-36 show the corresponding simulation results using contact angles in the range 110° - 120°. Similar trends were observed in the comparison of these experimental and simulation results. The presence of oil at a high saturation caused a shift in the T² distribution towards higher values similar to the observation in the mixed-wet state.

The magnetization for the mixed-wet condition decays faster than that of the oil-wet condition as shown in Figures 10-31 and 10-32. This is expected since both fluids wet the grain surfaces. For mixed-wet conditions surface relaxation of brine and bulk relaxation of the oil are both significant thereby resulting in a faster magnetization decay. For oil-wet conditions, the brine relaxes at its bulk relaxation rate (which is less than that of oil) while the oil relaxes at its bulk relaxation rate. This results in a slower magnetization decay which is observed in Figure 10-32. The principal qualitative prediction of our multiphase model is that in oil-wet conditions, the magnetization decay for water is slower since it cannot access the surface. Fig 10-35 from the experiments confirms this prediction with a clear signature from bulk water.
11.

Conclusions and recommendations for future work

11.1 Conclusions

For the sand packs studied in this work, successful comparisons of the simulated magnetization decays were made with experimental data. Computations of permeability and formation factor were made on micro-CT images and extracted networks which are consistent with experimental measurements. Hence, the maximal ball extraction algorithm can be used to extract networks from which single-phase transport properties in unconsolidated media can be predicted successfully.

We also simulated magnetization decay in a selection of sandstones sand carbonates. For consolidated media, the maximal ball algorithm met with mixed success. The extracted networks tended to predict a faster magnetization decay than simulations on the underlying micro-CT image. In contrast, networks generated by the process-based method gave more consistent results. The maximal ball method over-estimated the surface area, leading to the generation of slit-like elements in which surface relaxation was very fast. For all the networks extracted using the maximal ball method, comparison of the simulated T2 distributions of these networks are narrower than those of the corresponding micro-CT images. This suggests that in the maximal ball algorithm some fine details of the pore structure are lost during extraction.

Overall, in single-phase flow we were able to predict permeability, formation factor and NMR response with reasonable accuracy in most cases, which serves to validate the network extraction algorithm and to serve as the starting point for the prediction of multiphase properties. We simulated magnetization decay during multiphase flow in both drainage and waterflooding for different rock wettabilities. In oil-wet media, we predict a slow decay and a broad distribution of T2, this is because water in the centres of the pores has a low bulk relaxivity, since the grain surface is covered by oil layers, this suggests a straightforward technique to indicate oil wettability.
11.2 Recommendations for future work

In order to further validate the simulation results, further experiments should be conducted on consolidated media which can be compared with simulation results on both micro-CT images and extracted networks. The maximal ball network extraction algorithm can be further developed to be suitable for consolidated media. This unsuitability arises from the fact that the method seems to over-estimate pore surface area, leading to a faster magnetization decay. The increased surface area leads to increased shape factors; and so an improved way of determining shape factors in the maximal ball algorithm could result in better predictions.

Two-phase properties such as relative permeability and capillary pressures could be measured experimentally on sand packs and sandstones which can be compared with their corresponding simulation results; this will assist to further validate the network extraction algorithm. For the two-phase NMR simulations, this can be validated by performing simulations directly on the micro-CT image. The respective fluid configurations can be mapped to the appropriate pore voxels in the 3D image, since we know the voxels that define a given network element.

Our results suggests that oil-wet conditions are readily identified in NMR experiments, indicated by a slow magnetization decay from water in the centres of the pore space, protected from the grain surface by oil layers. This prediction needs to be tested directly by experiments. Overall, the aim is to use pore-scale modelling, verified against experiments to make reliable predictions of properties outside the range of conditions in the measurements. We could use drainage capillary pressure combined with a single water flood NMR signal to elucidate pore structure and wettability from which relative permeability could be predicted. A detailed and extensive experimental programme is necessary to test the ability of network modelling to give reliable predictions in these cases.
REFERENCES


Smolen, J. J., 1996, Cased hole and production log evaluation, PennWell Books, Tulsa, Oklahoma, USA


APPENDIX A-1

Manual of the NMR response simulation code

Description

The program for the simulation of NMR response is written in C++ and reads the basic keywords from the input file. The keywords in the single-phase and two-phase are basically the same except that the properties of the two fluids are entered for the two-phase fluid compared to the single-phase. All the keywords are necessary for the program to run, although there are default values embedded within the program. The keywords in the input file can be arranged in any order but however must be included in the input file. Comments in the data file are indicated by ‘%’, resulting in the rest of the line being discarded. All keywords should be terminated by ‘#’. The keywords for the micro-CT and network simulation are mostly the same except for a few explained below.

Keywords specific to Micro-CT Simulation:

1. **VOXEL_WALKERS**

This is the number of walkers to be assigned to each pore voxel; a larger number of walkers will result in longer computation time. The default value is 1. The value selected should take into consideration the voxel size of the image and its porosity. For example, an image having a voxel size of $300^3$ and a porosity of 33\% will have a total of 9 million pore voxels; if 1 walker is assigned to each pore voxel, there will be 9 million walkers which may be computationally expensive to run. Hence, the number of walkers to be assigned to pore voxels can be limited to a particular value as we have in the WALKERS_LIMIT keyword.

```
VOXEL_WALKERS
1
#
```
2. **WALKERS_LIMIT**

This is the total number of walkers to be assigned to the entire image. The code compares the total number of walkers to be assigned to the pore voxels in the image from the VOXEL_WALKERS keyword with the value input of WALKERS_LIMIT. If the total number of walkers calculated from the VOXEL_WALKERS keyword is greater than that of the WALKERS_LIMIT, the value input for the WALKERS_LIMIT keyword is used. If there are fewer walkers than the available pore voxels, walkers are then assigned to randomly selected pore voxels.

```
WALKERS_LIMIT
200000
#
```

3. **UNIT_DISTANCE**

The distance diffused by a walker at unit time step is chosen a function of the resolution of the image. It is expected to be a fraction of the resolution of the image, values in the range 0.1 and 0.3 are suitable. This will ensure that the random walkers take significant number of steps before encountering a grain surface. The time required to diffuse this distance (time-step) is then calculated from this unit distance by using equation (A.1.1):

\[
\Delta t = \frac{s^2}{6D}
\]  

(A.1.1)

where \( \Delta t \) is the unit time-step, \( s \) is the unit distance and \( D \) is the diffusion coefficient of the fluid.

```
UNIT_DISTANCE
0.2
#
```
4. **VOXEL_SIZE**

This is the voxel size of the image in one dimension. The image should have a cubic geometry. The voxel size should take into consideration the memory capacity of the computer. The maximum voxel size for a Pentium IV processor with 2GB RAM is 300.

```
VOXEL_SIZE
300
#
```

5. **RESOLUTION**

This is the resolution of the image in metres (m)

```
RESOLUTION
3.85E-6
#
```

6. **IMAGE_FILE**

This is the file containing the image, the required paths and initial of the file must be specified, better still the file should be placed in the same folder as the executable file.

```
IMAGE_FILE
Sandpack
#
```

**Keywords specific to Network Simulation:**

1. **WALKERS**

This is the initial total number of walkers to be assigned to all the network elements. Walkers are proportionally assigned to elements based on their volumes. This will ensure a uniform distribution of walkers in the whole network. The total number of walkers finally assigned to elements will be slightly less than this value, as a result of their relative pore volume distributions.
2. **TIME_STEP**

This is the time-step in seconds (s). The time-step of the walkers should be in the range 0.01ms to 0.3ms. This corresponds to a unit distance in the range 0.35µm to 2.0µm which is significantly less than the dimensions of a typical network element.

```
WALKERS
2000000
#
```

```
TIME_STEP
3.0E-4
#
```

3. **NETWORK**

This is the file containing the network, the required paths and initial of the file must be specified, better still the file should be placed in the same folder as the executable file. The network data comprises of 4 ASCII files which has the same format as that used by Statoil.

```
NETWORK
Sandpack
#
```

**Keywords specific to Micro-CT and Single-Phase Network Simulation:**

1. **DIFF_CONSTANT**

This is the diffusion coefficient of the fluid saturating the network or the micro-CT image in m²/s.

```
DIFF_CONSTANT
2.07E-9
#
```
2. RELAXIVITY

This is the surface relaxivity of the porous medium in m/s with respect to the fluid in contact with the surface. If a match with experimental data is desired, sensitivities can be performed using this keyword until a match with the experimental data is obtained.

```
RELAXIVITY
15.0E-6
#
```

3. BULK_RELAXIVITY

This is the bulk relaxivity of the fluid in seconds (s).

```
BULK_RELAXIVITY
3.1
#
```

Keywords specific to Two-Phase NMR Network Simulation:

1. DIF_CONST_OIL

This is the diffusion coefficient of oil in m²/s.

```
DIF_CONST_OIL
0.67E-9
#
```

2. DIF_CONST_WAT

This is the diffusion coefficient of water in m²/s. The diffusion coefficients of both oil and water are dependent on temperature and viscosity of the fluid. They are often determined from the correlations (Vinegar, 1995):

\[
D_o \approx \left( \frac{1.37}{(298)\eta} \right) \times 10^{-32}
\]  

(A.1.2)
\[ D_w \cong \left( \frac{2T}{(298 \eta)} \right) \times 10^{-12} \]  \hspace{1cm} (A.1.3)

where \( D_o \) and \( D_w \) are the diffusion coefficient of oil and water respectively in m²/s, \( T \) is temperature in K and \( \eta \) is the fluid viscosity in Pa.s.

3. **OIL_RELAXIVITY**

This is the relaxivity, \( \rho_o \) of the porous medium in m/s with respect to oil. It is much less than the relaxivity of the surface to water, \( \rho_w \). The ratio \( \rho_o / \rho_w \) is often in the range 0.1 to 0.4 (Looyestijn and Hofman, 2005).

4. **WAT_RELAXIVITY**

This is the relaxivity, \( \rho_w \) of the porous medium in m/s with respect to water.

5. **OIL_BULK_RELAX**

This is the bulk relaxivity of oil in seconds (s).
6. **WAT_BULK_RELAX**

This is the bulk relaxivity of water in seconds (s). The bulk relaxivities of oil and water are dependent on temperature and viscosity of the fluid and are often determined from the correlations (Vinegar, 1995):

\[
T_{2Bo} = \left(\frac{1.2T}{(298)\eta}\right)10^{-3}
\]  
(A.1.4)

\[
T_{2Bw} = \left(\frac{3T}{(298)\eta}\right)10^{-3}
\]  
(A.1.5)

where \(T_{2Bo}\) and \(T_{2Bw}\) are the bulk relaxation times in seconds (s) of oil and water respectively, while \(T\) is the temperature in K and \(\eta\) is viscosity in Pa.s.

7. **TWOPHASE_DATA**

This is the drainage two-phase data from the two-phase simulation code. This file contains the geometrical properties of network elements and their respective fluid configurations at a given water saturation during drainage.

8. **2PHASE_DATA_IMB**

This is the imbibition two-phase data from the two-phase simulation code. This file contains the geometrical properties of network elements and their respective fluid configurations at a given fluid saturation during imbibition.
9. SIMULATION_TYPE

This keyword specifies the type of NMR simulation; there are two options, drainage and imbibition. One of the two options must be selected by (‘T’) and the other should be set to (‘F’) depending on which simulation is desired.

```
SIMULATION_TYPE
% Drainage Imbibition
F T
#
```

10. NETWORK

This is the file containing the network, the required paths and initial of the file must be specified, better still the file should be placed in the same folder as the executable file. The network data comprises of 4 ASCII files which has the same format as that used by Statoil.

```
NETWORK
Sandpacks
#
```

10. CLAY_VOLUME

This is used to input the clay volume porosity of the network. If the porous medium is sand this keyword should be set to zero.

```
CLAY_VOLUME
0.056
#
```
General keywords: Applicable to all the simulation codes

1. TITLE

The basic output files are prefixed by the indicated title. The basic output files generated are the magnetization decay file (title_nmrResponse.csv) and the results summary file (title_Results.prt). The other files generated are used for $T_2$ inversion these files include, the abridged magnetization decay (M.csv) and the kernel matrix file (K.csv).

```
TITLE
Sample1
#
```

2. REPORT_TIME

This is the interval for reporting the magnetization decay, this keyword should be an integer, the value selected will be multiplied by the time-step to determine the time interval at which the magnetization decay values are reported.

```
REPORT_TIME
10
#
```

3. NUM_TIME_DATA

This is the number of data points in the magnetization decay that is needed for $T_2$ inversion. These selected data points are equally spaced within the magnetization decay spectrum. This corresponds to the number of data entries in the abridged magnetization decay file (M.csv).

```
NUM_TIME_DATA
100
#
```
4. **DECAY_CUT_OFF**

This keyword specifies the time in seconds (s) desired for the simulation to be terminated. The simulation ceases as soon as the reported time-interval reaches this value. The simulation can also stop as soon as all the walkers decay. The simulation is terminated by whichever condition is satisfied first.

```
DECAY_CUT_OFF
10.0
#
```

5. **INTER_ECHO_TIME**

This keyword is required if comparison of the simulation results with experimental data is desired. This is the inter-echo time used in the NMR measurement, it is used to calculate the magnetization decay due to relaxation in magnetic gradients. This relaxation mechanism is often negligible and in order to neglect it, the value assigned to the keyword should be set to zero.

```
INTER_ECHO_TIME
00.0E-6
#
```

6. **MAGNET_GRADIENT**

This keyword is also required if comparison of the simulation results with experimental data is desired. This is the magnetic gradient imposed during NMR measurement. It is used in combination with the inter-echo time to calculate the magnetization decay due to relaxation in magnetic gradients. To neglect this relaxation mechanism, the value assigned to the keyword should be set to zero.

```
MAGNET_GRADIENT
0.0
#
```
OUTPUT FILES

A. *title* _Results.prt* – This contains a summary of all the fluid and network or micro-CT properties used in the simulation. It also contains an abridged magnetization decay. For single-phase simulation in networks, this file contains the solid surface areas of the sides of triangular and square shaped elements in the network as given in equations (4.15 – 4.18) and the ratios of walkers that decay on these sides given in equations (4.19 – 4.22).

B. *title* _nmrResponse.csv* – This is an excel (comma separated variable, csv) file which contains the magnetization decay results at the selected time intervals specified in the input file. The first two columns in this file is the magnetization decay due to surface relaxation mechanism alone while the next two columns is the magnetization decay as a result of both surface and bulk relaxation mechanism. The last two columns is the magnetization decay due to surface, bulk and diffusion relaxations. If the INTER_ECHO_TIME and MAGNET_GRADIENT keywords are set to zero, then the last two columns are the same value as the previous two columns. For two-phase fluid simulation, two additional files *title* _nmrOil.csv* and *title* _nmrWat.csv* are generated the magnetization decay of the oil and water phases alone, while their associated *title* _nmrResponse.csv* file is a weighted average of the two fluid phases.

C. *M.csv* – This is an excel file used for the inversion of the $T_2$ distribution from the magnetization decay. This file contains a single column of magnetization decays at selected point intervals, the total number of data points in this file is specified using the keyword NUM_TIME_DATA.

D. *K.csv* – This is a matrix file generated from the time intervals corresponding to the abridged magnetization decays (*M.csv*) and exponentially spaced $T_2$ values.
APPENDIX A-2

Diffusion in micro-CT images

The following equations show the conditions that must be specified for walkers in a particular pore to diffuse into specific neighbouring pores. The basic condition that must be satisfied is that the unit distance diffused at each time step is much less than the resolution of the image. This will ensure that walkers do not diffuse beyond their neighbouring voxels.

If a walker is in voxel X, the following conditions of the coordinates of the walker must be satisfied for the walker to diffuse into any of the neighbouring pore voxels.

1. Initial position in voxel X \((x_1, y_1, z_1)\)  
   \[ 
   x_1 > L \\
   y_1 > L \\
   0 < z_1 < L 
   \]  

   Final position in Voxel 1 \((x_2, y_2, z_2)\)  
   \[ 
   x_2 = x_1 - L \\
   y_2 = y_1 - L \\
   z_2 = z_1 
   \]
<table>
<thead>
<tr>
<th>Step</th>
<th>Initial Position in Voxel $X(x_i,y_i,z_i)$</th>
<th>Final Position in Voxel ( x_2,y_2,z_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>( 0 &lt; x_i &lt; L ) ( y_i &gt; L ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = x_i ) ( y_2 = y_i - L ) ( z_2 = z_i )</td>
</tr>
<tr>
<td>3.</td>
<td>( x_i &lt; 0 ) ( y_i &gt; L ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = L - \text{abs}(x_i) ) ( y_2 = y_i - L ) ( z_2 = z_i )</td>
</tr>
<tr>
<td>4.</td>
<td>( x_i &gt; L ) ( 0 &lt; y_i &lt; L ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = x_i - L ) ( y_2 = y ) ( z_2 = z_i )</td>
</tr>
<tr>
<td>5.</td>
<td>( 0 &lt; x_i &lt; L ) ( 0 &lt; y_i &lt; L ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = x_i ) ( y_2 = y_i ) ( z_2 = z_i )</td>
</tr>
<tr>
<td>6.</td>
<td>( x_i &lt; 0 ) ( 0 &lt; y_i &lt; L ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = L - \text{abs}(x_i) ) ( y_2 = y_i ) ( z_2 = z_i )</td>
</tr>
<tr>
<td>7.</td>
<td>( x_i &gt; L ) ( y_i &lt; 0 ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = x_i - L ) ( y_2 = L - \text{abs}(y_i) ) ( z_2 = z_i )</td>
</tr>
<tr>
<td>8.</td>
<td>( 0 &lt; x_i &lt; L ) ( y_i &lt; 0 ) ( 0 &lt; z_i &lt; L )</td>
<td>( x_2 = x_i ) ( y_2 = L - \text{abs}(y_i) ) ( z_2 = z_i )</td>
</tr>
</tbody>
</table>
9. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 9 \((x_2, y_2, z_2)\)
\[
\begin{align*}
x_1 &< 0 \\
y_1 &< 0 \\
z_1 &< L
\end{align*}
\quad
\begin{align*}
x_2 &= L - \text{abs}(x_1) \\
y_2 &= L - \text{abs}(y_1) \\
z_2 &= z_1
\end{align*}
\]

10. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 10 \((x_2, y_2, z_2)\)
\[
\begin{align*}
x_1 &> L \\
y_1 &> L \\
z_1 &> L
\end{align*}
\quad
\begin{align*}
x_2 &= x_1 - L \\
y_2 &= y_1 - L \\
z_2 &= z_1 - L
\end{align*}
\]

11. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 11 \((x_2, y_2, z_2)\)
\[
\begin{align*}
0 < x_1 < L \\
y_1 &> L \\
z_1 &> L
\end{align*}
\quad
\begin{align*}
x_2 &= x_1 \\
y_2 &= y_1 - L \\
z_2 &= z_1 - L
\end{align*}
\]

12. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 12 \((x_2, y_2, z_2)\)
\[
\begin{align*}
x_1 &< 0 \\
y_1 &> L \\
z_1 &> L
\end{align*}
\quad
\begin{align*}
x_2 &= L - \text{abs}(x_1) \\
y_2 &= y_1 - L \\
z_2 &= z_1 - L
\end{align*}
\]

13. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 13 \((x_2, y_2, z_2)\)
\[
\begin{align*}
x_1 &> L \\
0 < y_1 < L \\
z_1 &> L
\end{align*}
\quad
\begin{align*}
x_2 &= x_1 - L \\
y_2 &= y_1 \\
z_2 &= z_1 - L
\end{align*}
\]

14. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 14 \((x_2, y_2, z_2)\)
\[
\begin{align*}
0 < x_1 < L \\
0 < y_1 < L \\
z_1 &> L
\end{align*}
\quad
\begin{align*}
x_2 &= x_1 \\
y_2 &= y_1 \\
z_2 &= z_1 - L
\end{align*}
\]
15. Initial position in voxel X \((x_1,y_1,z_1)\) Final position in Voxel 15 \((x_2,y_2,z_2)\)

\[
\begin{align*}
    x_1 &< 0 \\
    0 &< y_1 < L \\
    z_1 &> L \\
    \Rightarrow \quad & x_2 = L - \text{abs}(x_1) \\
    & y_2 = y_1 \\
    & z_2 = z_1 - L
\end{align*}
\]

16. Initial position in voxel X \((x_1,y_1,z_1)\) Final position in Voxel 16 \((x_2,y_2,z_2)\)

\[
\begin{align*}
    x_1 &> L \\
    y_1 &< 0 \\
    z_1 &> L \\
    \Rightarrow \quad & x_2 = x_1 - L \\
    & y_2 = L - \text{abs}(y_1) \\
    & z_2 = z_1 - L
\end{align*}
\]

17. Initial position in voxel X \((x_1,y_1,z_1)\) Final position in Voxel 17 \((x_2,y_2,z_2)\)

\[
\begin{align*}
    0 &< x_1 < L \\
    y_1 &< 0 \\
    z_1 &> L \\
    \Rightarrow \quad & x_2 = x_1 \\
    & y_2 = L - \text{abs}(y_1) \\
    & z_2 = z_1 - L
\end{align*}
\]

18. Initial position in voxel X \((x_1,y_1,z_1)\) Final position in Voxel 18 \((x_2,y_2,z_2)\)

\[
\begin{align*}
    x_1 &< 0 \\
    y_1 &< 0 \\
    z_1 &> L \\
    \Rightarrow \quad & x_2 = L - \text{abs}(x_1) \\
    & y_2 = L - \text{abs}(y_1) \\
    & z_2 = z_1 - L
\end{align*}
\]

19. Initial position in voxel X \((x_1,y_1,z_1)\) Final position in Voxel 19 \((x_2,y_2,z_2)\)

\[
\begin{align*}
    x_1 &> L \\
    y_1 &> L \\
    z_1 &< 0 \\
    \Rightarrow \quad & x_2 = x_1 - L \\
    & y_2 = y_1 - L \\
    & z_2 = L - \text{abs}(z_1)
\end{align*}
\]

20. Initial position in voxel X \((x_1,y_1,z_1)\) Final position in Voxel 20 \((x_2,y_2,z_2)\)

\[
\begin{align*}
    x_1 &> L \\
    y_1 &> L \\
    z_1 &< 0 \\
    \Rightarrow \quad & x_2 = x_1 - L \\
    & y_2 = y_1 - L \\
    & z_2 = L - \text{abs}(z_1)
\end{align*}
\]
Pore-scale simulation of NMR response in porous media

21. Initial position in voxel X \((x_1, y_1, z_1)\)  
Final position in Voxel 21 \((x_2, y_2, z_2)\)  
\(x_1 < 0\)  
\(y_1 > L\)  
\(z_1 < 0\)  
\(x_2 = L - \text{abs}(x_1)\)  
\(y_2 = y_1 - L\)  
\(z_2 = L - \text{abs}(z_1)\)

22. Initial position in voxel X \((x_1, y_1, z_1)\)  
Final position in Voxel 22 \((x_2, y_2, z_2)\)  
\(x_1 > L\)  
\(0 < y_1 < L\)  
\(z_1 < 0\)  
\(x_2 = x_1 - L\)  
\(y_2 = y_1\)  
\(z_2 = L - \text{abs}(z_1)\)

23. Initial position in voxel X \((x_1, y_1, z_1)\)  
Final position in Voxel 23 \((x_2, y_2, z_2)\)  
\(0 < x_1 < L\)  
\(0 < y_1 < L\)  
\(z_1 < 0\)  
\(x_2 = x_1\)  
\(y_2 = y_1\)  
\(z_2 = L - \text{abs}(z_1)\)

24. Initial position in voxel X \((x_1, y_1, z_1)\)  
Final position in Voxel 24 \((x_2, y_2, z_2)\)  
\(x_1 < 0\)  
\(0 < y_1 < L\)  
\(z_1 < 0\)  
\(x_2 = L - \text{abs}(x_1)\)  
\(y_2 = y_1\)  
\(z_2 = L - \text{abs}(z_1)\)

25. Initial position in voxel X \((x_1, y_1, z_1)\)  
Final position in Voxel 25 \((x_2, y_2, z_2)\)  
\(x_1 > L\)  
\(y_1 < 0\)  
\(z_1 < 0\)  
\(x_2 = x_1 - L\)  
\(y_2 = L - \text{abs}(x_1)\)  
\(z_2 = L - \text{abs}(z_1)\)

26. Initial position in voxel X \((x_1, y_1, z_1)\)  
Final position in Voxel 26 \((x_2, y_2, z_2)\)  
\(0 < x_1 < L\)  
\(y_1 < 0\)  
\(z_1 < 0\)  
\(x_2 = x_1\)  
\(y_2 = L - \text{abs}(x_1)\)  
\(z_2 = L - \text{abs}(z_1)\)
27. Initial position in voxel X \((x_1, y_1, z_1)\) Final position in Voxel 27 \((x_2, y_2, z_2)\)

\[
\begin{align*}
x_1 &< 0 & x_2 &= L - \text{abs}(x_1) \\
y_1 &< 0 & y_2 &= L - \text{abs}(y_1) \\
z_1 &< 0 & z_2 &= L - \text{abs}(z_1)
\end{align*}
\]

From the above analysis, voxels 2, 4, 6, 8, 14 and 23 have large surface area in contact with the reference voxel X, as such most of the inter voxel diffusion takes place in these directions. However voxels 1, 3, 7, 9, 11, 13, 15, 17, 20, 22, 24 and 26 all have an edge connected to the reference voxel 5, as such very few inter voxel diffusion takes place through this edges. The remaining 8 voxels are the corner point voxels and simply because of very minute point contact with the reference voxel, very few walkers diffuses through these points.
APPENDIX A-3

T2 inversion from magnetization decay

The method used for the inversion of $T_2$ distributions from magnetization decays is based on a curvature-smoothing regularization (Chen et al., 1999) and is adapted from Toumelin, (2003). From the multiexponential equation used to represent a distribution of $T_2$ constants of a porous medium, (Kenyon, 1997):

$$\frac{M(t)}{M_0} = \sum_{i=1}^{N} a_i \exp\left(-\frac{t}{T_{2i}}\right)$$  \hspace{1cm} (A.2.1)

where $a_i$ is the volume fraction of pores of size $i$ that decay with relaxation time $T_{2i}$ and $M(t)/M_0$ is the normalized magnetization decay at time $t$. Equation (A.2.1) can be expressed in matrix notation by:

$$\overline{M} = \overline{K} \cdot \overline{A}$$  \hspace{1cm} (A.2.2)

where $\overline{M}$ is an $M \times 1$ matrix, $M$ is the number of data points specified by the keyword (NUM_TIME_DATA) in the input file. This matrix is read from the output data file (M.csv). $\overline{K}$ is an $M \times N$ kernel matrix, where $N$ is the total number of exponentially spaced $T_2$ values. The $T_2$ values are initially selected over a given range (for example 100 data points between 0.1ms and 10,000ms). $\overline{K}$ is constructed using the expression:

$$K_{i,j} = \exp\left(-\frac{i t}{T_{2j}}\right)$$  \hspace{1cm} (A.2.3)

and it is read from the output file, (K.csv). $\overline{A}$ is an $N \times 1$ matrix, which is the output in the inversion algorithm.
The elements in this matrix correspond to the volume fraction of pores of size $i$ that decay with the exponentially spaced relaxation times $T_{2i}$. The inversion method uses an $N \times N$ weighted matrix, $\overline{W_m}$ and a regularization parameter $\lambda$ such that:

$$\overline{A} = \left( \overline{W_m}^T \cdot \overline{W_m} + \lambda^2 \overline{W_m} \right)^{-1} \cdot \overline{W_m}^T \cdot \overline{M}$$  \hspace{1cm} (A.2.4)

The weighted matrix is a fourth order derivative matrix constructed from:

$$\overline{W_m} = \begin{bmatrix} 5 & -4 & 1 & \cdot & \cdot & \cdot & 1 \\ -4 & 6 & -4 & 1 & 0 & 0 & 0 \\ 1 & -4 & 6 & -4 & \cdot & \cdot & \cdot \\ & 1 & -4 & 6 & -4 & 1 \\ & & 1 & -4 & 6 & -4 & 1 \\ & & & 0 & 0 & 6 & -4 & -4 \\ & & & & 1 & -4 & 6 & 5 \end{bmatrix}_{N \times N}$$  \hspace{1cm} (A.2.5)

The regularization parameter $\lambda$ is determined from

$$\lambda = \frac{\left( \overline{M} - \overline{K} \cdot \overline{A_1} \right)^T \cdot \left( \overline{M} - \overline{K} \cdot \overline{A_1} \right)}{\overline{A_1}^T \cdot \overline{A_1}}$$  \hspace{1cm} (A.2.6)

$\overline{A_1}$ in the equation above corresponds to the matrix obtained using a regularization parameter equal to 1, i.e:

$$\overline{A_1} = \left( \overline{W_m}^T \cdot \overline{W_m} + \overline{W_m} \right)^{-1} \cdot \overline{W_m}^T \cdot \overline{M}$$  \hspace{1cm} (A.2.7)
The following steps are followed for the inversion of $T_2$ distributions from magnetization decay.

1. Read matrix $\mathbf{M}$ from the output file, (M.csv).

2. Read matrix $\mathbf{K}$ from the output file, (K.csv).

3. Construct weighted matrix $\mathbf{W}_m$ using equation (A.2.5).

4. Retain the exponentially spaced $T_{2i}$ used to construct the kernel matrix, $\mathbf{K}$ as matrix $\mathbf{T}$.

5. Determine $\mathbf{A}_1$ from equation (A.2.7).

6. Determine the regularization parameter, $\lambda$ from equation (A.2.6)

7. Define the following expressions;

$$
\mathbf{K}\mathbf{K}^{\text{ex}} = \mathbf{T}^T \mathbf{K} \mathbf{T}
$$

(A.2.8)

$$
\mathbf{K}\mathbf{M}^{\text{ex}} = \mathbf{T}^T \mathbf{M}
$$

(A.2.9)

8. Determine $\mathbf{A}$ from the equation:

$$
\mathbf{A} = \left( \mathbf{K}\mathbf{K}^{\text{ex}} + \lambda \mathbf{2W}_m \right)^{-1} \cdot \mathbf{K}\mathbf{M}^{\text{ex}}
$$

(A.2.10)

Equation (A.2.10) is another form of equation (A.2.4)
9. Negative values in the matrix $\mathbf{A}$ are set to zero and their indices are deleted from the rows and columns of the matrices $\mathbf{K}^{\text{ex}}$, $\mathbf{K}^{\text{m}}$, and $\mathbf{W}_m$. The resulting matrices are then substituted into equation (A.2.10) to determine new matrix $\mathbf{A}$. This process is repeated until all the elements in the matrix $\mathbf{A}$ are all positive.

The elements in the matrix $\mathbf{A}$ are the volume fractions of pores of size $i$ that decay with a relaxation time $T_{2i}$. A plot of these volume fractions and their respective relaxation times is the $T_2$ distribution of the porous medium. This inversion method outputs the frequencies corresponding to each transverse relaxation time $T_{2i}$. NMR measuring equipments are embedded with software that invert $T_2$ distributions from measured magnetization decays; an example is the WinDXP software that is found in most MARAN bench top spectrometers (Resonance instruments) which was used for the experimental measurements in this work.

![Comparison of T2 distributions](image)

Figure A.2.1: Comparison of the $T_2$ distributions inverted using Win DXP software with that obtained using the curvature smoothing method.
Comparisons were made between the $T_2$ distribution obtained using the WinDXP software from Resonance Instruments and that obtained using the curvature-smoothing regularization method (Chen et al., 1999; Toumelin, 2003) discussed in this appendix are shown in Figure A.2.1. These comparisons validate the curvature smoothing code that was used for the inversion of $T_2$ distributions from simulated magnetization decays.
APPENDIX A-4

Flowchart for the simulation of NMR response in networks

START

Place \( N \) walkers randomly in network elements; set \( N_r = N \), \( N_{st} = 0 \), for each walker, determine, \( x(0), y(0), z(0) \)

Spherical 3D displacement of walkers of radius \( R \) where \( R = \sqrt{6D_0 \Delta t} \) from time \( t \) to \( t + \Delta t \). Generate new coordinates \( x(t), y(t), z(t) \)

For all walkers; \( i = 1, 2, 3, \ldots \ldots \ N_r \)

Walker enters one of connected throats. Determine new \( z(t) \)

- yes is \( z(t) < 0 \) or \( z(t) > L \) no walker in a throat

- no contact with grain surface?
  - yes is \( z(t) < 0 \) or \( z(t) > L \) no
  - no is walker killed?
    - yes Walker enters new pore
    - no return to previous position

- no

Generate new \( x(t), y(t), z(t) \)

- retain \( x(0), y(0), z(0) \)
- remove walker

Plot \( M_r \) vs Time

Add bulk relaxation mechanism

- \( M_r = M_0 \exp(-t/T_{1a}) \)
- \( M_t = N_r / N \)

set \( N_r = N_{st} \); \( N_{st} = 0 \)

is \( i = N_r \) ?

Porosity (a.u.)

\( T_2 \)