Chapter 2

LITERATURE REVIEW

2.1 An overview of Network Modelling of Multiphase Flow in Porous Media

2.1.1 Introduction

Pore network modelling (PNM) is concerned with the description of fluid flow and physical transport in a domain with geometric and topological properties and scale that approximate that of the void spaces found in geologic or synthetic porous media. The void spaces are conceptually described in terms of a system of larger compartments or pores connected by a network of narrower channels or throats. Rules are then developed to specify the possible arrangements of fluids within pores and throats, and to govern the movement of fluids or the transport of a range of physical quantities (e.g. current, tracers, dissolved substances, etc) under given conditions. Individual pores and throats have sizes on the order of microns (1x10^{-6} m), but by aggregating flow behaviour over a large number of these network elements (usually hundreds, to tens of thousands elements – spanning a few millimetres to several centimetres), macroscopic flow properties such as permeability, relative permeability vs. saturation (K_r-S) functions, electrical properties, capillary pressure vs. saturation (P_c-S) functions etc, of the particular porous medium represented by the network model can be determined.

Fatt (1956) is widely credited to have been the first to use network models to study fluid flow in porous media and to derive multi-phase flow properties such as P_c-S and K_r-S curves, in a bid to address the shortcomings of the bundle of parallel tubes as a model for representing flow through porous media. Since the pioneering work of Fatt, PNMs have been redesigned and implemented in a variety of ways to study a wide range of observed phenomena including solution gas drive, the role of wettability in two-phase and three-phase flow under drainage and imbibition processes, viscous fingering, and diffusive transport (Ramstad et al,

In comparison to other approaches for describing fluid flow in porous media e.g. analytical techniques, numerical techniques such as Lattice Boltzmann methods, Stokes solution in single pores of special geometry, etc, PNM – even in its basic implementations – has been quite successful in providing useful explanations for many experimentally observed phenomena and in predicting macroscopic transport properties (Blunt et al, 2001).

The push for greater predictive power in the modelling of more complex multiphase flow processes has, however, driven the search for more rigorous description of both the void space and the physics governing fluid flow. This has been facilitated by new insights gained from micromodel experiments, improved imaging techniques and better algorithms. The remainder of this section briefly describes the most salient developments in the construction of predictive networks.

### 2.1.2 Predictive Network Construction Approaches

#### 2.1.2.1 The Regular Lattice Network

The simplest network is a regular lattice of interconnected elemental tubes, usually with cylindrical cross sections (Figure 2-1). The network elements represent pores which are randomly assigned radii according to a statistical distribution. A network of regular lattice is generally described by two parameters: its coordination number (the average number of elements meeting at a common point, a measure of connectivity) and a pore size distribution. Although simulations performed on networks so idealised could still yield important insight into the nature of fluid flow in porous media (for example, networks of cubic lattice with pore elements of circular cross section were used by Jerauld and Salter (1990) to reproduce important features of relative permeability curves as observed in experiments), it is evident that they fail to adequately characterize the complexity of real porous media in terms of geometry and topology.
An equivalent network of a given real porous media could, however, be obtained by adjusting the network coordination number by randomly removing pores to match the coordination number of a specific sample. Early networks of unconsolidated sandstones were ‘anchored’ this way to permit a more realistic determination of two-phase flow properties. Dixit et al (1997) found, using regular cubic lattice networks, that reducing the coordination number from 6 to 4 had a stronger influence on hysteretic relative permeability curves than varying the pore size distribution or the pore-scale displacement mechanisms (snap-off and piston-type).

One of the most influential theories in the field of pore scale modelling – invasion percolation theory – was developed by Wilkinson and Willemsen (1983) to describe drainage in porous media by performing calculations on lattice network of spherical pores connected by cylindrical throats. The fundamental mechanisms of imbibition displacement processes – piston-like, snap-off, and cooperative pore-body filling – were described by Lenormand et al (1983) using regular networks of rectangular cross-sections. As well as reproducing the qualitative trends in the behaviour of transport properties of porous media (Kr-S, Pc-S curves, etc) in response to changes in pore-scale features (PSD, connectivity) and displacement mechanisms (drainage, imbibition), lattice networks have been used to quantitatively predict transport properties too. Rajaram et al (1997) successfully predicted Kr-S curves by fitting Pc-S curves constructed from a regular lattice network to experimental Pc-S curves through careful tuning of network parameters related to spatial pore size correlations and the standard deviation of pore size distributions.
Despite the evident utility of regular lattice models for gaining fundamental insight into pore-scale displacement mechanisms, their description of the topology of the pore space still leaves out a lot of what’s known about geologic porous media: the irregularity of pore space geometry, the random distribution of coordination number and the existence of short range pore size correlations, that introduces a high level of uncertainty into the quantitative predictive results that can be obtained with lattice models. The construction of more geologically realistic networks that incorporate the appropriate amount of detail in a computationally efficient way is a nontrivial task. Network extraction from directly or stochastically reconstructed pore spaces is the most common approach for constructing predictive networks (Al-Kharusi and Blunt, 2007; Silin et al, 2006, 2003; Valvatne and Blunt, 2004; Gladkikh and Bryant, 2003; Blunt et al, 2002; Øren et al, 1998). A statistical approach that uses routinely available experimental data from e.g. mercury intrusion experiments, to derive representative pore size distribution, medium connectivity and pore volume distribution has also been developed (McDougall and Sorbie, 2002; McDougall et al, 2001). The broad features of both approaches will be discussed next.

2.1.2.2 Predictive Network Extraction from Pore Space Reconstruction

2.1.2.2.1 Pore Space Reconstruction methods

The methods may be broadly classified into two types:

1) **Direct Methods** – non-destructive acquisition of 3D images of the pore space using Micro Computed Tomography (Micro CT). By analysing the spatial variations in attenuation coefficients recorded from a series of X-rays directed at a sample from multiple directions, the distribution of grains and void space can be distinguished and mapped (Coker et al, 1996; Baldwin et al, 1996; Rintoul et al, 1996; Spanne et al, 1994; Dunsmuir et al, 1991). Micro CT is currently able to resolve rock images to about a few microns although sub-micron level of resolution may be needed to satisfactorily image microporosity in carbonate rocks (Knackstedt et al, 2006). Micro CTs are also expensive and therefore not readily available. Figure 2-2 compares 3D images of a Fontainebleau rock generated by Micro CT and three other methods.
2) **Indirect methods** – this involves the recombination of 2D digital images of real or synthetic porous media into 3D models of the pore space.

Following on from the geometrical studies of random sphere packings by Finney (1970), Bryant et al (1992; 1993) reported the first networks extracted from a simulated geological porous media representation. Starting from a benchmarked random packing of equal-sized spheres, geological processes of compaction and cementation were simulated by moving the sphere centres closer together in the vertical direction and by allowing spheres to swell and overlap. Networks extracted from these pseudo-rock void spaces were found to give better predictions of the relationship between porosity and permeability for Fontainebleau sandstone compared to statistically equivalent but uncorrelated networks. They were however still *synthetic* networks with constant coordination number. This process-based pore space reconstruction approach has been extended to more complex rock forming processes including sedimentation, compaction and digenesis (Øren and Bakke, 2002; Bakke and Øren, 1997).

The construction of 3D pore space from serial 2D thin section images of real rocks opens the possibility of recreating the in situ connectivity with much higher accuracy. The creation of a 3D voxel-based representation is usually achieved by building a pseudo-3D training image from binary data acquired from 2D sections and then running a standard 3D multipoint geostatistical simulation. Okabe and Blunt (2005) generated 3D pore space
images of Fontainebleau and Berea sandstone samples using this stochastic technique that compared favourably with Mirco-CT generated images.

Alireza et al [2011] presented an algorithm similar to Okabe and Blunt (2005) that is capable of reconstructing 3D porous media when only a single 2D section is available. The algorithm works by extracting a few points from a 2D training image as conditioning data. A 2D multi-point stochastic simulation procedure that is conditioned to the selected conditioning data is then performed to generate a stochastic realization that serves as a new 2D seed image. Sequential application of this procedure generates a 3D image that is a stack of the simulated 2D realizations. Simulations of relative permeability during drainage and imbibition on networks extracted from this stochastically reconstructed pore space yielded similar results to extracted networks from 3D micro-CT images of the same rock sample. The approach of Alireza et al [2011] is faster than that of Okabe and Blunt (2005) because it does not require the construction of 3D training images and thus dispenses with computationally intensive 3D multipoint simulations. Both approaches are, however, only applicable to media with stationary properties, such as sandstones, and not vuggy carbonate rocks.

2.1.1.1 Network Extraction Methods
Flow simulation is rarely carried out directly on the reconstructed pore space image. This is especially true for multiphase flows, where the highly irregular geometry and topology of the pore space greatly multiplies the possible set of rules needed to adequately describe the flow process. In order to perform practical multiphase flow simulations at a length scale that minimises finite size effects and therefore allows macroscopic flow properties to be fully described, a skeleton of the reconstructed 3D image that carries the essential geometric and topological information in a condensed form is extracted and used as the simulation grid, see Figure 2-3. A number of network extraction methods have been reported, two of the most widely used are discussed below.
Figure 2-3: Comparison of two topologically different networks, each consisting of 512 pore bodies. (a) A regular cubic lattice with a constant coordination number of 6. (b) A topologically realistic network constructed from a 3D voxel-based representation of the pore space with an average coordination number of 3.6 (Bakke and Øren, 1997).

**Delaunay tessellation algorithms:** this has often been used to extract networks from pore space constructed from randomly packed spheres (Gladkikh and Bryant, 2003; Mason and Mellor, 1995; Bryant et al, 1992, 1993). Pore bodies and throats are defined by the voids formed between the surfaces of four nearest spheres. Prior knowledge of sphere coordinates permits easy calculation of pore and throat geometric properties such as areas and volumes. Networks extracted by Delaunay tessellation have a maximum coordination number of 4, Figure 2-4.

Figure 2-4: A tetrahedral cell formed by joining four nearest-neighbour grain centres ABCD (from Gladkikh and Bryant, 2003)

**Medial axis algorithms:** in this approach, the extracted network corresponds to lines (medial axes) running through loci along the geometric centre of the interconnected void space, Figure 2-5. Because the medial axes run throughout the entire void space, they share its connectivity and therefore its topology. To create a medial axis, the 3D image would first be segmented into a binary image comprising only grains and voids. Then at selected (or all) points along the voxel-based 3D pore space, voxels are simultaneously eroded or burned from the grain surface towards the void centre until one voxel remains.
The maximum inscribed radius centred at the voxel (called the bond number) is recorded. There is no standard definition for a pore or node – it has been defined as the point at which three or more medial axes intersect (Lindquist and Venkatarangan, 1999). Pore radius is defined as the maximum radius of a sphere centred at the node which just contacts the grain surface (Figure 2-6). A pore throat is defined as the voxel with the minimum burn number along a path connecting two throats. Medial axis algorithms are more versatile compared to Delaunay tessellation and have been used to extract networks from 3D images generated by micro-CT (Jiang et al, 2007; Prodanović et al, 2006; Lindquist and Venkatarangan, 1999) and images generated stochastically (Hidajat et al, 2002). Networks generated by Medial axis algorithms can, however, exhibit large differences in topological properties depending on how pores and throats have been defined (Silin et al, 2006, 2003).

![Figure 2-5](image)

Figure 2-5: The concept of medial axis in a schematized two-dimensional binary system, the dashed lines represents the medial axis

![Figure 2-6](image)

Figure 2-6: Schematic of the overlap of inscribed radius, nodes represent point of intersection of three or more medial axis branches (from Al-Raoush et al, 2003)

### 2.1.1.2 Predictive Network Anchoring Methods

Anchoring methodologies have been developed to tune regular lattice networks of specific rock samples into geologically equivalent analogues. Anchoring methodologies use statistical information derived from routinely available laboratory data to build networks without going through the laborious pore space reconstruction and network extraction procedures.
2.1.1.2.1 The 3Rs Method

This method was introduced by McDougall and co-workers (McDougall et al, 2001; McDougall and Sorbie, 2002) and used to characterise networks that make no explicit distinction between pores and throats. Information about throat size distribution, measures of network connectivity and the distribution of pore volume are obtained from mercury injection data. After each element in the network has been assigned a capillary or throat radius, its volume and conductance are calculated using power law relationships according to Equation (2-1).

\[
\begin{align*}
V &= \bar{C}\pi r^\nu L 10^{(6\nu-12)} \\
g &= \frac{\bar{A}\pi r^\lambda 10^{(6\nu-24)}}{8\mu L}
\end{align*}
\]  

(2-1)

where, \( C \) and \( \bar{A} \) are volume and conductance pre-factors, \( r \) the capillary entry radius [m], \( L \) the pore length [m], \( \mu \) the viscosity [PaS], \( g \) the conductance [m\(^3\)/secPa], \( \nu \) the volume exponent and \( \lambda \) the conductance exponent.

The exponents are approximated by fitting the so called R-plot (a plot of capillary entry radius vs. mercury saturation obtained by inverting the experimental \( P_c-S_{\text{Hg}} \) data via the Young-Laplace equation). The fitting process is enhanced by an accessibility function, \( A(r) \), that weights the number of invaded pores to the number that would have been invaded if each pore had a direct connection to the inlet. Further enhancements to the method have focused on constraining the range of the exponents by use of independent experimental data such as residual saturation [McDougall and Sorbie, (2002)]. One of the drawbacks of the 3Rs approach is its inadequate modelling of film and layer flow which could lead to the erroneous prediction of wetting phase relative permeability at low saturations. Despite some limitations of the 3Rs approach, it had been successfully used to anchor networks to experimental data (Bondino et al, 2009) and will later be employed in Chapter 7 of this thesis to construct a network which will be used to analyse a depressurization experiment.
2.1.1.2.2 Extensions of the 3Rs Approach

van Dijke and co-workers (2007c) presented a version of the 3Rs approach that uses the correlations between measured pore space microstructure data – pore radii, length and shape factor – in Equation (2-2) to derive expressions for the power law volume ($v$) and conductance ($\lambda$) exponents as in Equation (2-3).

$$l_i = l_{\text{min}} \left( \frac{r_i}{r_{\text{min}}} \right)^\alpha \quad G_i = G_{\text{min}} \left( \frac{r_i}{r_{\text{min}}} \right)^\beta$$

(2-2)

where $r_{\text{min}}$, $G_{\text{min}}$ and $l_{\text{min}}$ are minimum values of measured radius, shape-factor and length respectively.

A network constructed using this approach computed the permeability of Fontainebleau sandstone as 1008mD which compared reasonably well with 760mD, computed using a node-bond model of the same sample by Valvante and Blunt (2004). This discrepancy might be due to the fact that pore-pore connectivity correlations were not captured by the model.

$$v = 2 + \alpha - \beta$$
$$\lambda = 4 - \alpha - \beta$$

(2-3)

where $v$ and $\lambda$ are the volume and conductance exponents, respectively, $\alpha$ and $\beta$ are curve fitting parameters determined from Equation (2-2).

Ezeuko (2009) described an anchoring algorithm that takes full advantage of the increased ease of access to pore-space microstructure – information from Micro CT scans, information about connectivity, pore size distribution, pore volumetric, and pore aspect ratios. To implement the radius-length correlation, an effective radius was randomly assigned to each pore according to the measured pore size distribution function. Pore lengths were assigned using trend lines ($l_{\text{max}}(R)$, $l_{\text{min}}(R)$) that specify lower and upper limits for a given pore radius. Network connectivity was matched by a bond dilution process that was linked to the radius-length correlation function, where a bond of radius $R$ is removed only if $l_i(R) > l_{\text{max}}(R)$, $l_i(R) < l_{\text{min}}(R)$. Pores were assigned shape factors using a procedure identical to the pore length assignments. The permeability of the same
Fontainbleau sample used by van Dijke et al (2007c) and Valvatne and Blunt (2004) was predicted by the network constructed using the ‘stochastic’ approach of Ezeuko (2009) as 717mD. Comparisons of simulation results of oil-water drainage and oil depressurization obtained by networks anchored using van Dijke et al’s (2007c) method and that anchored using Ezeuko’s method showed persistent disparities.

Despite impressive recent advances in network reconstruction and extraction techniques there is no generally agreed criteria for judging the predictive quality of extracted networks. The flow properties of a network extracted from a given rock sample are affected by the extraction algorithm and workflow employed. Different extraction algorithms emphasise different features of a porous medium. For example, whilst the medial axis algorithm generates more representative pore space connectivity, the maximal ball algorithm is better at identifying the pore bodies (Bondino et al, 2012). According to Sorbie and Skauge (2011), there is, however, a more fundamental reason why predictions (especially of two-phase flow properties such as relative permeability) from extracted networks should be used with great caution: the number of input parameters needed to build a predictive network model far exceeds the actual system parameters. Inspired by the observations of Sorbie and Skauge (2011), Bondino et al (2012) compared two-phase oil and water relative permeabilities ($K_r$) from 3 networks extracted from micro-CT images of a Clashach sample by two independent research groups using 3 different extraction algorithms. One research group used a Veronoi diagram-based method (denoted as S1_N1 in Figure 2-7) whilst the other group used two variants of the watershed transform approach (denoted S2_N2 and S3_N3 in Figure 2-7). As can be seen in Figure 2-7, the authors observed large variations in both the oil and water $K_r$ ($K_{ro}$ and $K_{rw}$) between the three networks which would have led to significantly different recovery forcasts. A recognition of the over-parameterization inherent to network extraction workflows (subjective assumptions about the partitioning of the pore space between pores and throats, the distribution of pore lengths to radii ratios, etc) has led some authors (Battad et al, 2011) to suggest that an objective criteria for determining a priori whether one extracted network is better than the other is unattainable with current technology, and that the ‘correctness’ of a network might be a function of the context in which it is used.
Figure 2-7: (a) Drainage, and (b), (c) Imbibition $K_r$ computed on networks extracted from 3D micro-CT images of Clashach sandstone using different extraction algorithms (from Bondino et al, 2012). S1_N1= Veronoi diagram-based, S2_N2= watershed transform approach I, and S3_N3= watershed transform approach II.

2.1.2 Review of Basic Concepts Relevant to Multiphase Flow in Porous Media

The pore scale phenomena that are the subject of this thesis will be described against a background of concepts that are more fundamental. We briefly examine some of these concepts in this section.

2.1.2.1 Surface and Interfacial Tension

The existence of a finite boundary between two fluids, say a liquid and air, is an indication of differences in the strength of intramolecular attractions within each fluid. Since there is stronger intra-phase molecular attraction between liquid molecules, a liquid in the presence of air will tend to assume a shape that minimizes its surface-to-volume ratio. This is why water droplets spontaneously assume a spherical shape. Thus, there is always a net tensile force pulling the liquid-air interface towards the liquid, making the interface behave like a uniformly stretched membrane. Surface tension of a liquid is thus defined as the work required to increase the area of a surface isothermally by a unit amount; commonly used units are dynes/cm or N/m. It is the same as the free surface energy of a substance per unit area. If a fluid other than air is involved, the surface tension is referred to as the interfacial tension and denoted by $\sigma$. It is one of the most important parameters for evaluating immiscible displacement in porous media.

2.1.2.2 Contact Angle and Wettability

Consider a solid surface in contact with water and oil as shown in Figure 2-8. At equilibrium three forces must be balanced: the first is the solid-water surface tension ($\sigma_{ws}$) which acts towards the centre of the water droplet; secondly, the solid-oil
interfacial tension ($\sigma_{os}$) directed away from the droplet centre; and finally the oil-water interfacial tension ($\sigma_{ow}$) which acts tangentially to the angle at which the oil-water interface intersects the solid surface – the contact angle. This force balance yields Equation (2-4), known as the Young-Dupre equation.

$$\sigma_{so} = \sigma_{sw} + \sigma_{ow}\cos\theta$$

(2-4)

Equation (2-4) can be generalised for any fluid pair. The contact angle has a range between $0^\circ$ and $180^\circ$. Its precise value depends on the mineralogy of the solid surface and the fluid pair.

The magnitude of the contact angle indicates the degree of affinity of a fluid to a particular solid surface in the presence of another fluid or its wettability. However, because of the non-uniformity of the materials that make up the grains of even the smallest rock samples, contacts angles are often reported as a range in practice. For example, with respect to Figure 2-8, if $65^\circ < \theta \leq 0^\circ$, the solid is considered water-wet; if $105^\circ < \theta \leq 180^\circ$, oil-wet; and if $65^\circ < \theta \leq 105^\circ$, intermediately wetted or mixed-wet.

![Force balance acting on a liquid drop in equilibrium](from Sahimi, 2011)

**2.1.2.3 Wetting Films, Wetting and Spreading Layers**

The experiments of Lenormand et al (1984), and Dullien et al (1989), using micromodels and bead packs, respectively, have shown that in multiphase flow through porous media thin layers of the wetting phase adhere to the crevices and grooves in the pore walls and run throughout the system – thus, potentially creating a system-wide hydraulically connected wetting phase that may result in very low wetting phase saturations post drainage. The thickness and conductivity of these wetting layers, as measured by Dullien et al (1989) for example, depend on the roughness of the pore wall. For smooth walls the thickness was estimated to be in the order of nanometres and the layers are known as
films. When the pore wall is rough the thickness increases to a few microns. Wetting films are stabilized by molecular forces in contrast to wetting layers that are stabilized by capillary forces. Different approaches have been proposed to capture flow through wetting layers in network models. van Dijke and Sorbie, (2002) considered layers that are continuous but non-conductive. The great majority of attempts to model wetting layer flow involve the assignment of simple geometric cross sections (e.g. triangles, squares, stars, etc) to pores and throats which are then used directly to calculate effective transport properties (Al-Kharusi and Blunt 2007: Øren et al, 1998; Fenwick and Blunt, 1998; Blunt, 1998).

The spreading coefficient is an important parameter that characterises the interfacial interaction between three immiscible fluids that are in contact. For a gas, oil, water system, the spreading coefficient, $C_s$, may be defined as:

$$C_s = \sigma_{gw} - (\sigma_{go} + \sigma_{ow})$$  \hspace{1cm} (2-5)

If $C_s > 0$ and the system is water-wet or mixed-wet, then oil may spread between water and gas. This allows oil to maintain hydraulic connectivity even at very low saturations and consequently lead to very high oil recovery factors.

Mani and Mohanty (1997) described a model that captures the effect of oil spreading on residual oil saturation during gas injection into a water-wet network of regular lattice. In the model, the spreading oil films did not actually contribute to the oil saturation but were assumed to have a finite conductivity that permits isolated oil ganglia (oil clusters trapped by water-oil interface on all sides) to be invaded at lower capillary pressures. Oil residual saturations in non-spreading systems were found to be lower than in spreading systems.

Again, just as for wetting layers, spreading layer volume can be more carefully tracked by assigning arbitrary non-circular shapes to pore and throat cross-sections (Blunt et al, 2002; Valvatne and Blunt, 2004). An example of a spreading layer representation within a triangular pore cross-section may be as a lens – sandwiched between the curvatures of
water-oil and oil-gas interfaces, the thickness of which will depend on the capillary pressure, the wettability, and the half angle of the corners of the triangle.

### 2.1.2.4 Capillary Pressure and Interfacial Forces

Consider a spherical air bubble of radius $R$ encased in a liquid membrane that is in turn surrounded by air, Figure 2-9. To minimise free surface energy the bubble will tend to shrink just as the air pressure within it increases in response to the volume decrease. The change in free surface energy associated with a decrease in radius from $R$ to $R - \Delta R$ is $-\Delta G = \Delta A\sigma = 8\pi R \Delta R \sigma$. At the same time, the air outside the bubble expands and its pressure decreases. The net work associated with the shrinkage-expansion is given by $-\Delta W = (P_i - P_o) \Delta V = (P_i - P_o)(4\pi R^2 \Delta R)$, where $P_i$ and $P_o$ are the pressures inside and outside the bubble (Sahimi, 2011). Since the net work must be equal to the free surface energy change, we have

$$P_i - P_o = \Delta P = \frac{2\sigma}{R} \quad (2-6)$$

![Figure 2-9: A spherical air bubble at equilibrium.](image)

Equation (2-6) is in fact a specific version of the more general Young-Laplace equation (Equation (2-7)) which can be applied to non-spherical curved surfaces, where $R_1$ and $R_2$ are the two principal radii of curvature.

$$\Delta P = \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \sigma \quad (2-7)$$

Capillary pressure may be defined as the pressure change across a bounded fluid-fluid interface. Imagine two immiscible fluids, e.g. CO$_2$ and water, in contact inside a cylindrical tube as shown in Figure 2-10. If the pressures in the CO$_2$ phase ($P_{g}$) and in the water phase ($P_{w}$) are measured at an infinitesimally small distance from both sides of the interface, then $P_{g} \neq P_{w}$. The pressure difference, $P_{g} - P_{w}$, corresponds to the capillary
pressure and represents a discontinuity in the pressure field. It is evaluated using the Young-Laplace equation (Equation (2-7)) as:

\[ P_c = \sigma_{gw} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(2-8)

For an interface in a cylindrical tube \( R_1 = R_1 = r\cos\theta \), where \( r \) is the radius of the tube, and Equation (2-8) reduces to:

\[ P_c = \frac{2\sigma_{gw}\cos\theta}{r} \]  

(2-9)

Figure 2-10: Two fluids at equilibrium in a circular cylinder

\( P_c \) is one of the principal parameters used to characterise multiphase flow phenomena, especially at the pore scale.

2.1.3 Implementation of Multiphase Flow Physics in Network Models

Rarely do pore network modelling studies have as a chief goal the determination of single phase flow properties like permeability, even though permeability might be determined at some stage for use in the evaluation of more pertinent macroscopic two- and three-phase flow parameters like relative permeability or used as a benchmarking parameter for network construction. The common consensus is that the mechanics of single phase flow are very well understood and single phase parameters can be readily determined in the laboratory with relatively simple setups. The laboratory determination of multiphase properties is, unfortunately, not so straightforward. In the case of three-phase flow, it is actually very complicated to carry out and difficult to interpret. Hence the vast majority of pore network modelling studies have been devoted to the understanding and prediction of macroscopic multiphase flow properties in terms of microscopic displacement mechanisms. Displacement in physical terms is a causal outcome of a larger force overcoming a smaller one which results in some movement in the direction of the net
force. A displacement event also tacitly implies the existence of a boundary between the displaced object and the displacing object. In pore network modelling, the displacement of an interface separating two-fluids of given viscosities and densities by an external force is described in terms of three principle forces, namely: capillary, gravity and viscous forces. To accurately quantify the contribution of each of these forces, it is usually necessary to isolate one force at a time by temporarily setting the other two to negligibly low values. The principle of force isolation has led many researchers to adopt suitable boundary conditions that have been judged adequate to describe a given problem. It is in this respect that pore network models can be classified into two broad classes: (a) Quasi-static and (b) Dynamic pore network models.

2.1.3.1 Quasi-Static Network Models
These models assume pore-level multiphase displacement to be governed by equilibrium capillary pressure only. Viscous and gravity forces are neglected, sometimes for physically cogent reasons such as the simulation of slow displacement through a network with limited spatial extent – typically enclosing a volume of a few mm$^3$, while in other cases the boundary condition is imposed artificially in order to isolate the effect of a particular parameter, e.g. the contact angle. The immiscible displacement of one fluid by another, e.g. gas displacing water, takes place in a series of discrete equilibrium steps in which the pressure of the displacing phase is successively increased while keeping that of the displaced phase constant. A gas injected at one face of a water-wet network and initially 100% saturated with water, will invade any water-filled pore at the gas-water interface if the current difference between the gas and water pressure exceeds the equilibrium capillary entry pressure of the pore as given by the Young-Laplace equation. At each stage of displacement, the invading phase saturation ($S_g$) in the network increases while the defending phase saturation ($S_w$) decreases. For every change in gas saturation, higher gas pressures would be required to achieve the same saturation change because, according to Equation (2-9), pores with the smallest capillary entry thresholds are invaded first and those with the largest radii are invaded last. Of course, some pores may never be invaded regardless of their radius, simply because they are inaccessible – due to trapping or pore shielding. The displacement process just described is known as drainage, where a non-wetting phase displaces a wetting phase. In an imbibition process, the wetting phase (water) displaces the non-wetting phase (gas) and can be achieved by increasing the
water pressure while keeping gas pressure constant. In an imbibition process, the smallest pores are generally invaded first. The process can be extended to three-phase flow with the use of appropriate interfacial tensions and modified filling rules.

Quasi-static models are by far the most widely used description of pore level events and are implemented on every class of networks – whether painstakingly extracted from reconstructed pore space or simply constructed from a regular lattice, and with every pore shape. Their rate-independence has led quasi-static models to be described as invasion percolation models, a term used for all classes of network models based on the percolation model introduced by Lenormand and Bories (1980). A selective sample of the use of quasi-static models for studying two-phase and three-phase flow phenomena is given below.

Jerauld and Salter (1990) used a quasi-static network model to study the effect of pore/throat aspect ratio on drainage/imbibition relative permeability hysteresis behaviour. They found that an increase in throat-throat correlation changed the shape of the relative permeability curve in a way that reduces the wetting phase relative permeability. Lin and Slattery (1982), Mohanty and Salter (1982), Sahimi et al (1986), and Blunt and King (1990, 1991) used models similar to Jerauld and Salter (1990) to compute relative permeability vs. saturation curves. With a similar model, Blunt (1997) showed that contact angle has a significant impact on the shape and end-point of non-wetting relative permeability curves. Blunt (1997) reported that proper representation of spatial correlations was critical to reproduce even qualitative trends in measured data. The model was later extended to capture wettability effects based on the work of Kovsecek et al (1993).

Fischer and Celia (1999) predicted two-phase relative permeability curves using a regular lattice network with correlated pore-throat radii that is also calibrated to a capillary pressure curve. The match to experiment was, however, poor. By combining pore size distribution and connectivity information from a network extracted from a reconstructed network and throat size distribution information from experimental capillary pressures, Tsakiroglou and Payatakes (2000) obtained very good match of capillary pressure curves and absolute permeability.
Dixit et al (1996) investigated the effect of wettability on oil recovery during waterflooding in a two-phase system using an invasion percolation model implemented on a 3D regular lattice network. Mixed-wet and fractionally wet media were considered. Wettability alterations were achieved by running complete flooding sequences – primary drainage, aging, spontaneous water imbibition, forced water drive, spontaneous oil imbibition and forced oil drive, that include some contact angle hysteresis. By analysing the generated capillary pressure curves, they were able to explain a number of experimentally observed phenomena, such as the higher oil recovery in weakly water-wet cores compared to strongly water ones, using the concept of a capillary surface. The model was later extended by Dixit et al (2000) to explain the discrepancy between the USBM and Amott wettability tests in terms of pore scale displacement mechanisms.

Øren et al (1998) simulated two-phase primary drainage and water imbibition for a set of water-wet and mixed-wet systems with a quasi-static model implemented on a network extracted from reconstructed sandstone. Predicted capillary pressure and relative permeability curves for water-wet samples showed good agreement with experimental data. The results for the mixed-wet systems were also encouraging. The model was later extended by Lerdahl et al (2000) to three-phase flow in water-wet systems.

Tsakiroglou and Payatakes (2000) used a 3D network extracted from pore space reconstructed from thin sections to predict mercury injection capillary pressure curves and absolute permeability. The numerical results (capillary pressure and absolute permeability) were found to be in good agreement with experimental data.

Heiba et al, (1984) presented one of the first network models to simulate three-phase (oil, water, and gas) flow. Using a regular lattice network that considered spreading phenomenon, they showed that gas and water relative permeabilities were functions of their saturation only. Oil was different. Oil isoperms had curvatures which suggested that oil relative permeability is also a function of the saturation of other phases.

Øren et al, (1994) used an invasion percolation algorithm that ran on a 2D regular lattice water-wet network to study the effect of spreading on oil recovery by tertiary gas
injection. Higher recoveries were calculated for spreading systems compared to non-spraying systems because of the tendency of early gas breakthrough in non-spraying systems. The authors compared the results to those obtained from micromodel experiments of Øren et al (1992) and they showed good agreement.

van Dijke et al. (2006, 2007a, 2007b) presented a thermodynamic criteria of three-fluid configurations in angular pores of non-uniform wettability by building on the work of Helland and Skjaveland, 2006; van Dijke et al., 2004; Piri and Blunt, 2004; van Dijke and Sorbie, 2003. They found that the thermodynamic criteria for layer formation and collapse were consistent with entry pressures for bulk displacement, although criteria for three-phase fluid configurations were found to be much more restrictive than then existing geometrical criteria. Quasi-static three-phase simulations involving gas injection in a waterflooded network with star-shaped pores was used to generate a comprehensive range of fluid configurations that may be generalized to other pore shapes. Al-Dhahli et al (2011) used these thermodynamic criteria to account for film/layer flow and layer collapse in a three-phase network model which they used to make predictions of three-phase relative permeability for a reconstructed carbonate rock of mixed-wettability.

Piri and Blunt (2004, 2005a, b) presented a quasi-static network model that incorporates an impressive level of pore-scale physics including the effects of contact angle hysteresis, film flow, connectivity, pore and throat size distributions, together with a description of up to 30 different fluid configurations, to predict two-phase and three-phase relative permeability for a Berea sandstone as reported by Oak (1990). They reported accurate predictions of both two-phase and three-phase experimental relative permeability data from Oak (1990).

2.1.3.2 Dynamic Network Models

In many multiphase flow situations, the assumption of negligible viscous forces becomes inadequate to describe fluid-fluid interface movements. Examples of such situations include near-well flows during the implementation of most enhanced oil recovery processes – gas injection, waterflooding, polymer flooding, etc, in which project economics dictate the imposition of large flow rates; flow in fractures; flow in processes that involve reduced or low interfacial tensions (<1mN/m) such as near-miscible gas
injection, gas condensate reservoirs, and surfactant flooding. Each of these processes may generate viscosity-dependent local fluid pressure gradients of the same or of higher order of magnitude as the equilibrium capillary pressures operating across the interface. Dynamic network models have therefore been developed to account for the contribution of local viscous pressure gradients to multiphase flow. A commonly used parameter for gauging the potential impact of viscous forces is the capillary number \( Ca = q \mu / \sigma \), which, reflects the ratio of viscous to capillary forces.

For a displacement process with a finite capillary number \( Ca > 1 \times 10^{-7} \), determining the next position(s) of the interface involves a solution to two sets of problems: (1) the viscous pressure field solved by assuming conservation of flow at each node or at the centre of each pore, and (2) the evaluation of the positions of the interface in each pore or throat given the current net pressure drop across the pore or throat and its conductivity.

The volumetric flow rate through a pore or throat with an interface is generally expressed by Poiseuilles’s flow with capillary pressure as:

\[
Q = g(\Delta P - P_c) = \frac{\pi r^4(\Delta P + P_c)}{8\mu L} \tag{2-10}
\]

where, \( \Delta P \) is the viscous pressure drop across the interface, \( g \) the pore/throat conductivity, \( r \) the pore/throat radius, \( \mu \) the displacing fluid viscosity, and \( L \) the pore/throat length.

While for single phase flow,

\[
Q = \frac{\pi r^4 \Delta P}{8\mu L} \tag{2-11}
\]

The formulation of pressure equations from flow equations that include capillary pressure could lead to nonlinear flow problems in at least two ways. Firstly, in networks consisting of pores and throats, the capillary pressure might vary during a pressure solution as the meniscus moves from a pore or throat into a contiguous throat or pore (Koplik and...
Lasseter, 1984,1985). Capillary pressure variation also occurs if pores or throats are of non-uniform cross sections. Secondly, the flow through a pore might vary between a finite value (positive or negative) or might be zero during a pressure solution, depending on whether it is trapped or not (Dahle and Celia, 1990). In order to avoid the complexities associated with non-linear problems, researchers have often adopted formulations that convert the nonlinear flow problem into linear forms by use of effective conductance across fluid interfaces in addition to constraints that specify conditions under which interfaces may advance or recede (Koplik and Lasseter, 1984,1985; Dias and Payatakes, 1986a, 1986b).

A great deal more complexity could be avoided by isolating the capillary pressure from the solution of the pressure field by using pseudo-single phase pore conductivities to derive the flow conservation equations at each node (McDougall and Sorbie, 1993). A Washburn (1921) type approximation could then be used to calculate intra-pore distance travelled by the interface within an explicitly specified time.

Dias and Payatakes (1986a, 1986b) studied the effect of capillary number and viscosity ratio on the displacement efficiency of water to oil in a water-wet network. The network flow elements were made up of constricted tubes of diverging-converging geometries and with randomly assigned sizes. Assuming creeping flow, the authors derived linear flow and pressure equations the solution of which gave instantaneous pressures at the network nodes. Inlet and outlet boundary pressures were determined by calculating the pressure gradient required to drive a flood of water with a capillary number equal to a predetermined value in a fully water-saturated network. Once the instantaneous nodal pressures and the appropriate Washburn (1921) type capillary pressure drop across the interface have been computed the next position of the interface can be calculated. Due to the non-uniform cross-sectional profile of the network elements, very small time steps are taken so that the flow rate over the pore segment through which the interface moves remains constant. Results show that at favourable viscosity ratios (M=μ_o/ μ_w < 1) the displacement efficiency, measured by the percentage decrease in the oil residual saturation, increased as the capillary number increases for \( Ca > 10^5 \). When the viscosity ratio is unfavourable (M>1), however, displacement efficiency improved only for \( Ca > 5 \times 10^5 \).
Koplik and Lasseter, (1984, 1985) presented a dynamic pore network model that was similar to that of Dias and Payatakes (1986a, 1986b) in terms of the formulation of the pressure equations but which was much slower, and this restricted simulations to very small networks – typically 10x10. The network was represented by cylindrical throats and circular pores with randomly distributed radii, in a 2D but non-planar domain (a domain consisting of two layers of intertwined network elements, with some elements overlapping but not necessarily touching, allowing the network to retain some of the topological character of fully 3D domains whilst also permitting easy visualization and high computational efficiency), see Figure 2-11. The pressure is determined implicitly by solving a set of five coupled linear equations. The initially non-linear equations are recast in a linear form by prescribing specific rules about how the interface leaves or exits a pore or throat. Water was injected at one face of a water-wet network initially saturated with oil of identical viscosity. A number of simulations were performed to investigate the impact of the capillary number and network properties on the rate of change of water saturation but the results were inconclusive due the general instability of the algorithm marked by oscillation of menisci near pore-throat boundaries.

Figure 2-11: A non-planar 2D network of a porous medium (from Koplik and Lasseter, 1985)

Lenormand et al (1988) developed a dynamic model with very close resemblance to that of Leclerc and Neale (1988) to study displacement patterns for Ca and M that spanned several orders of magnitude. The network is described by a 2D regular lattice, with the volume elements (pores) situated at the sites of the lattice and the conductive elements (throats) corresponding to the bonds. The flow rate through a bond containing an interface was given by an equation similar to Equation (2-10), but with the viscosity term
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weighted to the fraction of the throat occupied by the invading and defending phases, representing a kind of local microscopic relative permeability. The capillary pressure was considered constant and only drainage processes were modelled – this means that only positive flow was considered, thus leading to a non-linear problem. The linear problem was solved through a relaxation technique. Using the flow conservation equation (flow is assumed to be zero between two nodes separated by an interface if the net entry pressure is negative), the pressure field is updated several times (typically four) until a satisfactory stability is achieved. The next stage involves moving the interface inside the pores until a pore becomes completely filled. The time taken to fill this pore is taken as the time step. The simulation results were subsequently used to develop a phase diagram of three principal regimes – stable displacement, viscous fingering and capillary fingering – that was mapped onto a Ca–M plane. Comparison of the simulation results with micromodel experiment results of Lenormand et al (1983) showed very good agreement. Sahimi et al (1998) generalized this model to include the effect of pore bodies on the displacement process.

McDougall and Sorbie (1993) described a network model which they used to study unsteady-state two-phase displacement during waterflooding for a range of viscosity ratios, flow rates and levels of pore-scale heterogeneity. Both water-wet and oil-wet conditions were considered. The model implemented a meniscus tracking algorithm that permits moving interfaces in multiple pores to be tracked synchronously when flow rates are high. The impact of viscosity ratio and flow rate (or capillary number) largely followed a similar trend as reported by Lenormand et al (1988). A modified version of this model for the simulation of the full range of viscous-driven and gravity-driven displacement processes for a wide range of flow rates/capillary numbers and viscosity ratios will be presented in the next chapter of this thesis.

In recent years attention has been turned to more dynamic descriptions of film and wetting layer flows. The model of Blunt et al (1992) was extended by Blunt and Scher (1995) to include wetting layers that were assigned a fixed conductance. Mogensen and Stenby (1998) developed a dynamic model of imbibition that permits stepped interface advancement within a pore for both piston-like and snap-off displacement. Singh and Mohanty (2003) presented a network that accounts for wetting layers by a two-step
pressure solution procedure – one for the wetting layers and the other for bulk flow. The model of Al-Gharbi and Blunt (2005) accounted for the effects of wetting films of varying thickness, depending on the capillary pressure, by the use of equivalent hydraulic resistance to calculate the pore pressures. The rule-based model of Hughes and Blunt (2000) was extended by Idowu and Blunt (2009) to include simultaneous pore filling for imbibition displacement under high viscous pressure gradients. Tørå et al (2012) presented a fully dynamic two-phase model that captures the effects of dynamic wetting layers and viscous forces in both drainage and imbibition processes. The model was used to study the electrical resistivity of reconstructed sandstone at different capillary numbers.

2.1.4 Gravity-Perturbed Flow

When two immiscible fluids of different densities come into contact, hydrostatic equilibrium requires that the lighter fluid stays on top of the heavier fluid. Most multiphase flow situations in porous media involve fluid phases with contrasting densities. Thus, gravity forces will almost invariably play a role in multiphase flow, even though this is often ignored in order to simplify analysis. Other practical considerations such as very small fluid density contrasts and small length scales may justify ignoring gravity as a significant contributor to multiphase flow. When density contrasts are large, as in gas-liquid displacement, or when length scales are extensive, then the impact of gravity forces can no longer be neglected. Examples of practical applications where gravity effects play a significant role in multiphase flow include: the migration of oil from a source rock into an initially water-saturated reservoir rock, the flow of injected or aquifer water into an oil saturated reservoir rock to improve oil recovery, the flow of injected or gas-cap gas into oil saturated regions of a reservoir to improve oil recovery, the flow of solution gas within a supersaturated liquid, water infiltration into air saturated rocks encountered in the field of ground water hydrology, the migration of CO$_2$ injected for storage in deep aquifers, etc. There is, therefore, a lot to be gained from understanding the fundamental nature of the impact of gravity on multiphase flow. The large body of published experimental and pore-scale modelling studies of gravity effects that have accumulated over the past three decades is a reflection of this fact. Experiments have provided the background and anchor for the development of numerical
models. It is therefore fitting to begin with a review of experiments designed to study gravity effects during multiphase flow in porous media.

Dumoré (1970) explored the impact of the average capillary pressure in bead packs, defined as: \( P_c = \sigma \sqrt{\phi/k} \), on gas migration in two different types of multiphase flow scenarios. In the first case, air was slowly injected at the bottom of bead packs saturated with a kerosen-Novasol mixture while the second scenario involved the evolution of solution gas from a live oil as a result of pressure depletion below bubble point. With regards to the injection experiments, two bead packs were used: the high perm pack with an average \( P_c \) of 0.22psi and the low perm pack a \( P_c \) of 0.29psi. Injection rate was selected so that viscous pressure gradients were negligible. The injected gas in both packs did not form a continuous phase from the injection point to the outlet but evolved as a discontinuous phase. Nevertheless, the gas saturation distribution pattern varied from one pack to the other. For the high perm pack a conically shaped gas saturation region developed through which the injected air was transported. This was called the dispersion regime. In the low perm pack, the air evolved through a narrow channel, creating the non-dispersion flow. Final saturation was visibly much greater in the dispersion regime than in the non-dispersion regime, Figure 2-12. By the author’s account, flow dispersion was caused by both the low \( P_c \) in the high perm pack and the uniformity in \( P_c \) distribution across the pack which drives rising bubbles into adjacent pores simultaneously, splitting them up. The bead packs used in the solution gas drive experiments had \( P_c \)s of 0.15psi and 0.70psi, corresponding to the high perm and low perm packs respectively. The solution gas evolved in a network of channels in both packs but the channels were much thicker in the high perm pack than in the low perm pack. Final gas saturation distribution was again higher in the high perm pack than in the low perm pack, reminisce of the difference between the dispersion and the non-dispersion injection experiments.
Birovljev et al (1995) showed clearly the distinct stages of evolution of an invasion percolation cluster under the influence of an increasing gravitational gradient. The 2D porous medium, made from 1mm diameter glass beads and closely packed between two polymethylmethacrylate plates, was mounted on a stand to permit the angle of inclination between the plane of the model and horizontal to be varied. After saturating the medium with a glycerol-water mixture, air was injected through a small hole at one end of the cell. The hole was sealed after a large IP cluster had been created. The entire cell was then rotated about its horizontal axis at a velocity of 4° per hour. As the inclination angle was increased, the strength of gravity or more precisely the Bond number - defined as the ratio between gravity and capillary forces \( Bo = \Delta \rho g a^2 / \sigma \sin \theta \), where \( a \) is the pore radius), increases. The IP (invasion percolation) cluster at first became elongated in the direction of gravity and subsequently migrated when a critical inclination angle was reached. Migration describes a sequence of displacement steps that involves drainage (gas displacing water) at the upper front and imbibition (water displacing air) at the lower front of the migrating cluster. Imbibition led to cluster fragmentation which resulted in temporary halts to migration. At higher inclination angles migration was restarted, but between migration cycles cluster fragments continued to propagate along the gravity gradient, usually at a rate faster than the rate of formation of the original IP cluster. Branch-like cluster structures were created after a number of migration events, Figure 2-13.
Auradou et al (1999) presented experimental studies of the impact of the competition between uncorrelated capillary forces and correlated gravity forces during drainage in a porous monolayer. Air, considered the non-wetting phase, was injected at one end of a porous medium – formed by a horizontally oriented rough fracture joint filled with glass beads which was saturated with the wetting phase (either pure water or a glycerol-water mixture). Three strength levels of the gravitational force $1g_0$, $2g_0$, and $3g_0$ were considered using a centrifuge. The smoothing of the boundary of the air invasion structures was accompanied by a decrease in air saturation as the strength of gravity increased, Figure 2-14. For the $6g_0$ experiment, buoyancy was strong enough for the air clusters to migrate, Figure 2-15. Migration was observed to occur as a sequence of cluster expansion at the top and retraction or imbibition at the bottom which may cause cluster fragmentation. Fragmentation was followed by a long period of stagnation until the inlet reconnects up with the fragment after which another migration, coalescence and fragmentation cycle restarts.
Using a series of experiments, Meakin et al (2000) examined the effects gravity on the displacement of a wetting fluid by a lighter non-wetting fluid in quasi-two dimensional and three dimensional granular porous media under both gravity stabilized and gravity-destabilized displacement processes. For the 2D gravity-stabilized displacement, air was injected at a slow rate at the upper edge of the porous medium saturated with a high density water/glycerine mixture. Gravitational force was increased by increasing the inclination of the initially horizontal quasi-2D porous medium. The growth of the active front was found to stabilize as the inclination angle increased (Figure 2-16). In the 2D gravity-destabilized displacement air was injected at the lower end of the porous medium instead of the upper. The resulting pattern consists of fingers of the non-wetting phase extending into the wetting phase and directed upwards. The fingers thinned out and eventually migrated, fragmented and bifurcated as the inclination angle was increased (Figure 2-17). Results of the 3D experiments broadly followed the same trends as the 2D experiments. Meakin et al (2000) found that a modified version of the simple invasion percolation algorithm that accounts for the effects of bubble migration gives realistic simulations of the most important features of gravity stabilized and destabilized displacement processes.
Geistlinger et al (2006) proposed a stability criterion that predicts grain-size and flow-rate dependent transitions from coherent to incoherent flow which were observed in their gravity-destabilized injection experiments in two-dimensional tanks filled with glass beads. In the experiments, compressed air was injected through a needle close to the bottom of a water saturated bead-packed Plexiglas tank (40cm x 45cm x 1.2cm), at a constant rate of about 10mL/min. The experiments were conducted under no bulk flow condition. Three glass bead sizes, denoted as 0.5mm-, 1mm-, and 2mm-GBS (glass bead sediment), with grain size intervals of 0.25-0.5mm, 0.75-1.0mm, and 2.0-2.2mm, respectively, were used. The images of the spatial gas saturation distributions (Figure 2-18) and the plots of the injection entry pressure profiles with time (Figure 2-19) clearly indicate a predominantly gravity-driven (a consequence of the no bulk flow) transition from coherent flow (or gravity fingered regime) to incoherent flow (or migratory regime) as the bead size diameter increased. The stability criterion proposed to explain these results considers steady state tortuous gas flow as a core annulus flow and uses the Hagen-Poiseullle laminar flow equation to define a critical injection rate window (Equation (2-12)) outside of which, for a given range of pore radius within a porous medium, flow transitions from incoherent to coherent flow. Using the stability criteria in Equation
(2-12), the theoretical lower injection rate limit was calculated as 110mL/min for the 2mmGBS, and since the experimental injection rate was 10mL/min, it correctly predicted the observed incoherent flow behaviour in Figure 2-18(c). For the 1mmGBS, the critical rate window ranged between 5 and 22mL/min, suggesting a transient regime between coherence and incoherence. Lastly, the upper critical rate limit for the 0.5mmGBS was 0.6mL/min, which strongly indicate coherent flow behaviour. It might be of interest to note that the authors considered the dispersive nature of incoherent flow to be aided by the high symmetry of the glass beads which may be akin to the uniformity in the capillary pressure field proposed by Dumoré (1970).

\[ Q_{\text{crit}} = \frac{\pi \Delta \rho g}{8 \mu_g} R_c^4 \]  

(2-12)

where, \( Q_{\text{crit}} \) = the critical rate, \( \Delta \rho \) = density difference, \( g \) = gravitational constant, \( R_c \) = radius of mean capillary, \( \mu_g \) = gas viscosity

Figure 2-18: Gas flow patterns in quai-2D bead packs of different characteristic bead sizes – (a) 0.5 mm-GBS, (b) 1.0 mm-GBS, and (c) 2.0 mm-GBS. GBS means glass bead sediment (from Geistlinger et al, 2006).

Figure 2-19: Entry pressure versus time for three different GBS, from (from Geistlinger et al, 2006).
Cinar et al (2009) reported a series of gravity-stabilized and gravity-destabilized experiments at Bond numbers ($B_o = \frac{\Delta \rho g a^2}{\lambda}$, where $\Delta \rho$ is the density difference, $d$ the characteristic length taken as the pore diameter, $\lambda$ the interfacial tension, and $g$ the gravitational acceleration) and capillary numbers ($Ca = \frac{\mu_i u}{\lambda}$, where $\mu_i$ is the viscosity of the injected fluid and $u$ the injection velocity) of the order of $10^{-3}$ and $10^{-4}$, respectively. Even though the Ca range considered imposed viscous forces whose contribution to the flow process could not be ignored, the experiment employed a wetting (glycerol-rich water with a density of 1.123g/cm$^3$) and non-wetting (heptane-rich oil with a density of 0.679g/cm$^3$) phase pair with properties that are relevant to the study of CO$_2$ evolution in saline aquifers. Five experimental runs were performed by introducing the non-wetting phase at different injection rates across the top or bottom faces of a vertically oriented 29.5cm high 2D porous medium made from uniform glass beads. Only two of the runs will be discussed here. As shown by Figure 2-20 and Figure 2-21, the displacement process was more efficient when injection is from the top (gravity stabilized) than from the bottom (gravity destabilized). In the gravity destabilized case, there was simultaneous growth of multiple independent non-wetting phase channels occurred from the onset of injection which might be due more to the influence of both the high Ca regime and the high viscosity ratio between the two fluids ($M = \frac{\mu_d}{\mu_i} = 13$, where $\mu_d$ is the viscosity of the displaced fluid) than the impact of gravity. Gravity apparently contributed to the general upward flow bias but the extent of its contribution is not clear.

Figure 2-20: Gravity-stabilized drainage at an unfavourable viscosity ratio ($B_o = 1.25 \times 10^{-3}$, $Ca = 1.2 \times 10^{-4}$, $M = 13$), Cinar et al (2009).
We next review a range of pore network modelling algorithms that have been developed over the years to better characterise and explain the disparate gravity-induced multiphase flow phenomena observed in these experiments.

2.1.4.1 Pore Network Modelling of Gravity Effects

In the quasi-static limit of multiphase flow, were the effect of viscous forces can be ignored, gradient invasion percolation has been found to be an efficient and relatively accurate algorithm for describing the impact of gravity on multiphase flow behaviour (Tsimpanogiannis and Yortsos, 2004; McDougall and Mackay (1998); Wagner et al, (1997); Birovljev et al (1995). The gradient invasion percolation is a version of the standard IP as described by Wilkinson and Willemsem (1983) but with additional terms that account for the buoyancy forces created as a result of density differences between two fluids in contact.

Birovljev et al (1995) described a gradient invasion percolation algorithm that was extended to include migration processes. The network was represented by a regular square lattice of sites and bonds which were assigned random numbers \( p \) and \( p' \), respectively, that ranged between 0 and 1. These random numbers were used to calculate invasion and withdrawal thresholds depending on whether a site (or bond) is occupied by a wetting fluid (WF) or a non-wetting fluid (NWF). As long as a WF site is not trapped, its probability of invasion corresponds to the value of its random number. The withdrawal thresholds were, however, determined using a combination of the assigned random numbers and a ranking parameter that accounts for the local configuration of the interface according to the established four dominant imbibition mechanisms: the I1, I2,
piston and snap-off types. Under this formulation, the I2 and snap-off imbibition during withdrawal could cause fragmentation. A migration event was considered possible if the threshold described by Equation (2-13) is less than zero, where $\Delta y$, the last term of the equation, represents the height difference between an invasion and a withdrawal site, and $f$ a gradient parameter that might be used to vary the strength of the buoyancy force – much like changing the inclination angle of the cell in the experiment of Birovljev et al (1995) as described above. A migration step consisted of an invasion of a WF site (or bond) and withdrawal from a NWF site (or bond). The model was used to qualitatively reproduce the buoyancy-driven migration of an IP cluster that was observed in the experiment of Birovljev et al (1995) with results that compared favourably in terms of the fragment size distribution post migration (compare Figure 2-13 and Figure 2-22).

$$\Pi = \Pi^i - \Pi^w - f \Delta y \quad (2-13)$$

where, $\Pi^i$ is the invasion threshold and $\Pi^w$ the withdrawal threshold.

The modified invasion percolation algorithm presented by Wagner et al (1997) was similar to the gradient invasion percolation algorithm of Birovljev et al (1995) but with slight differences. There are two main differences between the two models. First, in Wagner et al’s (1997) model buoyancy force was included in the invasion threshold regardless of whether a migration event is possible or not, and secondly, the withdrawal threshold does not account for the local configuration at the interface. Using a gravity destabilized configuration in which a non-wetting phase was injected at the bottom end of a 2D
regular lattice network saturated with a wetting phase, a range of displacement patterns was obtained. Large continuous non-wetting phase invasion structures, oriented in the direction of the buoyancy gradient were observed when the gradient parameter was small. For high values of the gradient parameter, the structures were thinner and disconnected due to fragmentation. For intermediate gradient parameters, fragmentation resulted in the formation of secondary migration pathways or branches. Notice that even at the highest values of the gradient parameter the flow pattern remained confined to narrow channels and did not at any point transition to a more dispersed flow pattern as observed in the experiments of Dumoré (1970) and Geistlinger et al (2006). This appears to be a principal limitation of algorithms that are exclusively based on the gradient invasion percolation, where pores are filled one at a time (Tsimpanogiannis and Yortsos, 2004; Zhang et al, 2000; Maekin et al, 2000).

Ezeuko et al (2010) extended the model of McDougall and Mackay (1998) to allow for simultaneous interface advancement in all pores at the invasion front of a migrating cluster in which the invasion threshold have been exceeded. The model successfully reproduced the important qualitative features of the dispersion and non-dispersion experiments of Dumoré (1970), marking a significant advance in our understanding of gravity-driven flow behaviour. Using 2D regular lattice networks, Ezeuko et al (2010) went on to investigate the impact of mean capillary radius, network connectivity, interfacial tension and pore size distribution variance on buoyancy-driven migration during the depressurization of an oil saturated network. They identified four distinct gas flow regimes depending on the value of the Bond number, namely, the capillary (Bo<=1), the fingering (Bo<=1), the braided (Bo>1), and the dispersive (Bo>1) regimes. Flow dispersion was found to be more likely under conditions of large mean capillary radius, small PSD variance, low interfacial tension, and high network connectivity.

### 2.2 CO₂ Sequestration in Saline Formations

The link between anthropogenic CO₂ emissions and global climate change is no longer ambiguous. As a greenhouse gas CO₂ has contributed the most to the increase in global temperatures for the past one hundred years or so (Figure 2-23). Some of the observed effects – the increased concentration of CO₂ in the atmosphere, the warming of the ocean and the atmosphere, the diminishing amounts of snow and ice, and the rising sea level
(based on direct measurements and remote sensing from satellites and other platforms, and on Paleoclimate reconstructions) – are unprecedented for over decades to millennia (Stocker et al, 2013). These effects will persist for hundreds of years to come even when all anthropogenic emissions cease today. The goal of most global climate change mitigation strategies is therefore not to reverse the process but to stabilize it within defined thresholds by limiting emissions. One of the most promising emission reduction strategies that has been proposed is Carbon Capture and Storage (CCS). CCS involves the collection of potential emissions from large scale point sources – coal fired power plants, cement factories, etc., and then subsequent disposal into deep geologic formations. Among the three possible options of geologic formations for CO₂ storage – depleted oil and gas reservoirs, deep saline aquifers, and un-mineable coal beds – deep saline aquifers have by far the largest volumetric storage capacity (91.8 – 97.5% of geologic storage capacity in North America, Nghiem et al, 2009) and are more widely distributed globally.

We next outline the theoretical assumptions that underlie the conceptual understanding of the ultimate fate of CO₂ when injected into saline formations.

![Figure 2-23: Global mean surface temperature increase as a function of cumulative total global CO₂ emissions from various lines of evidence (from Stocker et al, 2013).](image)

In Figure 2-23, multi-model results from a hierarchy of climate-carbon cycle models for each RCP (Representative Concentration Pathways - a set of simulation model scenarios for forecasting future changes in global climate) until 2100 are shown with coloured lines and decadal means (dots). Some decadal means are labelled for clarity (e.g., 2050
indicating the decade 2040−2049). Model results over the historical period (1860 to 2010) are indicated in black. The coloured plume illustrates the multi-model spread over the four RCP scenarios and fades with the decreasing number of available models in RCP8.5. The multi-model mean and range simulated by CMIP5 (Coupled Model Intercomparison Project Phase 5) models, forced by a CO₂ increase of 1% per year (1% yr⁻¹ CO₂ simulations), is given by the thin black line and grey area. For a specific amount of cumulative CO₂ emissions, the 1% per year CO₂ simulations exhibit lower warming than those driven by RCPs, which include additional non-CO₂ forcings. Temperature values are given relative to the 1861−1880 base period, emissions relative to 1870. Decadal averages are connected by straight lines. For further technical details see Stocker et al (2013): IPCC (Intergovernmental Panel on Climate Change) Summary for Policymakers. These data highlight the fact that cumulative CO₂ emission is linearly correlated with average global temperature rise and that global warming is most likely to continue beyond the present century.

2.2.1 CO₂ Trapping Mechanisms in Saline Aquifers

CO₂ is a gas with a density of around 1.98 kg/m³, about 1.67 times that of air, at standard temperature and pressure conditions (National Institute of Standards and Technology, NIST: 20 °C, and 14.7psia; International Union of Pure and Applied Chemistry, IUPAC: 0 °C, and 14.5psia). It has critical point of 7.38 MPa (1070.38psia) at 31.1 °C and above this point it behaves as a supercritical fluid i.e. a fluid that no longer exist as a distinct gaseous or liquid phase and with physical properties between those of a gas and a liquid. Figure 2-24 shows the pressure-temperature phase diagram of CO₂, and the variation of CO₂ density with temperature and pressure. It depicts the extent and proportions of a number of important points, boundaries and regions. We can see that at the temperature and pressure conditions likely to be encountered in deep saline aquifers, injected CO₂ is most likely to exist as a supercritical fluid. We can also observe that although ScCO₂ (supercritical CO₂) would be much heavier than air at similar conditions, it will still be lighter than water (or brine, density 958.4kg/m³ at 100°C) under the most probable conditions that prevail in saline aquifers.
Figure 2-24: Physical properties of CO₂ (a) CO₂ pressure-temperature phase diagram, (b) Variation of CO₂ density with temperature and pressure (from Annex of Metz et al, 2005)

CO₂ is soluble in water (brine), and in the aqueous phase forms the carbonic acid H₂CO₃, which will undergo further dissociation into bicarbonate (HCO⁻³), hydron (H⁺) and carbonate (CO₃⁻²) ions in proportions that depend on the pH levels.

Based on what is known about the physical and chemical properties of CO₂ and brine, CO₂ injected into brine can be expected to be sequestered in four main forms – as a free phase accumulation beneath a structural or stratigraphic trap, as a residual (and dispersed) free phase held in place by capillary forces, as an aqueous phase dissolved in brine, and as a precipitated mineral. The proportion of CO₂ sequestered in each of these forms differ from one saline formation to another and it is considered to depend on a wide range of factors including the formation geology (thickness, geometry, faults, etc), its petrophysics (permeability, porosity, fractures, etc), its mineralogy, its depth (temperature and pressure), brine salinity, etc. The contribution of each trapping mechanism also changes with time. Higher proportions of injected CO₂ will be expected to be either dissolved or mineralised with the passage of time, Figure 2-25. Each trapping mechanism will now be examined in brief.
2.2.1.1 Structural and Stratigraphic Trapping

CO₂ is likely to exist as a supercritical phase under temperature and pressure conditions in deep saline formations suitable for storage. Even though ScCO₂ (supercritical CO₂) is denser than gaseous CO₂, there will nevertheless be a large density difference between ScCO₂ and saline water (brine). The injection of CO₂ into a brine saturated formation will therefore create buoyancy forces that drive the ScCO₂ towards the top of the formation. The rate of buoyancy rise will depend on formation properties – it will generally decrease with decrease in formation permeability, and the shape of the rising plume will be determine by the nature of large scale heterogeneities within the formation (layers, shale lenses, etc). Eventually, the further rise or migration of the CO₂ will be prevented when it encounters low permeability or impermeable boundaries of the surrounding formation – caprock – that confines the brine bearing formation in a structural or stratigraphic trap. CO₂ still rising from the source is assumed to accumulate beneath the caprock and subsequently spread laterally. This of course assumes that the caprock is completely sealing, a situation rarely encountered in practice. Brine bearing formations relevant to CO₂ storage are large scale geological structures – typically spanning several kilometres – and the occurrence of high conductivity flow pathways such as fractures and faults within the caprock or sealing formation is always possible. Furthermore, a caprock may not even exist. A comprehensive analysis of leakage risk is, therefore, indispensable in any CO₂ storage evaluation. Despite the associated uncertainties, most of the injected CO₂ in the initial storage phase - which may last for tens to hundreds of years, will be sequestered in structural and stratigraphic traps.
2.2.1.2 Residual Trapping

As CO$_2$ migrates towards the upper parts of the formation under buoyancy forces, brine flows in the opposite direction simultaneously. But imbibition (displacement of CO$_2$ by brine, brine considered the wetting phase) will only displace a fraction of the initial CO$_2$ saturation, leaving the rest as disconnected structures that are trapped by capillary forces. The process by which a fraction of the rising CO$_2$ plume becomes permanently trapped by capillary forces is called residual trapping. Residual trapping is highly desirable because it renders the free CO$_2$ permanently immobile and thus reduces the risk of leakage by limiting the amount of injected CO$_2$ that reaches the caprock. The extent of residual trapping depends on the specific properties of the formation under review and some authors have estimated that 15 – 25% of the injected CO$_2$ may be trapped this way (Holtz, 2002). Reliable estimates of residual trapping are difficult to make due, in large part, to the limitations of current migration models related to the upscaling of flow coefficients. One of the main tasks of CO$_2$ storage reservoir engineering is the development of strategies that maximise residual trapping.

2.2.1.3 Solubility Trapping

CO$_2$ is soluble in brine and its CO$_2$ solubility is dependent on brine salinity and temperature. Dissolution rate increases with increase in the amount CO$_2$-brine interface contact area and thus reliable estimates of CO$_2$ migration patterns is essential to accurately quantify the solubility trapping capacity of a saline aquifer. CO$_2$ saturated brine becomes slightly denser than a CO$_2$ free brine by approximately 1%, depending on brine salinity (Bachu and Adams, 2003). This density contrast may set off convective currents in which denser brine near the CO$_2$-brine interface sinks through the lighter unsaturated brine just as the lighter brine flows in the opposite direction. Convective mixing enhances solubility trapping and its impact increases with increase in the vertical permeability of the formation (Ennis-King and Paterson, 2003; Lindeberg and Wessel-Berg, 1997). Solubility trapping can also be enhanced if the aquifer is connected to an active hydrodynamic flow system rather than being confined in a hydrologically isolated structure. The contribution of solubility trapping increases with time, and depending on formation petrophysical properties and hydrodynamics, brine salinity and temperature, a significant fraction (up to 30%) of injected CO$_2$ may be dissolved in a matter of decades,
(Doughty et al, 2001). Assuming no leakage, all injected CO$_2$ will eventually dissolve in brine – this may take centuries to occur (McPherson and Cole, 2000).

### 2.2.1.4 Mineral Trapping

Dissolved CO$_2$ in brine dissociates into a number of ions: H$^+$, HCO$_3^-$, CO$_3^{2-}$, to produce a weak acid. Equation (2-14) indicates the kind of reaction involved:

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+ \tag{2-14}
\]

The newly formed ions go on to react with ions already present in the host brine and with some of the minerals (non-carbonate calcium-, iron-, magnesium-rich minerals) making up the reservoir rock, leading to the precipitation and dissolution of other minerals, e.g. calcite. Equation (2-15) gives an example of a mineral precipitation and dissolution reaction.

\[
\text{Calcite} + \text{H}^+ \leftrightarrow \text{Ca}^{++} + \text{HCO}_3^- \tag{2-15}
\]

The reversible nature of Equations (2-14) and (2-15) suggests that it may be difficult to predict a priori whether mineral trapping will be cumulative. Further, the complex web of thermodynamic, kinetic, flow and transport processes involved over a spectrum of time scales may result in net mineral precipitation within the reservoir formation or the caprock – creating a self-sealing mechanism. On the other hand, a net mineral dissolution might propagate through the sealing formation, starting from the caprock-reservoir boundary, creating possible leakage pathways (Czernichowski-Lauriol et al, 2006) and diminishing storage security. The conversion of CO$_2$ into stable minerals is considered the most permanent form of geological storage (Gunter et al, 1993), although the fraction of injected CO$_2$ trapped in this form is believed to become significant only after thousands of years have elapsed (Metz et al, 2005).

Like most key questions regarding CO$_2$ storage evaluation, reducing uncertainties associated with the quantification of the rate and extent of mineralization can be achieved through numerical simulations that are properly parameterised and well constrained by experimental and observational data. The most common approaches to
numerical modelling of CO₂ storage are presented next, with special emphasis on the migration processes of free and dissolved CO₂ phases.

2.2.2 Modelling Options for CO₂ Storage in Saline Formations

Numerical modelling of geosequestration of CO₂ has evolved rapidly in the past two decades in terms of the capability to simulate the various flow, transport, and geochemical interactions between CO₂ and brine. From an historical perspective, most numerical models of CO₂ storage processes are hybrid models because they borrow heavily from legacy codes from the field of petroleum engineering, geohydrology, and geochemistry. The approaches do not actually fall into clear cut categories but are rather distributed on a continuum defined by the range of questions that is to be addressed. Nevertheless, two broad modelling approaches may be discerned: 1) Fully Coupled models and 2) Flow and Transport models.

2.2.2.1 Fully Coupled Models

These models describe non-isothermal, multiphase flow, coupled to multicomponent reactive transport – via convection, dispersion and advection, and including geomechanical effects, in three dimensional porous media. The coupling between flow, transport and geochemical processes is represented by the changes to permeability due to mineral precipitation and dissolution reactions. The associated equations may include: relative permeability and capillary pressure functions, mass and energy balance equations; equations of state formulations for calculating PVT properties; flash equations to determine component partitioning and phase compositions; geomechanical equations to describe the changes in rock properties and stress states in response to variations in pore pressure, fluid content, etc; an extensive table of geochemical reaction equations. The attraction of fully coupled models stems from their apparent completeness. However, their implementation is often plagued by numerical difficulties, arising primarily from the non-linearities inherent in their formulation. More importantly, identification of well calibrated parameters (flow, kinetic, thermodynamic, equilibrium constants, initial formation stress states, faults and fracture geometries, etc), appropriate coupling strategies and representative chemical reaction paths always present significant challenges (Court et al, 2011). These challenges are often resolved by selection of generic inputs that have little justifiable physical basis, making any outputs from these models
irrelevant to the practical questions being asked. Despite these limitations, coupled models can provide qualitative predictions about important processes involved in CO$_2$ storage, which will continue to improve as these models become increasingly constrained by experimental and observational data. Examples of these models include: TOUGH2 (Pruess et al, 2004), NUFT (Nitao, 1998), FLOTRAN (Lichtner, 2003).

### 2.2.2.2 Flow and Transport Models

It is often necessary to apply some simplifying assumptions to models in order to obtain clear and rapid estimates of the broad system behaviour which will serve as a basis for more detailed future studies. To determine the extent of a CO$_2$ plume and the associated pressure perturbations during the period of injection, for example, the impact of geochemical trapping might be far less important than the interaction between viscous and gravity forces. In this case geochemistry might be de-coupled or ignored altogether. If no significant temperature changes are expected and rock deformation considered too small to make any significant impact, then non-isothermal and geomechanical effects could be ignored without loss of accuracy. It is of course not always straightforward to identify beforehand which parameters are important or not, and some codes allow for governing equations to be de-coupled selectively. Examples of codes with well-tested flow and transport modules include Eclipse (Schlumberger, 2013), GEM (CMG, 2013), TOUGH2 (Pruess et al, 2004). Simplifications might also be applied to the representation of the flow domain. The so called vertically-integrated models could be used to resolve a 3D flow domain into a 2D domain if the flow along the horizontal direction is considered much more important to the understanding of the behaviour of a system than flow in the vertical direction. With respect to modelling CO$_2$ storage, vertically integrated models might be appropriate for a formation with a disproportionally larger lateral dimensions compared to its thickness.

### 2.2.3 Current Limitations of Numerical Models to Describe CO$_2$ Migration during Storage

Compared to depleted oil and gas reservoirs, whose geological structure and petrophysical properties are fairly well understood from the extensive information gathered in the exploration, development and production phases using many different probing techniques, deep saline aquifers are relatively unknown geological entities. In the
17 years since the launch of the Sleipner project in the North Sea (the first commercial scale CO\(_2\) injection into a saline formation) only two additional large scale CO\(_2\) storage projects have come on stream, with about a dozen pilot and demonstration projects at several stages of implementation (Michael et al, 2010). While these projects clearly demonstrate the technical feasibility of CO\(_2\) storage in saline formations and also furnish pertinent data for formulating best practice guidelines for future projects, the first principal set of questions that was asked in the IPCC (Intergovernmental Panel on Climate Change) Special Report on CCS (Metz et al, 2005) is still largely unanswered – “How is CO\(_2\) stored underground? What happens to the injected CO\(_2\)? What are the phyisco-chemical processes involved? What are the geological controls?”.

Current monitoring techniques are able to detect the large scale subsurface migration footprints of injected CO\(_2\) but the detailed quantitative information about its spatio-temporal phase distributions that is needed to answer practical questions about storage capacity and security will probably always require numerical simulation studies.

All the physical and chemical processes of importance in CO\(_2\) sequestration in saline formations – residual, solubility, mineral and, to some extent, hydrodynamic trapping, and leakage path analysis – are fundamentally pore scale phenomena. We focus here on the flow processes. Although most practical questions about storage capacity and security are probably best answered by reservoir or basin-scale models, made up of representative elementary volumes (gridblocks) of sizes many orders of magnitude larger than the largest pores in the physical rock, these models must somehow represent the pore scale mechanisms in an efficient and realistic way.

The considerable increase in the number of numerical simulation studies of flow processes during CO\(_2\) storage have significantly advanced our understanding of the impacts of reservoir heterogeneity, relative permeability hysteresis, density-driven convection, injection strategies, etc on CO\(_2\) migration and trapping (Michael et al, 2009). Outstanding issues, technical and theoretical, remain to be addressed however. Two of the outstanding knowledge gaps are: 1) the inability to obtain reliable upscaling of CO\(_2\) solubility and residual (relative permeability) trapping, and CO\(_2\) migration through convective mixing; 2) Insufficient understanding of leakage mechanisms and hence the
high uncertainty in leakage potential quantification. It is very likely that any attempts to close these knowledge gaps will draw heavily upon what can be discovered about the fundamental pore scale mechanisms that control CO₂-brine interactions.

Pore scale studies of CO₂-brine interactions have also been carried out to explore different topics relevant to CO₂ sequestration. The range of topics include: the impact of geochemistry on poro-perm evolution (Algive et al, 2009); the impact of rock properties on capillary/residual trapping efficiency (Pentland et al, 2011, 2010; Iglauer, 2011; Bandara, 2011), solubility trapping efficiency (Izgec and Demiral, 2005; Suekane et al, 2008) and relative permeability characteristics (Bachu and Bennion, 2008); the influence of the balance between capillary, viscous and buoyancy forces on CO₂ migration (Polak et al, 2011). The following summarises - in chronological order, recent research findings on the physical interactions between CO₂, brine, and porous media microstructure using both experiments and pore scale modelling.

2.2.4 Experiments of CO₂-Brine Interactions in Porous Media

Recent progress in experimental research into multiphase flow process behaviour in porous media have been encouraged and enabled by the improved capability to non-intrusively visualize in-situ fluid flow. Micro-CT techniques are by far the most commonly used. Izgec and Damiral (2005) performed CO₂ injection experiments on carbonate plugs (7-10cm long an 3.81-4.72 in diameter) that were recovered from the Midyat aquifer formation located in Diyarbakir, South Turkey to investigate the impact of CO₂ injection rate, brine salinity, core orientation, and system temperature and pressure on core porosity and permeability. Significant dynamic changes to core permeability (1 – 250%) and porosity (<10%) were observed (using X-ray scanners) during CO₂ injection and these changes were found to strongly depend on core orientation. Injection of CO₂ into horizontally oriented cores led to a continuous decrease in permeability as injection proceeded even as the porosity increased slightly. In vertically oriented cores, however, injected CO₂ moved rapidly upwards due to buoyancy and permeability increased sharply at the initial stages of injection before stabilizing above the original value. The results were explained in terms of the surface contact area available for mineralization. The contact area in horizontal cores was greater than in the vertical cores and this permitted rapid CO₂ dissolution which dropped near inlet pH and which in turn led to the formation
of calcite particles that blocked the flow path. Brine salinity (0 – 5% by weight), system temperature (18°C – 50°C) and CO₂ injection rate (3 – 60mL/min) had noticeable but far less significant effects on porosity and permeability changes.

Bachu and Bennion (2008) conducted a series of experiments on several core samples collected from sandstone, carbonate and shale formations in central Alberta, western Canada, to measure the impact of rock and fluid properties on relative permeability and capillary pressure behaviours at laboratory conditions representative of the in-situ conditions of deep saline formations suitable for CO₂ storage. The 13 rock samples spanned a wide range of permeability (0.00000294mD – 66mD) and pore size distribution. Both drainage (CO₂ displacing brine) and imbibition (brine displacing CO₂) experiments were considered for pressure and temperature windows above the supercritical point of CO₂ (8.6 – 27MPa and 35°C – 75°C), and brine salinity between 27 and 248 g/L. Capillary pressure was found to depend mainly on the pore size distribution – increasing with decrease in pore sizes – but was also indirectly affected by the temperature and pressure condition through the IFT (increasing as the IFT increases). End point relative permeability to CO₂ for both drainage and imbibition was found to decrease as IFT decreased, while irreducible water saturation (for drainage) and irreducible CO₂ saturation (for imbibition) increased as IFT increases. IFT also had a strong impact on the shape of the relative permeability curves. No clear correlation was found between pore characteristics and irreducible water and CO₂ saturations. The effect of viscosity ratio between brine and CO₂ was assumed to be negligible.

Suekane et al (2008) reported the results of an experiment on a Berea sandstone core (34mm in diameter and 110mm long) aimed at estimating the amount of residual and solubility CO₂ trapping after a number of imbibition and drainage cycles. Trapped CO₂ saturation was calculated from the relationship between volume and pressure during isothermal expansion. The proportion of total injected CO₂ trapped (residual and dissolved) ranged between 24.8 – 28.2% for the seven combinations of temperature and pressure conditions considered (40 – 45°C; 8.9 – 10MPa).

The work of Pentland et al (2010) suggests that residual CO₂ saturations in Berea sandstones could be even higher (up to 37% for an initial maximum saturation of 90%) if
CO₂-brine displacement is carried out under immiscible conditions i.e. when CO₂ saturated brine or carbonated brine is used from the start of the drainage – imbibition cycles of the experiment. In their experiment, supercritical CO₂ was injected into a Berea sandstone core saturated with a carbonated brine to establish an initial CO₂ saturation. The maximum initial CO₂ saturation was found to be strongly dependent on the type of coreflood method used – the porous plate method produced a higher initial CO₂ saturation than the unsteady state displacement method because of the high capillary pressures that are imposed in the former. To generate residual CO₂ saturation, the CO₂ saturated core was then waterflooded at an injection rate selected to yield a capillary number of ~ 1x10⁻⁷. Residual CO₂ saturations of 25 – 28% for corresponding maximum initial CO₂ saturations of 35 – 40% were measured in the unsteady coreflood method, while the porous plate method yielded a residual CO₂ saturation of 37% for an initial CO₂ saturation of 90%. Pentland et al (2010) recommended the adoption of the porous plate method for determining irreducible water saturations for CO₂-brine systems, although the degree to which the maximum initial CO₂ saturations obtained with this method are representative of field values was not indicated.

Polak et al (2011) used a binary fluid system consisting of a glycerol-rich dense phase and an n-heptane-rich lighter phase as brine and CO₂ surrogates, respectively, to investigate the impact of the balance between capillary, viscous and gravity forces on displacement efficiency. The set up consists of glass beads packed between two vertical glass plates to form a pseudo-2D porous medium. The CO₂ proxy was injected at the bottom of the model at a constant rate. Two sets of bead sizes were considered, with estimated permeability of 40.2D and 161.0D. The density difference and IFT between the two fluids were given as 476kg/m³ and 34mN/m, respectively. The most vertically biased flow was observed at the lowest injection rate in the high permeability (low capillary pressure) bead pack and this resulted in less in-situ fluid being displaced. High injection rates were found to cause viscous fingering which, paradoxically, led to an increase in in-situ fluid displacement.

Results of many experiments on CO₂ storage in brine suggest that a significant fraction of total injected CO₂ could be trapped via residual and capillary trapping although there is considerable variation across rock types. Iglauer et al (2011) directly imaged trapped
supercritical (50°C and 9MPa) CO₂ clusters in a homogeneous sandstone (Doddington) core using micro-CT. CO₂ was injected into an initially brine saturated core – this represents primary drainage during the initial migration of CO₂ into the aquifer. This was then followed by the injection of a CO₂-saturated brine – representing secondary imbibition at the trailing edge of a CO₂ plume. CO₂ trapping occurs during the imbibition stage and this process is controlled by the competition between snap-off and piston-like imbibition mechanisms according to the system wettability. Because the ScCO₂/brine/sandstone system was not considered strongly water-wet by the authors, there was limited number of snap-off events which broadly reduced capillary trapping and led to fewer small residual clusters. The measured residual CO₂ saturation was 24.9%, somewhat lower than 35%, recorded in an analogue n-octane-brine experiment that used the same Doddington sandstone but in a strongly water-wet condition. Despite the relatively low residual saturation, the presence of clusters of all sizes was expected to provide large surface area dissolution and reaction, thus enhancing storage security. Pentland et al (2011) reported a similar experiment on a Berea sandstone and obtained a maximum residual CO₂ saturation of 37%, about 50% higher than the value obtained by Suakane et al (2008) using the same rock sample. While carefully correcting for CO₂ solubility effects El-Maghraby and Blunt (2012) showed that, for a Berea sandstone, gaseous CO₂ (at 4.2MPa and 50°C) exhibited less residual trapping (18.8%) than a supercritical (4.2MPa and 50°C) CO₂ (23.7%). Andrew et al (2013) reported trapped supercritical CO₂ as residual phase in a 2.809x10⁻¹² m² permeability Bentheimer sandstone sample of 32 ±0.9% and in a 1.4x10⁻¹² m² Ketton carbonate sample of 20.2±1.2%.

A technique for rapid measurements (in hours rather than weeks) of CO₂-brine capillary pressure curves at reservoir conditions and for quantification of capillary pressure heterogeneity was demonstrated by Pini et al (2012). To construct the capillary pressure curves, CO₂ was injected into a carbonated-water-saturated core at injection rates that were successively increased in discrete steps. The stabilized pressure drop across after each rate increase was simply taken as the capillary pressure, with the condition that the wetting phase (brine in this case) across the face of the core sample. CO₂ saturation was calculated as the average value from the analysis of micro-CT scan slices of the core. Two core samples were used – the homogeneous Berea sandstone (9.6cm long, with 276mD) sample and the heterogeneous Arqov sandstone (6.7cm long, with 28mD) sample. The
shape and value of the $P_c$ curves showed a strong dependence on rock sorting and pore size distribution. As is typical, the Berea $P_c$ curves displayed an initial broad plateau followed by a sharp rise, while the Arqov curves were characterised by a steady rise from the beginning. Sub-core (2.5x2.5x1mm$^3$) $P_c$ curves were generated using voxel-based saturation values on the inlet slice. The broad characteristics of the $P_c$ curve of each core sample were found to be preserved at the sub-system scale. A plot of $P_c$ curves for 20 voxels randomly selected from the inlet slice of each core indicated greater variation for the heterogeneous Arqov sample that for the homogeneous Berea sample.

The impact of fluid connectivity on non-wetting phase capillary trapping efficiency has been investigated by Herring et al (2013) for four different porous media: a Bentheimer sandstone, a sintered glass bead column, a loose packed glass bead column, and a column packed with crushed tuff. Fluid connectivity was characterised in terms of a normalized Euler number (Euler number is a topological parameter defined as $\chi = \beta_0 - \beta_1 + \beta_2$, where $\beta_0$, $\beta_1$, and $\beta_2$ are the zeroth, first and second Betti numbers respectively. $\beta_0$= number of distinct elements of fluid, $\beta_1$= number of redundant loops in the structure of each fluid component, and $\beta_2$= number of enclosed voids in each fluid component. The normalised Euler number is the ratio between the Euler number of the non-wetting fluid after a displacement event and the Euler number of the non-wetting fluid at 100% sample saturation). The results of air–brine (primary drainage) and brine–air (secondary imbibition) flooding sequences for each of the four porous media were analysed from X-ray CMT images taken during the displacement processes. Air was used as proxy for CO$_2$. The normalised Euler number was found to be proportional to the CO$_2$ saturation, reaching a value of 1.0 at a CO$_2$ saturation of 100%. CO$_2$ injected in Bentheimer sandstone displayed a higher connectivity (or normalised Euler number) as a function of CO$_2$ saturation than in glass beads and tuff sample. On the Euler number vs. fluid saturation plot, most of the data points for the sintered glass sample fell within a narrow CO$_2$ saturation range (80 – 95%). Results of the Bentheimer sandstone indicated that capillary trapping (Sr/Si: Sr being the residual saturation and Si the initial saturation), was inversely proportional to the initial CO$_2$ saturation. This suggested that enhancing CO$_2$ storage by capillary trapping will require minimizing the initial CO$_2$ connectivity. Capillary trapping also decreased as injection capillary number (Ca) increased.
The role of interface pinning by capillary forces during gravity-driven counter-current flow of two immiscible fluids has been reported by Zhao et al (2013). The experiment was set up such that the interface separating the two fluids was vertical at initial conditions. The onset of gravity segregation and its eventual extent was evaluated by the evolution of this interface. The authors found that capillary forces pinned a portion of the initial interface in position and above this pinned interface the lighter fluid spread laterally to the right whilst below it the heavier fluid spread to the left (Figure 2-26). The experiments were conducted in rectangular, quasi-2D cells with glass beads that range in size from 300 – 600µm. Three pairs of immiscible fluids were used to investigate the impact of contact angle, interfacial tension, and density difference. Air was used throughout as the lighter fluid and paired with three models of ambient heavier fluids (silicone oil, propylene glycol, and glycerol-water mixture). They showed that the interface pinning was caused by the hysteresis in capillary pressure – the difference between drainage and imbibition capillary pressures along the pinned portion of the interface. The hysteresis in capillary pressure described was independent of contact angle hysteresis and inherent in the fundamental difference between drainage and imbibition displacement processes – drainage produces highly curved interfaces whilst in imbibition the interfaces are much flatter.

Figure 2-26: The migration and spreading of a buoyant nonwetting phase (air: dark) in a porous medium filled with a denser wetting phase (silicon oil: light). Note the initial interface stopped moving at a finite distance due to the pinning effect of capillary pressure hysteresis (from Zhao et al, 2013)

The overwhelming number of experiments aimed at understanding CO₂-brine interactions at the pore scale have been mainly concerned with exploring the impact of rock fabric on the mechanisms of capillary and residual trapping at a wide range of temperature and pressure conditions. The common feature of these experiments is the assumption that residual and capillary trapping occur under capillary dominated flow processes in a two-
stage sequence of displacement events – CO₂ drainage then brine imbibition, that follow each other in orderly and predetermined steps. Gravity forces are generally ignored, understandably to avoid unwanted complications or due to equipment limitations. However, in the large scale systems that these results are presumably intended to apply gravity plays an important role, the nature of which is not captured or may actually be concealed by the capillary dominated displacement processes assumed in these experiments. It is by viewing the migratory process as a whole that we can see how the simultaneous evolution of the drainage and imbibition fronts creates characteristic cluster size distributions and trapping patterns that illuminates the dynamic nature of these scale dependent processes. PNM offers a robust platform for examining these issues from first principles – e.g. the link between snap-off imbibition mechanisms and the pore microstructure.

2.2.5 Network Modelling of CO₂-Brine Flow Processes during CO₂ Storage

Network Modelling of CO₂-brine interactions in porous media is not well explored. The few published accounts that could be found are discussed below.

Ferer et al (2001) developed a pore-network model to simulate the immiscible displacement of brine by CO₂ in a water-wet porous medium which was used to study the effects of viscosity ratio and capillary number on displacement and saturation patterns. The network was represented by a 2D diamond lattice consisting of pores and throats with randomly distributed sizes and finite volumes. To effectively manage the non-linearities associated with solving a viscous pressure field coupled to finite pressure drops at the CO₂-brine interface, capillary pressure was assumed to vary along the pore throat, reaching a maximum value at the middle and decreasing according to a sine function away from the middle. For a viscosity ratio (μ_{CO₂}/μ_{H₂O}) of 0.05, CO₂ flow pattern was observed to be identical to the fingering pattern of an Invasion Percolation displacement with trapping (IPwt), and breakthrough CO₂ saturation remained stabilized at about 20% for capillary numbers ranging between 6.25x10⁻⁶ – 6.4x10⁻³. At a viscosity ratio of 1.0, the displacement pattern changed from an IPwt fingering to a more compact pattern as capillary number increases and CO₂ breakthrough saturation increased from 20% at a Ca of 6.25x10⁻⁶, to 50% at a Ca of 6.4x10⁻³. This result suggests that CO₂ residual trapping could be enhanced by increasing CO₂ viscosity.
Pentland et al (2012) performed simulations on extracted networks from a range of porous media, including four glass bead packs, a sand pack and a sandstone sample, in order to study the influence of pore space geometry on CO$_2$ trapping by capillary forces. The networks were extracted using a maximal ball network extraction algorithm of Dong and Blunt (2009) to obtain pore body and pore throat distributions as well as coordination numbers. The network simulations attempted to reproduce the drainage-imbibition results that were obtained from experiments on the porous media from which the networks were constructed. Simulation results showed residual saturation to be inversely proportional to pore throat diameter - the narrower the pore throat, the greater the residual saturation. Comparison of simulation and experimental plots of $S_r$ vs. $r_{throat}$ indicated similar trends although the overall match was not optimal. A limitation of the model that might be responsible for the discrepancy between calculated and experimental values was identified as the absence of the cooperative pore filling displacement process during imbibition.

2.3 Review of Oil and Gas Production from Porous Media through Depressurization

Crude oil at reservoir conditions is a multicomponent mixture of hydrocarbons at thermodynamic equilibrium and will separate into its constituent components of mainly light and heavy parts if the reservoir conditions change sufficiently enough. For example, the lighter or gaseous components of the oil start to separate out when the reservoir pressure drops below the bubble point. The appearance of free gas signals a departure from equilibrium between oil and the dissolved gas, i.e. the oil at the new condition contains more gas than it can dissolve or it becomes supersaturated. The first appearance of gas is in the form of isolated microscopic bubbles, and with continued pressure depletion these bubbles grow by drawing the excess mass from the supersaturated oil through diffusion. As the bubbles grow they expel oil from the pore space towards the producing wells. This is called solution gas drive and it is the oldest known mechanism by which oil has been produced.
Solution gas drive is one of three key processes through which oil can be produced during reservoir development by the primary depletion strategy (also known as depressurization), which involves simply withdrawing fluids from the reservoir, leading to a decline in pressure. The others – liquid expansion and rock compression, are more dominant when the pressure is still above the bubble point. The appearance and growth of bubbles within a depleting oil actually leads to a decrease in the pressure decline rate. However, the greater mobility of gas compared to oil means that a large fraction of the oil will be by-passed as both gas and oil flow towards the producing well, especially when the initially isolated gas bubbles eventually join up to form a reservoir-wide interconnected network of gas flow channels. Figure 2-27 shows a schematic of the pressure, oil production and oil property profiles during depressurization including highlights of crucial events. Thus, oil recovery purely by the primary depletion strategy is not very efficient and the standard practice in the oil industry has been to keep the reservoir pressure above the bubble point by water or gas injection, a procedure which may also have the added benefit of helping to push oil towards the producing wells.

![Schematic of fluid properties and pressure history typical of a field under depletion (from Koederitz et al, 1989)](image)

Although water and gas flooding represent substantial improvements in oil production strategy over the older depletion strategy, a significant quantity of oil may still be left unrecovered even after extensive flooding. Of all the available options for improving recovery from these watered-out reservoirs, depressurization is the cheapest in terms of operating and capital costs, the simplest to implement and the least harmful to the environment. There is therefore a revived interest in engineered depressurization as a means for enhancing oil recovery and extending the producing lives of mature fields (Goodfield et al, 2003; Lago, 2002; Naylor et al, 2001; Chugh et al, 2000; De Mirabal, 1996). But an optimal implementation strategy that maximizes incremental oil and gas
production and minimizes waste (energy) requires a sound and broad knowledge of the complex mechanisms that drive and govern the process. The following review highlights the conceptual issues involved, the diverse approaches that have been proposed to resolve them – through experiments, theoretical formulations and numerical modelling – and questions that have been resolved and others that remain to be fully addressed.

2.3.1 Experimental Studies of Depressurization

The first systematic studies of depressurization addressed the mechanism of bubble formation and the factors that control it. Kennedy and Olsen (1952) observed the formation of gas bubbles in a C1/kerosene mixture containing silica and calcite crystals, under different depletion rates. They found bubble formation frequency to increase with both depletion rate (Figure 2-28) and the level of supersaturation. At a supersaturation of 30psi no bubbles formed, while at a supersaturation of 770psi, a great number of bubbles were formed in a very short time. Bubbles were also seen to form preferentially on the crystal surfaces rather than on the confining glass surfaces, with the silica and calcite crystals having identical effects. A degree of supersaturation was also observed by Stewart et al (1952) during a series of depressurization experiments on various oil-saturated limestone cores. Oil recovery by depressurization was found to vary considerably (12 – 52%) depending on the limestone sample used. The authors concluded that this variation in recovery was due to the differences in pore structure and connectivity (presence of solution cavities, fissures, etc). The high level of heterogeneity within limestone was also proposed to explain the discrepancy in gas/oil relative permeability functions between internal and external gas drive processes. But because the authors came to the conclusion in a later paper (Stewart et al, 1954) that depletion rate is a dominant factor that determines the amount of bubble formation (bubble formation increases with increase in depletion rate) and that laboratory depletion rates were several orders of magnitude greater than practical field depletion rates, they postulated that relative permeability obtained from an external gas drive process might be used to predict solution gas drive performance for non-uniform porosity limestone reservoirs. Wieland and Kennedy (1957) observed that supersaturations in excess of 14 – 25psi (depending on rock sample) were necessary for bubble nucleation to commence and also found bubble formation frequency to be dependent on the rock type but within a range that might be explained by variations in interfacial tension. Handy (1958) in a
corroboration of the observations of Stewart et al (1954), reported an increase in oil recovery by solution gas drive as depletion rate (production rate) increases and that the higher the oil viscosity the lower the production rate for which the increased recovery was observed. Like Stewart et al (1954), Handy (1958) again also found for lower depletion rates that solution gas drive recovery was predicted by external gas drive relative permeability data. Two clear conclusions may be drawn from these early studies of solution gas drive: 1) Some level of supersaturation is required for bubble nucleation to commence and 2) Bubble nucleation frequency and bubble density increases with increase in depletion rate.

![Figure 2-28: Bubble density as function of pressure decline rate(from Kennedy and Olson, 1952)](image)

More direct visual observations of the in-situ processes during depressurization have yielded new insights into the mechanisms involved in bubble formation and growth. Chatenever et al (1959) performed an impressive series of depressurization experiments on thin glass bead packings and thin sections of limestone and sandstone samples all housed in transparent cells for easy visualization. The authors made several important observations including 1) nucleation potential might be correlated with medium permeability and heterogeneity – low degrees of supersaturation observed in low permeability and in heterogeneous samples, 2) The growth of nucleated bubbles – rather the nucleation of new bubbles, was the mechanism by which oil displacement took place, starting from the largest pores (Figure 2-29). The work of Dumoré (1970) sheds more light on the impact of permeability on a depressurization process. Dumoré (1970) conducted two sets of depressurization experiments – one at 4,500psi/year and the other at 450psi/year, on two bead packs of different permeabilities, 350D and 15D. The gas
saturation distributions in both packs and at both depletion rates formed vertical channels, but while in the 350D pack the channels grew and migrated to fill the entire width of the pack as disconnected agglomeration of gas bubbles, in the 15D pack the channels formed very regular networks at the end of the experiments, leading to lower mean saturations compared to the high permeability pack.

Figure 2-29: Stages of oil displacement by liberated gas from a lens-type high permeability pack following initial nucleation in the surrounding low permeability pack (from Chatenever et al 1959)

The efficiency of a depressurization process is commonly measured and understood in terms of the critical gas saturation i.e. the gas saturation at which the liberated solution gas becomes sufficiently mobile. Knowledge of critical gas saturation ($S_{gc}$) and at what pressure it might occur is also indispensable in answering key practical questions such as at what point in the depressurization process will sufficient amount of gas be released in order to fulfil gas contractual obligations and what capacity of back produced water facilities would be needed (Ligthelm et al, 1997). Values of $S_{gc}$ reported based on experiments on reservoir type core samples vary between 0.6% (Firoozabadi et al, 1992) to 26.4% (Madaoui, 1975) of pore volume. The dependence of $S_{gc}$ on depletion rate, interfacial tension, initial water saturation, oil viscosity, and system size has been widely studied. The results are often inconsistent or contradictory, partly due to differences in data acquisition and interpretation methods but perhaps mainly because of lack of clarity about the fundamental processes involved. Thus, as will be shown presently, there seems to be a prevailing consensus that each depressurization study is unique. An example of a fundamental difference of opinion, which unfortunately is common place with respect to the interpretation of specific aspects of depressurization, concerns the reproducibility of bubble nucleation. While researchers like Li and Yortsos (1991) consider bubble
nucleation to be essentially a random phenomenon that cannot be reproduced, the work of others like El Yousfi et al (1992, 1997) suggests nucleation is reproducible.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>$K_{mD}$</th>
<th>$S_{gc}$, %</th>
<th>DP Rate, psi/day</th>
<th>$S_{gc}$ vs. DP Rate</th>
<th>$S_{wi}$, fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petersen et al (Brent Group, Statfjord Field)</td>
<td>2004</td>
<td>990</td>
<td>6.4 - 12.2</td>
<td>115 - 731</td>
<td>increase with</td>
<td>0.179 - 0.619</td>
</tr>
<tr>
<td>Petersen et al (Brent Group, Statfjord Field)</td>
<td>2004</td>
<td>711</td>
<td>8.4 - 13.4</td>
<td>115 - 731</td>
<td>increase with</td>
<td>0.173 - 0.731</td>
</tr>
<tr>
<td>Drummond (South Brae Field - North Sea)</td>
<td>2001</td>
<td>292</td>
<td>2.5</td>
<td>99</td>
<td>-</td>
<td>0.23</td>
</tr>
<tr>
<td>Egermann and Vizika</td>
<td>2001</td>
<td>3.2</td>
<td>24.0</td>
<td>2304</td>
<td>-</td>
<td>0.55</td>
</tr>
<tr>
<td>Naylor et al (Miller Field)</td>
<td>2001</td>
<td>27</td>
<td>21.0</td>
<td>765</td>
<td>-</td>
<td>0.52</td>
</tr>
<tr>
<td>Naylor et al (Miller Field)</td>
<td>2001</td>
<td>492.5</td>
<td>6.0 - 16</td>
<td>89 - 26</td>
<td>increase with</td>
<td>0.70 - 0.73</td>
</tr>
<tr>
<td>Sahni et al</td>
<td>2001</td>
<td>2000, 2060</td>
<td>6.0 - 11.0</td>
<td>increase with</td>
<td>0.0213</td>
<td></td>
</tr>
<tr>
<td>Kumar et al</td>
<td>2000</td>
<td>1250, 1180</td>
<td>3.0 - 7.0</td>
<td>increase with</td>
<td>non-monotonic</td>
<td></td>
</tr>
<tr>
<td>Kamath and Boyer</td>
<td>1995</td>
<td>0.1</td>
<td>10.0</td>
<td>20</td>
<td>non-monotonic</td>
<td></td>
</tr>
<tr>
<td>Kamath and Boyer</td>
<td>1995</td>
<td>0.04</td>
<td>10.0</td>
<td>20 - 100</td>
<td>non-monotonic</td>
<td></td>
</tr>
<tr>
<td>Firoozabadi et al (Berea)</td>
<td>1992</td>
<td>605</td>
<td>1.1 - 2.0</td>
<td>increase with</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Firoozabadi et al (Chalk)</td>
<td>1992</td>
<td>2.7</td>
<td>0.6 - 1.2</td>
<td>increase with</td>
<td>0 Virgin - watered out</td>
<td></td>
</tr>
<tr>
<td>Kortekaas and van Poelgeest (Brent)</td>
<td>1991</td>
<td>230 - 1900</td>
<td>4.0 - 8.0</td>
<td>10 - 230</td>
<td>increase with Virgin - watered out</td>
<td></td>
</tr>
<tr>
<td>Kortekaas and van Poelgeest (Brent)</td>
<td>1991</td>
<td>200 - 1100</td>
<td>7.0 - 10.0</td>
<td>10 - 230</td>
<td>increase with Virgin - watered out</td>
<td></td>
</tr>
<tr>
<td>Moulu (St Maximin limestone)</td>
<td>1989</td>
<td>211.10</td>
<td>6.6 - 12</td>
<td>0.44 - 72.5</td>
<td>increase with Non-monotonic</td>
<td></td>
</tr>
<tr>
<td>Madaoui</td>
<td>1975</td>
<td>4.4 - 26.4</td>
<td>0.78 to 170</td>
<td>377 -</td>
<td>increase with</td>
<td></td>
</tr>
<tr>
<td>Handy</td>
<td>1958</td>
<td>7.41</td>
<td>5.0 - 16.0</td>
<td>172800</td>
<td>increase with</td>
<td></td>
</tr>
</tbody>
</table>

An often debated issue is how the critical gas saturation should be defined and quantified. Is it the gas saturation at which gas is first produced? This is obviously inadequate as it will be dominated by the nucleation and growth of bubbles near the production outlet. Yortsos and Parlar (1989) offered an improved definition of $S_{gc}$ as the saturation at the formation of the first spanning cluster. But this is still unsatisfactory because even when this definition might be easy to implement in modelling situations, spanning clusters may not be easily visualized in physical experiments. Furthermore, spanning clusters may never form in the presence of strong gravity and viscous forces. Thus the definition of $S_{gc}$ by Du and Yortsos (1999) as the gas saturation at the onset of bulk flow, may be considered more general. Lately, Tsimpanogiannis and Yortsos (2004) proposed a definition of $S_{gc}$ for systems with strong gravity and viscous forces as the saturation at the onset of migration. The foregoing demonstrate that interpretation of
depressurization studies does not follow any standard conventions and this fact must always be acknowledged in any attempt to compare results of different depressurization studies even when exactly the same set ups and samples have been used.

We next examine some of the factors that may affect the critical gas saturation. Table 2-1 gives a summary of a range of $S_{gc}$ values obtained by conducting depletion experiments on porous media with absolute permeability, $S_{wi}$, and depletion rates in the ranges 0.04 - 2060mD, 0 - 73%, and 0.44 - 172800psid/day, respectively. Increase in depletion rate is generally known to increase bubble density which will in turn lead to an increase in $S_{gc}$. But the data of Kamath and Boyer (1995) and that of Madaoui (1975) in Table 2-1 showed otherwise. For the two cores (0.04mD and 0.1mD) used by Kamath and Boyer (1995), increasing the depletion rate from 20psi/day to 100psi/day had no effect on the $S_{gc}$. The results of Kamath and Boyer (1995) supports the conclusion that tight cores may require far larger time scales for equilibration to occur. This means that extremely low depletion rates will be needed to reduce the $S_{gc}$ from the values achieved at typical lab depletion rates. The work of Stewart et al (1954) presents a set of data which illustrate how a depressurization experiment can be easily misrepresented. The authors reported an increase in oil recovery from 22% to 36% of the original pore space of a 200mD Cordova shellstone as the depletion rate was increased from 10psi/day to 230psi/day. Examination of Figure 2-30 from Stewart et al (1954) shows that the flow of gas (indicated by the relative permeability ratios) in fact began at a lower gas saturation (2%) in the 230psi/day experiment than in the 10psi/day experiment (7%).
Although some authors (Kortekaas and van Poelgeest, 1991) have questioned any correlation between $S_{gc}$ and permeability, in Table 2-1, except for the data of Firoozabadi et al (1992), the high $S_{gc}$ values tend to correspond to the cores with the lowest permeability values albeit in a somewhat non-monotonic way (assuming we ignore the effect of depletion rate for a moment). Chatenever et al (1959) have already reported that less permeable media might possess lower bubble nucleation thresholds. But the weak correlation between critical gas saturation and permeability in Table 2-1 could also be justified by considering that samples with smaller average pore radius would more likely support dendritic bubble growth patterns that are not easily biased by gravity or viscous forces.

Based on a series of experiments on a connate-water saturated 550mD core from the Brent field, Kortekaas and van Poelgeest (1991) observed two effects of a change in IFT on the depressurization process: an decrease in IFT led to a decrease in the rate of gas saturation build up, which in turn led to a decrease in $S_{gc}$ but in a non-monotonic way. Increasing IFT from 0.1mN/m to 0.25mN/m decreased $S_{gc}$ from 18.5% to 16.5%, but as IFT increased from 1mN/m to 5mN/m, $S_{gc}$ increased from 12% to 14% (Figure 2-31). Similar results have been reported by Mackay et al (1998) from experiments conducted on micromodels. The accepted explanation for this phenomenon is based on the energy balance principle. A decrease in IFT lowers the energy threshold for the formation of a new interface and bubbles therefore nucleate more rapidly. At very low IFTs bubble
nucleation becomes instantaneous, needing only the slightest degree of super-saturation to occur.

![Figure 2-31: The impact of gas/oil IFT on the gas saturation profile (from Kortekaas and van Poelgeest, 1991)](image)

Data on the impact of $S_{wi}$ on $S_{gc}$ does not show a clear pattern. Kortekaas and van Poelgeest (1991) reported a doubling of critical gas saturations from <4% to 5 - 8% as $S_{wi}$ was changed from virgin to watered-out conditions for three sandstone core samples (230mD, 550mD, and 1900mD) obtained from a Brent Group reservoir, while for two other samples (200mD and 1100mD) obtained from another Brent Group reservoir, an increase in $S_{wi}$ had a negligible effect on $S_{gc}$ – virgin and watered out stabilised between 7 - 10%. The differences in the trends of $S_{wi}$ and $S_{gc}$ between the two reservoirs were assumed to result from the differences in the mineralogical and morphological properties of the reservoir rocks. The two reservoirs were shown to have quite different clay structures, with one reservoir containing kaolinite-like sharp-edged booklets which could form preferred sites for bubble nucleation. The data of Peterson et al (2004) showed a consistent decrease in $S_{gc}$ as $S_{wi}$ increased over a range of depletion rates for two core samples (990mD and 711mD) from the Statfjord field in the North Sea. The authors Dominguez et al (2000), Mackay et al, (1998) and Hawes et al, (1994) all independently reported bubble nucleation in three phase systems to be more likely to occur in the less wetting oleic phase, suggesting that the wetting characteristics of a porous medium could have a significant impact on the depressurization process. Figure 2-32 reproduced results of micromodel experiments of Dominguez et al. (2000) and clearly shows the impact of
contact angle (or wettability) on nucleation density – bubble density increases as contact angle increases.

![Figure 2-32: Gas cluster distributions in a micromodel for various wettabilities. The number of growth sites decreases with the wettability (from Dominguez et al, 2000). The results were obtained for DP/DPsat = 0.63 and θ =0 rad (a), θ =0.66 rad (b) and θ =0.82 rad (c).](image)

2.3.2 Theories of Bubble Nucleation and Growth

Bubble production is a phenomenon that is of extreme importance to a wide array of geological, biological and commercial processes, such as the sudden degassing of magma that may cause volcanic eruptions, the formation of nitrogen in the blood stream of divers as they rise to the surface, the use of dissolved air bubbles in underground waste management to carry particulate species to the surface, the production of effervescence in carbonated beverages, etc. Thus the literature dealing with bubble production is vast. The aim of this review is to selectively highlight aspects of this literature that directly relates to the understanding of the mechanisms of depressurization in hydrocarbon reservoirs. An excellent comprehensive review of the subject can be found in Jones et al (1999) and Blander (1979).

Nucleation in the context of solution gas drive can be defined as the localized development of a distinct thermodynamic phase as a result of supersaturation. Supersaturation is a measure of the tendency of a gas-liquid system that is being depressurized to nucleate and it is expressed as a pressure difference between the gas and the liquid phases. Nucleation is possible only when the gas pressure ($P_g$) is greater than the liquid pressure ($P_l$). With the use of Henry’s law, this pressure difference ($ΔP$) may be expressed in terms of the gaseous phase mass concentration $C(t)$ and its solubility constant ($K$) according to the relation:
\[ \Delta P = P_g - P_l = KC(t) - P_l(t) \geq 0 \] (2-16)

2.3.2.1 Theories of Bubble Nucleation and Growth in Bulk Fluids

The classical mechanistic description of nucleation identifies broadly two nucleation types: (1) Homogeneous nucleation and (2) Heterogeneous nucleation.

Homogeneous nucleation occurs exclusively within the bulk liquid in the absence of any cavities before the liquid became supersaturated, Figure 2-33. High levels of supersaturations are required to initiate homogeneous nucleation. Even though bubbles formed in this way immediately migrate upwards, subsequent nucleation at or near a nucleation site is unlikely to occur. Equation (2-17) (see Blander and Katz, 1975 for full derivation) can be used to estimate the rate of bubble nucleation (number of bubbles formed per unit volume per unit time) under homogeneous conditions.

\[ J = A \exp \left( -\frac{B}{\Delta P^2} \right) = N \left( \frac{2\sigma}{\pi m \bar{b}} \right)^{1/2} \exp \left( -\frac{16\pi \sigma^3}{3kT \Delta P^2} \right) \] (2-17)

where \( m \) the mass of a molecule, \( \sigma \) the interfacial tension, \( N \) is the number of molecules per unit volume, \( kT \) is thermal energy, \( \bar{b} \equiv 2/3 \), \( A \) is the pre-exponential factor (associated with the number of molecules), \( B \) is associated with the energy required for the creation of the interface, and \( \Delta P \) the difference between the vapour pressure of the gas and the ambient pressure.

Heterogeneous nucleation occurs in two stages. Firstly, a sudden increase in supersaturation by a sudden drop in pressure leads to the formation of bubble nuclei in an otherwise initially homogeneous liquid phase that was free of any gas cavities. These initial bubbles may form inside pits on the surface of the container, on particles within the bulk liquid, on solid surfaces, and in the liquid itself. As the initial nuclei grow, migrate and
are produced, they leave behind gas-filled cavities from which the second phase of bubbles can be produced. The bubble nucleation rate after the initial seeding phase decreases drastically because of the lower supersaturation. Equation (2-18) may be used to calculate heterogeneous nucleation rate. Figure 2-34 shows a schematic representation of classical heterogeneous nucleation process.

\[
J = \frac{\overline{A}_n}{\Delta \rho} = N^{2/3} \left( \frac{2\sigma}{\pi mbF} \right)^{1/2} \exp \left( -\frac{16\pi \sigma^3 F}{3kT \Delta \rho^2} \right)
\]

Equation (2-18) has the same structure as Equation (2-17) but with the factors \( S \) and \( F \) introduced to account for wettability and the geometry of liquid-surface interface that host the nuclei. Blander, (1979) also found (based on calculation of the factor \( F \)) that increased steepness of cavity walls improves nucleation potential.

Figure 2-34: Classical heterogeneous nucleation, with impurities in the bulk fluid and crevices in the medium acting as catalysts.

Bubble nucleation is followed by bubble growth. The classic description of the bubble growth process in bulk fluid couples the equation of motion of the gas-liquid interface in an infinite ambient fluid under a constant ambient pressure, Equation (2-19), to the conservative equation of the diffusive species, Equation (2-20) (Szekely and Fang, 1973; Scriven, 1959).

\[
P_g - P_\infty = \frac{2\sigma}{R} + 4\mu \frac{\dot{R}}{R} + \rho \left( \frac{3}{2} \dot{R}^2 + R \ddot{R} \right)
\]

\[
\frac{\partial C}{\partial t} + \left( \frac{R}{r} \right)^2 \dot{R} \frac{\partial C}{\partial r} = D \left[ \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right]
\]

where in Equation (19), \( R \) is the instantaneous bubble radius, \( P_g \) is the pressure within the bubble, \( P_\infty \) is the pressure some distance from the bubble, \( \sigma \) the
interfacial tension, $\mu$ the fluid viscosity, and $\rho$ the fluid density. Where in Equation (20), $C$ is the concentration at a distance $r$ from the centre of the bubble and $D$ the molecular diffusion coefficient.

The terms on the right hand side of Equation (2-19) describe the contributions of surface tension, viscous forces and inertial effects respectively. Equation (20) describes the mass balance of dissolved gas diffusing across a region of spherical symmetry and of a constant mass density.

A solution to the problem of spherically symmetric growth controlled by diffusion was presented by Scriven (1959), Equation (2-21), and it gives the bubble radius as a function of the square root of the growth time $t$.

$$R = 2\beta \sqrt{Dt}$$

where, the dimensionless parameter $\beta$ is related to the supersaturation of the system.

We next examine theories of the nucleation and growth of bubbles within liquids that occupy porous media. Considerations of the topology and microstructure of porous media strongly suggests that not only would bubble growth patterns and rates of growth differ between bulk fluids and fluids that reside in constricted spaces in porous media but the inherent roughness of the pore walls may result in significantly different nucleation characteristics between depressurization in bulk fluids and in porous media. Figure 2-35, from the experimental observations of Dominguez et al, (2000), compares bubble growth in a Hele-Shaw cell and in a micromodel and vividly demonstrates that while the growth pattern in the bulk fluid is compact, in the porous media it is dendritic and ramified. Some of the earlier theoretical models of bubble growth in porous media do not sufficiently account for these features, leading to inconsistent and unsatisfactory results (Kashchiev and Firoozabadi, 1993; Hunt and Berry, 1956; Kennedy and Olson, 1952). Progress is however being made towards developing representative models of bubble nucleation and growth in porous media.
2.3.2.2 Theories of Bubble Nucleation and Growth in Porous Media

In the large body of literature published on phase transitions only few have addressed the problem of phase change within porous media but there is a general recognition that nucleation in porous media is predominantly heterogeneous in nature. The high levels of supersaturation required by homogeneous nucleation are not commonly observed in porous media (Shen and Debenedetti, 2003; Wilt, 1989). Porous media also possess features, such as the presence of impurities, cavities, and, in the case of hydrocarbon reservoirs, poorly wetted surfaces, all of which according to classical nucleation should favour heterogeneous nucleation processes.

Moulu (1989) presented a model of nucleation that adapted the thermodynamically based classical heterogeneous nucleation model for predicting nucleation behaviour in porous media using the expression:

\[ J = Z \exp \left( \frac{-16\pi \sigma^3}{3KT(P_g-P_o)^2} \right) \]  

(2-22)

where, \( J \) is the number of nuclei formed per unit time per unit volume, \( \sigma \) the interfacial tension, \( P_g - P_o \) the pressure difference between gas and oil (also indicative of supersaturation), \( KT \) the translational energy of a molecule, and \( Z \) a pre-factor (obtained by curve fitting earlier experiments) that attempts to capture diffusion effects and kinetic considerations.

Diffusion was modelled using Fick’s law and spherical symmetry, and the agreement with experiment was satisfactory.

![Figure 2-35: Comparison of the shape of a growing bubble in (a) a Hele-Shaw cell, and (b) a micromodel (Dominguez et al, 2000)](image)
Firoozabadi and Kashchiev (1996) used a classical expression for nucleation rate to investigate whether the process of nucleation in porous media is progressive (where new bubble nuclei continuously appear in the course of the depressurization process), or instantaneous (where all bubble nuclei form at once and only grow afterwards). The expression used to estimate the bubble growth rate, Equation (2-23), contains a time-independent shape factor $a$ to account for the irregular geometry of bubble growth in porous media.

\[
\left\{ \begin{array}{l}
V_g(t) = V_0 \int_0^t J(t') v_b(t, t') dt' \\
v_b(t, t') = ar^3(t - t') = a \left[ \int_{t'}^t G(t'' - t') dt'' \right]^3
\end{array} \right. \tag{2-23}
\]

where, $V_0$ is the initial volume of liquid, $v_b(t, t')$ the volume at time $t$ of a bubble nucleated at time $t' < t$.

By comparing predicted and experimentally observed supersaturation profiles at various pressure decline rates, Firoozabadi and Kashchiev (1996) came to the conclusion that nucleation in pre-existing cavities is more likely an instantaneous nucleation (IN) mechanism than a progressive nucleation (PN) mechanism. This is in sharp contrast to the conclusion reached by Yortsos and co-workers (Li and Yortsos 1993, 1991; Yortsos and Parlar, 1989) who suggested that nucleation in porous media is essentially heterogeneous and progressive. Yortsos and co-workers also proposed an expression for evaluating the nucleation threshold which assumes that crevices in the pores walls are the most active nucleation sites. In PN, the crevices may bud new nuclei or may already contain pre-existing bubbles. A crevice is assumed to be activated if the local supersaturation exceeds the capillary threshold of the crevice according to:

\[
(KC - P_l) \geq \frac{2a \cos \theta}{\omega} \tag{2-24}
\]

where, the term in the bracket represents the supersaturation, $K$ is the gas solubility constant, $C$ the local dissolved gas concentration, $P_l$ the local liquid
pressure, $\sigma$ the gas/liquid interfacial tension, $\omega$ the crevice radius (Figure 2-36) and $\theta$ the contact angle ($0 < \theta < \pi/2$).

Thus, it is easy to see that bubble density is a function of crevice size distribution. Since different crevices will activate at different degrees of local supersaturations, bubble density will depend on the depletion rate and how the overall porous medium microstructure governs the diffusive mass transfer process.

Bauget and Lenormand (2002) expanded the concept of a pre-existing bubble to include the possibility of bubble collapse by a review of equilibrium condition for bubble stabilization. They stated that if the mechanical equilibrium condition for gas and liquid in contact at a planar interface is given by:

$$P_G = P_L = P_{equ}$$  \hspace{1cm} (2-25)

where, $P_{equ}$ is the equilibrium pressure at saturation on the planar interface, $P_G$ the gas pressure and $P_L$ the liquid pressure.

For a bubble of radius $r$ in a liquid, the equilibrium conditions require that the liquid pressure be lower than the equilibrium pressure. The capillary pressure is defined as:

$$P_C = P_{equ} - P_L$$  \hspace{1cm} (2-26)

This is an unstable equilibrium and the smallest perturbations of the liquid pressure or bubble radius ($2\sigma/r \pm \varepsilon$) can lead to either a collapse or the activation of the bubble. Bauget and Lenormand (2002) showed that for nucleation from pre-existing crevices the stabilization of microbubbles depends strongly on pore wall roughness that allows a
meniscus to have any contact angle, adding that wettability is of secondary importance to explaining bubble density. They also show that entrapped microbubbles in cavities can withstand overpressurization because gas dissolution can only take place to the point where a new chemical and mechanical equilibrium condition are achieved after the adaptation of the meniscus curvature.

Li and Yortsos, (1995) presented a model of the growth in porous media of a nucleated bubble driven by the diffusive mass transfer of dissolved light components from liquid into the nucleated bubble. Mass transfer was governed by the standard convection-diffusion equation as expressed by Equation (2-27):

\[
\frac{\partial C}{\partial t} + u \nabla C = D \nabla^2 C \tag{2-27}
\]

where, \(D\) is the molecular diffusivity and \(u\) is the velocity. Through the ideal gas law, the net mass transfer into a bubble is given as:

\[
M_w \frac{dn_k}{dt} = \int_{A_k} D \frac{\partial C}{\partial n} dA \tag{2-28}
\]

where, \(M_w\) is the molecular weight of the gas, \(n_k\) the number of moles of gas in bubble \(k\), and \(A_k\) the normal surface area of bubble \(k\) through which gas can be transported.

The rise in internal bubble pressure (for a fixed volume) following gas diffusion was modelled as:

\[
V_k \frac{dp_g}{dt} = R_g T \frac{dn_k}{dt} \tag{2-29}
\]

where, \(V_k\) is bubble volume, \(T\) is temperature and \(R_g\) is gas constant (~ 8.314 JK-mol-1).

The internal bubble pressure continues to rise until it exceeds the lowest capillary threshold of the neighbouring liquid-filled pore. The bubble then expands into the new pore and its pressure and volume change according to the expression:
\[ p_g \frac{dv_k}{dt} + v_k \frac{dp_g}{dt} = R_g T \frac{dn_k}{dt} \] (2-30)

It seems that the best hope of ironing out some of the controversies and misunderstandings that surround the design and interpretation of depressurization experiments lies in the development of a conceptual tool that permit the examination of the issues involved from fundamental physical principles. Pore network modelling is an example of such a tool and the next chapter will present a description of a practical implementation strategy that borrows from the theoretical works of Yortsos and co-workers. The model to be presented builds on the work of McDougall and Mackay (1998), Bondino et al (2005) and Ezeuko et al, (2009) to examine more closely the impact of a range of system variables (gravity, IFT, spreading coefficient, presence of fractures, wettability, rock fabric) on the depressurization process using carefully calibrated laboratory data.

### 2.4 Chapter Summary

This chapter has surveyed the historical development of PNM as a numerical technique for describing fluid flow and transport in porous media at the microscopic level and quantifying porous media flow and transport properties at the macroscopic level. Examples of successful application of PNM to explain a range of multiphase flow phenomena have been presented whilst also highlighting current limitations that prevent its application to other phenomena. We then reviewed the fundamental physical principles – derived from experimental and theoretical studies – that ground our current understanding of the evolution of CO\textsubscript{2} injected into brine saturated porous media for storage, and the evolution of gas from oil undergoing depressurization in porous media.

The development of PNM has followed two main branches which are (a) the representation of the pore space and (b) the implementation of the flow physics. From the early days of capillary bundle models, the search for numerical analogues of rocks has come a long way. Whilst regular lattice networks offer a more realistic representation of the interconnectivity of porous media microstructure compared to the bundle of tube models, and are extremely useful for gaining fundamental qualitative insight into pore
scale phenomena, they are not very reliable for making rock-specific predictions. Prediction of flow and transport properties such as porosity, permeability, capillary pressure, and relative permeability characteristics require the use of geologically equivalent networks that capture the irregular nature of pore space geometry, the random distribution of coordination number and the existence of short range pore size correlations. The two broad approaches for generating predictive networks were reviewed: (1) the statistical anchoring approach – networks are generated using pore size distribution and pore space connectivity data available from routine laboratory measurements, such as mercury injection capillary pressure curves (MCIP) etc, and (2) pore space reconstruction approach – the generation of networks from digital images of real or synthetic porous media.

The review of the basic concepts in multiphase flow in porous media such as surface and interfacial tension, wetting and spreading phenomena, capillary and interfacial forces, introduced the fundamental building blocks upon which the implementation of microscopic flow mechanisms depends. The choice of the approach to use to implement multiphase flow physics on pore networks have historically been driven by the objectives of the study. In quasi-static models, microscopic displacement events are assumed to be governed by the equilibrium capillary pressure, with viscous and sometimes gravity forces considered negligible. Dynamic models on the other hand, account for the effects of viscous and gravity forces on multiphase flow behaviour.

The role of gravity as a perturbing force during the flow of a lighter fluid phase within a denser phase was examined from accounts of experimental and modelling studies. Depending on the flow configuration, gravity could be made to have a stabilizing or a destabilizing effect on flow. There is strong experimental evidence that gravity destabilized flow may take two distinct forms: either flow fingering at small to moderate gradients or spontaneous migration when the gradient is sufficiently high. While there have been substantial improvements in the modelling of gravity driven flow at both microscopic and macroscopic scales, most models have not adequately represented the essential features of buoyancy driven migration e.g. the dispersive flow phenomenon. One of the key goals of this thesis is to develop a model, described in the next chapter, which accounts for these often neglected features.
There is as yet scant experimental and field data to support the widely held assumptions about the trapping mechanisms of CO\textsubscript{2} injected into saline aquifers for storage. It is increasingly recognised that some assumptions inherent to standard simulation workflows (which have historically been used for evaluating hydrocarbon reservoirs) may not be optimised for evaluating CO\textsubscript{2} storage. This is in consideration of the differences in flow, transport and physico-chemical processes between CO\textsubscript{2} storage and hydrocarbon recovery and the fact that far less petrophysical and geological information is likely to be available about aquifers than oil and gas reservoirs. Frequently encountered modelling challenges – e.g. the inability to obtain reliable upscaling of CO\textsubscript{2} solubility and residual (relative permeability) trapping, or the lack of a well parameterised model of the initiation and propagation of CO\textsubscript{2} convective mixing – points to a theoretical knowledge gap about the fundamental microscopic processes involved. This thesis attempts to bridge some of this gap by exploring the complex interplay of a variety of microscopic processes affecting subsurface migration of CO\textsubscript{2} injected for storage.

Depressurization (the production scheme of simply withdrawing fluid from a reservoir and allowing dissolved gas to be liberated as the pressure falls below bubble point) has lately found new scope as an economically viable and an environmentally friendly option for exploiting mature oil and gas fields. But outstanding conceptual and theoretical issues have prevented the articulation of clear general principles that will aid the formulation of practical implementation guidelines in the field. Evidence from experiments about the fluid, rock, thermodynamic and operational factors that may control the efficiency of a depressurization process are not only scarce but often contradictory. The challenges of disentangling the role of various interdependent aspects of the depressurization process are made even worse by the ever varied approaches to data acquisition and interpretation. Nevertheless, based on experimental results and theoretical consideration, opinion is converging on some facts: that bubble nucleation in porous media is a heterogeneous process, mostly from pre-existing cavities; that recovery efficiency increases with an increase in the pressure depletion rate and a decrease in the interfacial tension.