

Transport Phenomena Modelled on Pore-Space Images

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Doctor of Philosophy**

Declaration

I hereby declare that this thesis titled ‘Transport Phenomena Modelled on Pore-Space Images’ is entirely my own work otherwise is appropriately acknowledged. This work has not been previously submitted in its entire or in part to any other academic institute for a degree.

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Abstract

Fluid flow and dispersion of solute particles are modelled directly on three-dimensional pore-space images of rock samples. To simulate flow, the finite-difference method combined with a standard predictor-corrector procedure to decouple pressure and velocity is applied. We study the permeability and the size of representative elementary volume (REV) of a range of consolidated and unconsolidated porous media. We demonstrate that the flow-based REV is larger than for geometry-based properties such as porosity and specific surface area, since it needs to account for the tortuosity and connectedness of the flow paths.

For solute transport we apply a novel streamline-based algorithm that is similar to the Pollock algorithm common in field-scale reservoir simulation, but which employs a semi-analytic formulation near solid boundaries to capture, with sub-grid resolution, the variation in velocity near the grains. A random walk method is used to account for mixing by molecular diffusion. The algorithm is validated by comparison with published results for Taylor-Aris dispersion in a single capillary with a square cross-section. We then accurately predict experimental data available in the literature for longitudinal dispersion coefficient as a function of Peclet number. We study a number of sandpack, sandstone and carbonate samples for which we have good quality three-dimensional images. There is a power-law dependence of dispersion coefficient as a function of Peclet

number, with an exponent that is a function of pore-space heterogeneity: the carbonates we study have a distinctly different behaviour than sandstones and sandpacks. This is related to the differences in transit time probabilities of solute particles travelling between two neighbouring voxels.

We then study the non-Fickian behaviour of solute transport in porous media by modelling the NMR propagators and the time-dependent dispersion coefficients of different rock types. The behaviour is explained using Continuous Time Random Walk (CTRW) theory: transport is qualitatively different for the complex porous media such as carbonates compared to the sandstone or sandpack, with long tailing and an almost immobile peak concentration.

We discuss extensions of the work to reactive transport and the simulation of transport in finely-resolved images with billions of voxels.

The publications as a result of this work are:

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1. Introduction

Accurate modelling of flow and transport in porous media is of great importance in many scientific and engineering fields and a considerable body of research has been devoted to understand, model and quantify transport in porous media. However, understanding and accurate interpretation of the physics of transport phenomena in porous media is still a challenge for researchers and different types of investigation – analytical, experimental, and numerical – have been applied to study the generic behaviour of flow and solute transport.

In this work, we model flow and dispersion directly on micro-CT images of porous media with a resolution of a few microns. We apply a finite-difference approach in conjunction with a standard predictor-corrector method to simulate the flow on the pore-space images. Then we estimate permeability of a set of micro-CT images and investigate the validity of Carman-Kozeny equation. In addition, we study existence and size of representative elementary volume (REV) at the lamina (mm) scale. We investigate the REV of different rock types based on their static and dynamic properties. Then we model dispersion of solute particles based on the simulated velocity field. The simulations have been performed on high-porosity unconsolidated porous media as well as sandstones and carbonate rocks. The results highlight the generic behaviour of each type of porous medium.

This dissertation presents an applied methodology to simulate flow and dispersion on pore-space images. It also provides new insights into physics of the flow and transport in porous media along with relevant information from the literature.

In chapter 2, a detailed literature review and background on modelling and experiment on transport phenomena at the pore scale is presented.

In chapter 3, the process of generating micro-CT images as the main input for flow simulation and the method to simulate fluid flow directly on the images are described. Post-processing the data out of a micro-CT scanner, a binarized file can be generated to present the morphology of a core with a resolution of few microns. In the next step, this image can be used as an input for a flow simulator. A finite-difference technique in conjunction with a standard predictor-corrector method has been applied to discretize and decouple the governing equations of flow at the pore scale. Permeability has been computed and the validity of Carman-Kozeny correlation to estimate permeability without solving for the flow has been discussed. Furthermore, the size of representative elementary volume for different types of porous medium based on their static and dynamic properties is presented and a comparative investigation is performed for sandpacks, sandstones and carbonates.

In chapter 4, we describe the methods employed to model the dispersion of solute particles. This method uses a random-walk technique to capture diffusion of particles and a novel streamline-based method to model advection on the pore-space images. While the random-walk method is a known approach in the literature for modelling diffusion, the streamline method for advection applies a novel velocity distribution within voxels based on the face velocities and is able to capture the no-slip boundary condition exactly on the solid surfaces. Then the asymptotic dispersion coefficients of different types of porous medium for different regimes based on Peclet number are discussed. The scaling of the dispersion coefficient with Peclet number in complex geometries such as carbonates differs from that found in sandstones and sandpacks. Furthermore, we employ transit time

probability analysis to interpret the effect of heterogeneity on scaling of dispersion in the power-law regime.

Chapter 5 is devoted to study pre-asymptotic – also known as non-Fickian or anomalous – dispersion in porous media. We show that the generic types of transport behaviour emerge from pore-scale heterogeneity at the pre-asymptotic regimes. NMR propagators and the time-dependent dispersion coefficient are studied for sandpack, sandstone and carbonate samples. We interpret the pre-asymptotic dispersion with the continuous time random walk method which can clarify effect of heterogeneity at the pore scale on non-Fickian dispersion which has been observed in experiments and simulations.

Finally, chapter 6 summarizes results and provides conclusions and recommendations for further research.

2. Background

2.1. Pore Scale Modelling and Imaging

The accurate determination of rock and flow properties in porous media is of importance in many fields ranging from the design of enhanced oil recovery methods and CO₂ storage to contaminant transport and biomedical studies (Sahimi, 1995, Bear, 1972). Conducting physical experiments for understanding these properties and transport phenomena in porous domains is extremely difficult; numerical models are important to probe the range of behaviour that is not studied experimentally.

Scales of interest associated with porous media may vary from the molecular level (on the order of 10^{-11} m) to a mega level (10^6 m). The pore scale is of the order of a typical pore size which is in the range 10^{-7} to 10^{-4} m. Modelling fluid flows at the pore scale of a porous medium can provide a predictive tool for estimating rock and flow properties at larger scales and serve as a platform to study the physics of transport phenomena in porous media.

Pore-scale modelling has proved to be a reliable numerical approach to study flow at the micro scale to predict averaged macroscopic properties of porous media that are not possible or difficult to obtain experimentally. It can be used to predict single and multi-phase properties (Blunt et al., 2002) and it has a wide range of application in different

branches including petroleum and chemical engineering, groundwater flow, foam flow, the food industry, and biomedical sciences (Sahimi, 1995, McGreavy, 1992, Chen et al. 1991).

With progress in computing capabilities and the availability of modern processing systems, pore-scale modelling can provide simulation on larger domains and offer more accurate results for a wider range of processes. Furthermore, inspired by development in micro-model experiments, magnetic resonance and tomography imaging techniques, there has been an explosion of interest in pore-scale modelling (Adler, 1992, Blunt, 2001). The availability of detailed information on the microstructure of porous media has made pore-scale modelling a unique opportunity to investigate phenomena which are impossible or difficult to be obtained by laboratory experiments. Reviews on advances in pore-scale modelling are given by Celia et al. (1995) and Blunt (2001).

To model transport phenomena at the pore scale, the starting point is a three-dimensional description of the rock of interest. It is routine to obtain high-resolution two-dimensional thin section images (Zinszner and Meynot, 1982, Thovert et al., 1993) from which a three dimensional representation is constructed. This can be achieved using object-based methods, where grains of different size and shape are deposited (Øren et al., 1998) or an image is obtained that reproduces the statistics of the two-dimensional pictures (Adler et al., 1990, Hazlett, 1997, Roberts, 1997, Okabe and Blunt, 2004). The advent of X-ray computed tomography (micro-CT scanning) has made it possible to obtain three-dimensional images with a resolution of a few microns (Flannery et al., 1987, Coenen et al., 2004) which is sufficient to capture the pore space of many reservoir rocks. Using images obtained this way, one can avoid approximations caused from process-based and statistical-based image reconstruction techniques. Figure 2.1 shows the micro-CT scanner used at Imperial College to obtain the images used in this work. A review on applications of X-ray tomography in hydrogeology is given by Wildenschild et al. (2002).



Figure 2.1: The micro-CT scanner at Imperial College that was used to capture the micro-structure of rock samples in this study.

Post processing these images, a matrix can be generated for a core which shows whether there is a solid or a pore inside the voxel. Zero means that voxel is a pore and one means it is a solid phase. The binarized images can serve as an input for flow simulation at pore scale. Then, different approaches can be applied to model the fluid flow on the generated images.

2.2. Methods to model flow

2.2.1. Network models

Traditionally the pore geometries obtained from micro-CT imaging are used to extract a network model that then simulates the flow in the networks. In network modelling which was pioneered by Fatt (1956) void spaces are represented by a network of pores connected by throats – see Figure 2.2. To extract a network from a pore geometry, one must use an algorithm for distinguishing the pores and throats. There are several algorithms in the literature for extracting a set of pore bodies and pore throats from a

micro-CT image: the medial axis based method (Lindquist et al., 1996), the Voronoi diagram based method (Ripley, 1981, Bryant and Blunt, 1992), and the maximal ball method (Silin et al., 2003).

Network modelling can provide helpful insights into the physics of flow at the pore scale and has been successful in understanding and predicting trends in recovery with wettability and predicting single and multi-phase flow properties in porous media (Blunt et al., 2002, Patzek, 2001, Øren et al., 1998), non-Newtonian flow (Lopez et al., 2003), dispersion modelling (Bijeljic et al., 2004), and flow in fractures (Hughes and Blunt, 2001). However, the extraction of networks from a three-dimensional image, which relies upon an idealization of the pore morphology and topology, involves ambiguities as it is not easy to distinguish between pore bodies and throats in network extraction algorithms (Dong and Blunt, 2009). Furthermore, some complex pore geometries cannot be captured with network models (Arns et al., 2007, Ovaysi and Piri, 2010).

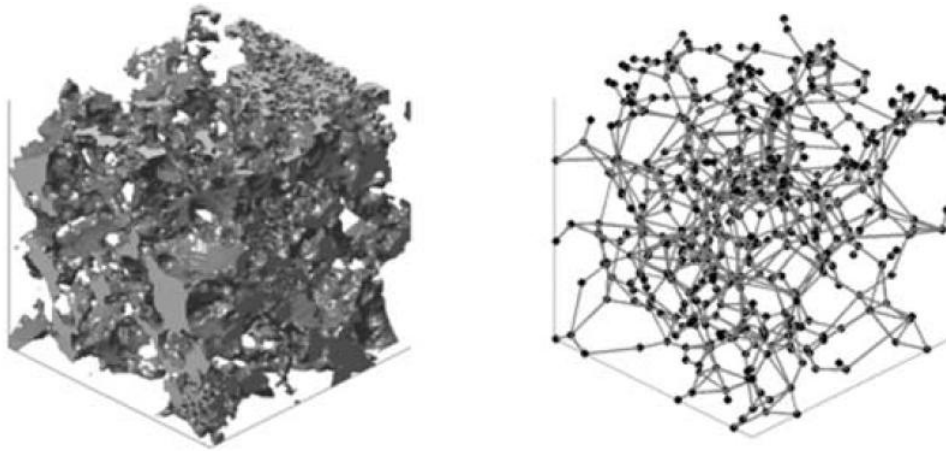


Figure 2.2: 3D section of micro CT image of Berea sandstone of 3×3×3 mm and its extracted network - reprinted from Bijeljic et al. (2004).

Given the mentioned limitations, it is natural to use three-dimensional binary images of pore-spaces to simulate transport phenomena directly on pore-space images to relax a number of simplifications inherent to network modelling, while the advances in X-ray tomography and three-dimensional image analysis techniques have made it possible to exploit the complex morphology of the pore spaces.

2.2.2. Direct numerical simulation

The availability of modern computing resources has made it possible to solve for fluid flow on micro-CT images without simplifications of the image geometry. For this aim, two approaches can be followed: conventional computational fluid dynamics methods which solve conservations of mass and momentum equations at the continuum scale; and unconventional numerical methods which solve flow at the mesoscopic scale using particles, of which the most commonly applied is the lattice Boltzmann method.

The lattice Boltzmann method is a popular platform for modelling flow in complex geometries (Maier et al., 1998, Pan et al., 2001, Pan et al., 2004, Jin et al., 2004, Knackstedt et al., 2004, Kang et al., 2006, Arns et al., 2007) because coding is straightforward and it can be readily parallelized (Piller et al., 2009). Although lattice Boltzmann is a powerful approach that is widely used, it is computationally demanding and requires the use of massively parallel computing approaches. At the same time, applying no-slip and constant-pressure boundary conditions is not straightforward (Noble et al., 1995, van Genabeek and Rothman, 1996, d’Humières and Ginzburgs, 2009).

Manwart et al. (2002) performed a comparative study of finite difference and lattice Boltzmann methods to simulate the permeability of three-dimensional porous media. They showed that in terms of memory, the lattice Boltzmann method required 2.5 times more memory than what was required by the finite-difference method. On the other hand, they stated that the computation times of the two methods are quite similar.

In this study, we use a finite difference approach to model the fluid flow. The finite difference method has been applied to model flow at the pore scale for a long time to predict the permeability of porous media (Adler, 1988, Schwartz et al., 1993, Kainourgiakis et al., 2005, Mourzenko et al., 2008, Silin and Patzek, 2009). Øren and Bakke (2002) applied a finite difference technique to solve for Stokes flow where pressure is assumed to vary only in the main direction of flow and obtained a good agreement for permeability predictions compared to experimental data for Fontainebleau sandstone. In addition, Øren et al. (2002) used a finite difference method for Stokes flow

to predict the permeability of three-dimensional reconstructions of the same sandstone at different porosity and further demonstrated a good agreement with the experimental data. Kainourgiakis et al., (2005) applied the same technique to predict the permeability of North Sea chalk and showed a good agreement with experimental data. Silin and Patzek (2009) estimated the permeability of slices taken through micro-CT image of a sandstone and then estimated the image permeability by taking the harmonic mean of the slices. In our work, we apply an efficient algorithm to compute permeability of porous rocks that allows us to use it on images containing up to 700^3 voxels.

For finite-difference simulation, the common assumption is that the flow at the pore scale can be considered creeping where inertial terms in Navier-Stokes equation can be ignored in comparison with viscous forces – also known as Stokes flow. Therefore, the governing equations of flow become linear. The only numerical challenge in solving Stokes flow is the coupling between pressure and velocity. In this study, we apply a numerical scheme based on pressure iteration (Patankar, 1980) and use a non-centered discretization to capture the no-slip boundary condition exactly on the surface of solid voxels. We have applied the method to simulate pressure and velocity directly on pore space images obtained from micro-CT scanning. We estimate permeability of a range of consolidated and unconsolidated porous rocks and study the effect of image size on predicted properties. In addition, we study the size of representative elementary volume (REV) of different types of porous media based on geometry-based and flow-based parameters.

2.3. Dispersion

When a miscible fluid is injected in a flowing fluid in a saturated porous medium, it will spread by various mechanisms including advection and diffusion. In the literature, dispersion is the spread or mixing of the miscible fluid due to all of these mechanisms (Bear, 1972). Dispersion occurs over multiple length scales from the pore to the field scale and the role of the pore scale has been shown to be of great importance (Sahimi, 1995, Rhodes et al, 2008). Dispersion is a non-steady and irreversible procedure and is of importance in many branches of science and engineering, such as enhanced oil recovery

techniques, sewage waste disposal, and ground water modelling (Sahimi, 1995, Bear, 1972, Adler, 1992).

In the absence of reaction between fluids and interaction of fluids and solid phase in porous media, dispersion is interplay of advection and diffusion. Advection is spreading of particles in porous media due to velocity variations between solid surfaces (caused by shear stresses) as well as velocity changes among pores due to the tortuosity of the pore space - Figure 2.3.

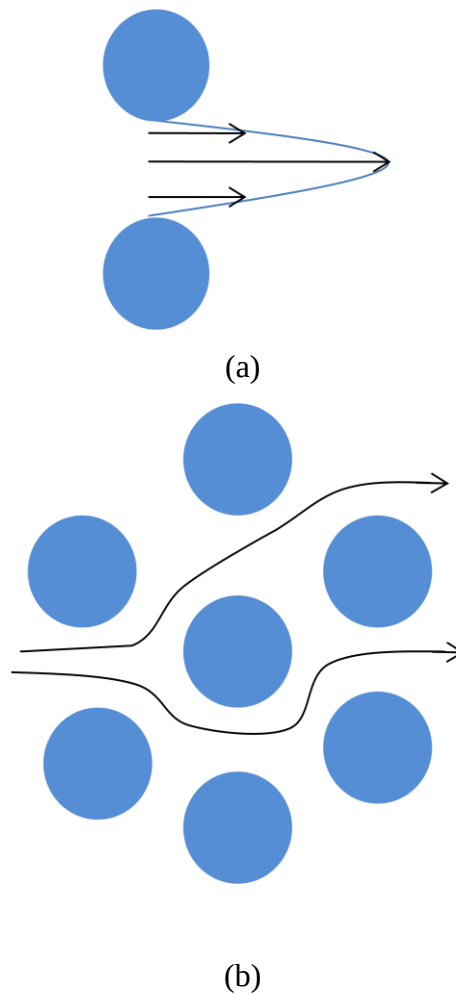


Figure 2.3: The advection contribution to the spreading of solute particles in porous media. The effect of velocity variation between two solid surfaces due to shear stress (a) and the effect of tortuosity of porous media on dispersion of solute particles (b) are shown schematically.

On the other hand, the diffusive spread of solute particles is due to the thermal motion of molecules. In a macroscopic approach, concentration gradients lead to a net diffusive flux; however diffusion – that is a random thermal motion – occurs even when there is no concentration gradient. Overall diffusion is a random motion with a net flux from high concentration to low concentration regions that results in a gradual mixing of the solute with an equilibrium state of uniform concentration.

Fick's law describes macroscopic diffusive net flux due to concentration gradient of solute species in a solvent:

$$J_{dif} = -D_m \nabla C \quad 2.1$$

where J_{dif} is net diffusive mass flux, C is concentration (mass per unit saturated pore space), and D_m is the diffusion coefficient. Diffusion coefficient is defined for a species in a solvent and has the dimension of L^2T^{-1} and is a function of temperature, fluid viscosity, and particle size. The diffusion coefficient in liquids is in range of $10^{-10} - 10^{-7} \text{ m}^2\text{s}^{-1}$.

From mass conservation we have,

$$\frac{DC}{Dt} = -\nabla \cdot J_{dif} \quad 2.2$$

Replacing equation 2.1 into the conservation of mass – equation 2.2 –, we obtain:

$$\frac{DC}{Dt} = D_m \nabla^2 C \quad 2.3$$

Taking into account the effects advection motion, the dispersion coefficient – D – can be replaced by the molecular diffusion in the equation 2.3 and in a Lagrangian reference frame we have:

$$\frac{DC}{Dt} = D \nabla^2 C \quad 2.4$$

In an Eulerian reference frame, the derivative with respect to time of a scalar is expanded through the multivariate chain rule and we obtain:

$$\frac{\partial C}{\partial t} + V \cdot \nabla C = D \nabla^2 C \quad 2.5$$

Equation 2.5 is known as advection-diffusion equation (ADE) in the literature (Sahimi, 1995, Lake, 1989, Bird et al., 1960). ADE has been traditionally the principal theoretical approach used to interpret and quantify solute transport in porous media.

For a one-dimensional transport in an infinite homogeneous porous medium where a plume with volume of W_0 is injected at $x=0$, the boundary and initial conditions are:

$$C(x,0) = 0 \quad 2.6$$

$$C(0,0) = C_0 \delta(x) \quad 2.7$$

$$C(\infty,t) = 0 \quad 2.8$$

Then the analytical solution for equation 2.5 can be presented as (Bear, 1972):

$$\frac{C(\xi,t)}{C_0} = \frac{W_0}{\phi} (4\pi Dt)^{-1/2} \exp\left(-\frac{(\xi - Vt)^2}{4Dt}\right) \quad 2.9$$

where ξ is displacement and ϕ is porosity of the porous medium. The concentration decays in time in an exponential form and can be treated as a Gaussian distribution function with mean and variance of $\bar{\xi} = Vt$ and $\sigma^2 = 2Dt$ respectively – see Figure 2.4.

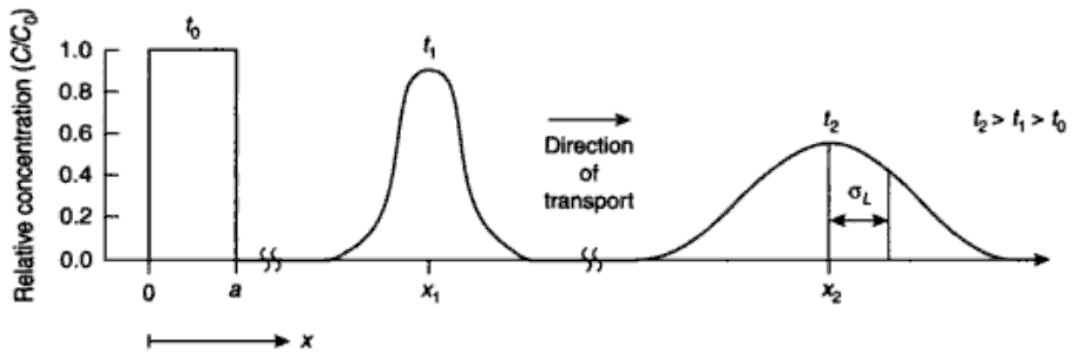


Figure 2.4: Fickian transport in a homogeneous one-dimensional porous medium. An injected plume will spread in a Gaussian profile with mean and variance of Vt and $2Dt$ respectively - reprinted from Fetter (1993).

In a homogeneous three-dimensional porous medium, we can assume an average macroscopic velocity in the main-direction of transport and then apply equation 2.9 to predict the average concentration in time. Based on ADE predictions, a plume of tracer in porous media will spread in a Gaussian manner and the second moment of the displacement grows linearly with time – this is named Fickian transport. However, from the early published research, fitting breakthrough curves with the ADE on column experiments, systematic errors have been reported that cannot be explained by measurement errors (Scheidegger, 1959, Aronofsky and Heller, 1957, Silliman and Simpson, 1987). These show that the fundamental assumption associated with the use of ADE that the dispersion coefficient is a constant, does not conform to experimental evidence at different scales. This regime of dispersion is called non-Fickian or anomalous dispersion. Following we will describe the dispersion coefficient of a porous medium in Fickian transport that can be used in ADE and can be measured as a property of a porous medium. Then we discuss non-Fickian transport at different length scales in porous media and CTRW as a framework able to interpret this anomalous behaviour.

2.3.1. Peclet number and asymptotic dispersion coefficient

In the literature, the asymptotic dispersion coefficient is studied for different regimes of Peclet number. Peclet number is a dimensionless number which describes the importance of advection in comparison with diffusion and is named after the French physicist - Jean Claude Eugène Péclet. This number is defined as the ratio of time needed for a particle to travel a characteristic length L by advection over the time needed to traverse the same length by diffusion (Sahimi, 1995, Bird et al., 1960).

$$Pe = \frac{u_{avg} L}{D_m} \quad 2.10$$

where u_{av} is the average velocity and L is the characteristic length of porous media. Average velocity is calculated from:

$$u_{av} = \frac{Q}{A\phi} \quad 2.11$$

where Q is volumetric flow rate in the model, ϕ is porosity, and A is the area perpendicular to the main direction of flow (the area of the inlet face).

Based on the Peclet number, dispersion for laminar flow is categorized in four separate regimes: restricted diffusion, transition, power-law, and mechanical dispersion (Pfannkuch, 1963, Sahimi, 1995, Koch and Brady, 1985). In the restricted diffusion regime, advection is negligible and diffusion controls the dispersion. This causes an isotropic dispersion in contrast with the other regimes of dispersion. In other words, a spherical plume spreads in a spherical shape while in regimes with advection effects the plume spreads as an ellipsoid, elongated in the main direction of flow, as indicated by the ADE.

In the restricted diffusion regime the dimensionless dispersion coefficient can be written as:

$$\frac{D}{D_m} = \frac{1}{\tau_{pm}} \quad 2.12$$

where D is dispersion coefficient, D_m is the molecular diffusion coefficient, and τ_{pm} is tortuosity of the porous medium.

In the transition regime, diffusion still is the main mechanism of dispersion but advection contributes to dispersion. It is not straightforward to have an equation to show the dependency of longitudinal dispersion coefficient on Peclet number in this regime. The transition regime is followed by a power-law regime. In the power-law regime there is a balance between advection and diffusion. In this regime, the dimensionless dispersion coefficient increases with Peclet number as a power-law scaling:

$$\frac{D}{D_m} \sim Pe^\delta \quad 2.13$$

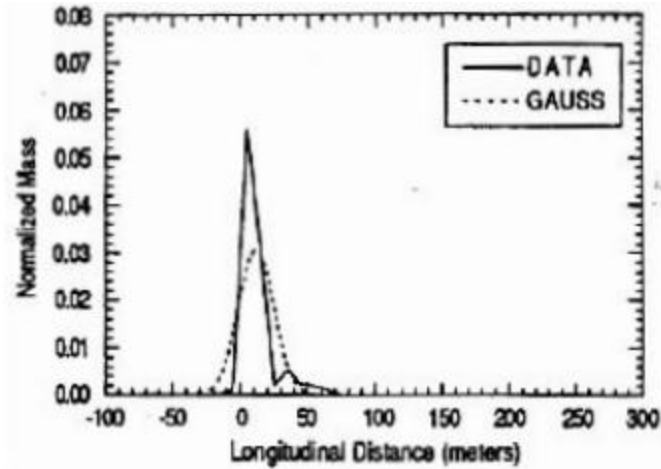
where δ depends on the heterogeneity of the porous medium (Bernabe and Bruderer, 2001).

For higher Peclet numbers, dispersion enters mechanical regime. In this regime, the role of diffusion is almost negligible and dispersion is purely governed by the velocity field in the porous medium. In this regime, dimensionless dispersion coefficient grows linearly with the Peclet number.

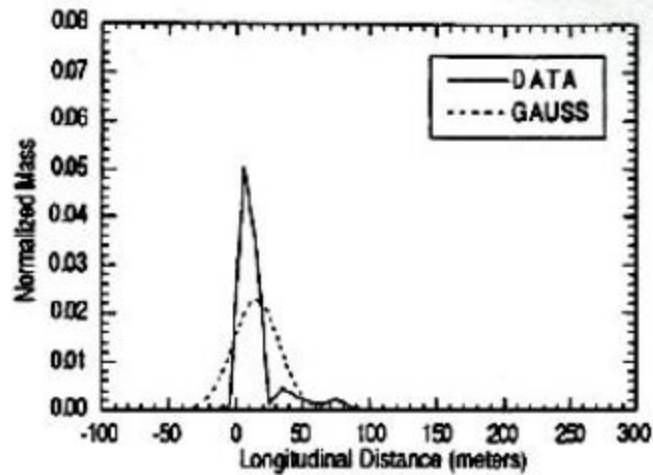
$$\frac{D}{D_m} \sim Pe \quad 2.14$$

2.3.2. Non-Fickian transport

The concept of anomalous or non-Fickian transport was pioneered by Montroll and Scher (1973) and has been demonstrated from the field to pore scales (Silliman and Simpson, 1987, Papathanasiou and Bijeljic, 1998, Adams and Gelhar, 1992, Levy and Berkowitz, 2003, Gouze et al. 2009). In a field scale experiment, Boggs et al. (1992) introduced a pulse of tracer to groundwater in a heterogeneous alluvial aquifer at the MADE site near Columbus, Ohio in the USA and deployed a three-dimensional network of wells to sample reservoir fluid over a 20 month period. Figure 2.5 shows the plume concentration as a function of longitudinal distance obtained from experiment. The concentration profile is highly asymmetric in the lateral plane. The dashed line shows the best Gaussian fit based on the ADE solution in an equivalent porous medium. The agreement is very poor and the ADE cannot capture the long tail and high peak associated with heterogeneous porous media.



(a)



(b)

Figure 2.5: The normalized mass of tracer versus distance on a field scale experiment (solid line) along with a Gaussian fit using the advection-dispersion equation (dashed line). Fickian transport is not able to capture the long tail and early time arrivals and the immobile high peak in heterogeneous porous media - reprinted from Boggs et al. (1992).

The non-Fickian behaviour has also been observed at the laboratory scale. Figure 2.6 illustrates a non-Fickian transport through a sandpack (Levy and Berkowitz, 2003). In contrast to prediction from the ADE, the dye plumes do not have a Gaussian profile. In addition, different plumes spread in non-identical asymmetrical shapes with a long tail. This is contrary to ADE predictions that an initially spherical dye plume will spread in a Gaussian profile to evolve an elliptic shape – see Figure 2.7.

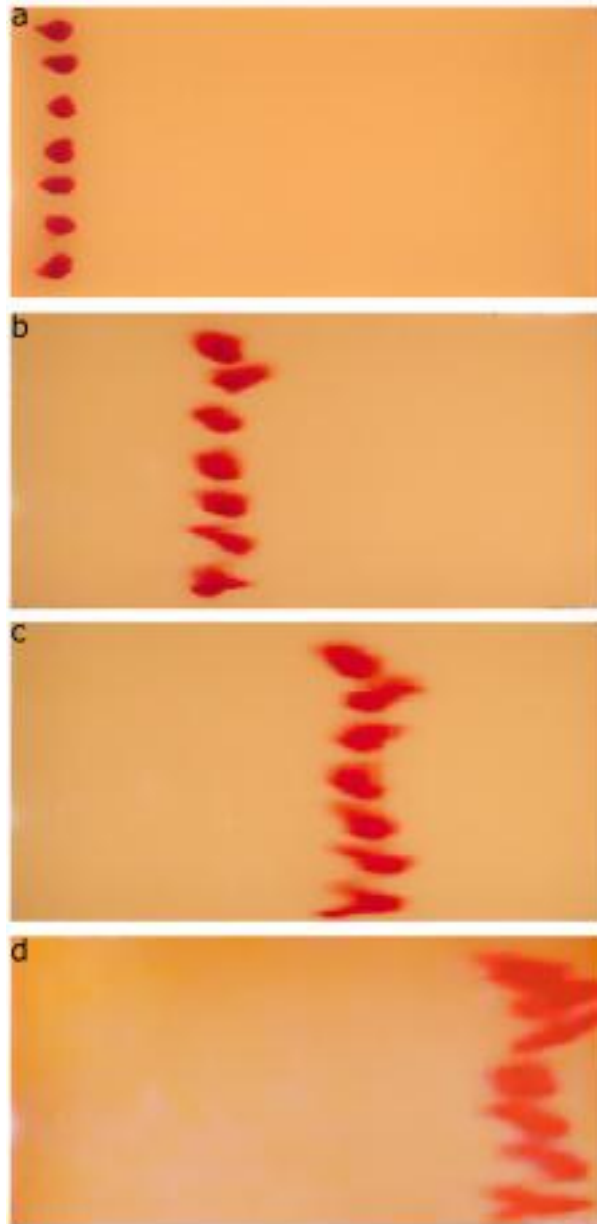


Figure 2.6: Transport of seven dye tracers through a saturated sandpack. The dimensions of the flow cell are 86 cm (length), 45 cm (height), and 10 cm (width). The injection is made at the constant rate of 53 mL/min from left to right and the tracers spatial profiles are captured at $t = 20$ (a), $t = 105$ (b), $t = 172$ (c), and $t = 255$ (d) minutes after injection. The non-Fickian transport can be seen in time through the porous media - dye plumes are not symmetrical ellipses. Furthermore, due to heterogeneity of the porous media shape of each of seven dye tracers is not the same as the other - reprinted from Levy and Berkowitz (2003).

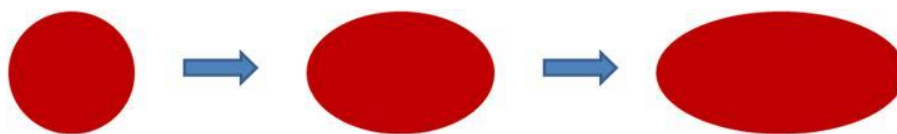


Figure 2.7: Evolution of a dye tracer in time as predicted by the ADE. It is symmetric in lateral plane and an initially spherical plume will spread in an elliptic shape as it moves through a porous medium.

2.3.3. NMR measurements

First, a brief description of basics of the nuclear magnetic resonance – NMR - imaging technique is given: a rigorous treatment can be found in Gladden (1994) and Callaghan (1991). NMR imaging is an advanced technique based upon the quantum magnetic properties of atoms' nuclei. A nucleus can be regarded as a particle spinning on its axis, which implies that nucleus has the property of nuclear spin angular momentum. Furthermore, as the nucleus is charged its intrinsic spin gives rise to a tiny magnetic dipole moment. The magnetic dipole moment of an atomic nucleus is directly proportional to its spin angular momentum. The vector sum of all individual magnetic moments of the spin nuclei yields a total magnetic moment or magnetisation. After placing the sample in a magnetic field, the spin system is excited by irradiation of the sample with electromagnetic radiation in the radio-frequency (RF) range of an appropriate frequency. This results in the nuclei absorbing photons from this radiation. When the irradiation stops, spin system begins to lose its energy by photon emission through relaxation processes, returning to thermodynamic equilibrium. The coil surrounding the sample detects an oscillatory emf signal of the current, induced by the decay of magnetisation, which is governed by the relaxation processes. In spatially resolved NMR, a sample experiences the magnetic field which is intentionally varied along required directions. In NMR measurement of movement the velocity encoding gradients are applied. NMR probes at the scale which contains a large number of molecules i.e. molecular ensembles present within the sample studied.

Advances in magnetic resonance imaging techniques and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) have made it possible to study anomalous transport experimentally at the pore-to-core scales (Seymour and Callaghan, 1997, Tessier et al., 1997, Tessier and Packer, 1998, Mantle et al., 2001, Scheven et al., 2005, Mitchell et al., 2008). A review on recent developments in magnetic resonance imaging techniques and their applications in porous media is given by Gladden and Mitchell (2011). Figure 2.8 shows NMR imaging results presenting the probability of molecular displacement for a set of evolution times through a bead pack, Bentheimer sandstone, and Portland carbonate (Scheven et al., 2005). All the samples imaged are cylindrical with a diameter of 37.5mm and length of 70mm. The coordinates are rescaled by the nominal mean displacement. For a homogeneous porous media like a bead pack, a Gaussian distribution can be observed approximately from very early time confirming Fickian transport. However, for more heterogeneous porous media, it is evident that the peak concentration is virtually immobile in time with a highly dispersed fast-moving tail: particles reside for a long time in slow or no-flow regions, close to the solid, in dead-end pores or in narrow pore spaces, eventually diffusing out and moving rapidly through the better connected, wider regions. These observed responses cannot be explained via an ADE solution.

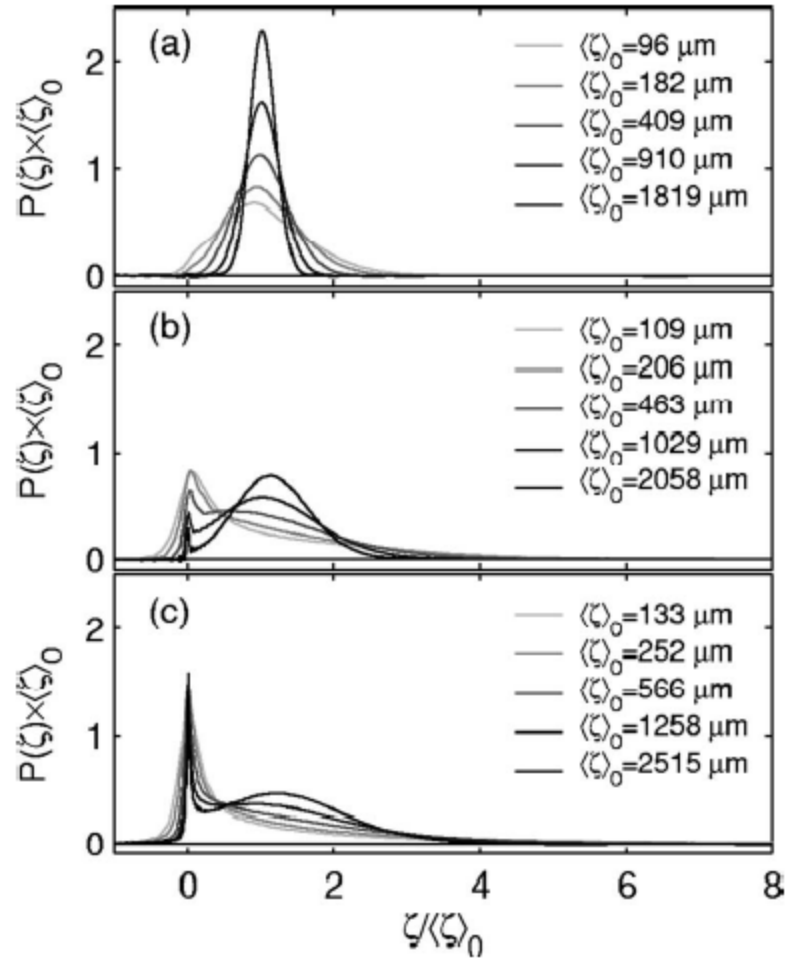


Figure 2.8: Probability of molecular displacement of water versus displacement measured using NMR in a bead pack (a), Bentheimer sandstone (b), and a Portland carbonate (c). The coordinates are rescaled by nominal mean displacement. The Gaussian distribution indicating a Fickian transport can be observed for homogeneous bead pack while for rock samples (the sandstone and the carbonate) an immobile high peak along with a long tail is observed which shows that the ADE cannot predict the transport in more heterogeneous samples accurately - reprinted from Scheven et al. (2005).

2.3.4. CTRW

These limitations associated with the ADE as described in the previous section have been a challenge over many years and a considerable body of research has been devoted to develop a theoretical approach able to quantify the scale-dependent transport in porous media accurately (Dagan, 1989, Gelhar, 1993). Continuous Time Random Walks

(CTRW) have proven to be a highly successful theory to quantify non-Fickian transport at a variety of scales (Berkowitz et al., 2006, Levy and Berkowitz, 2003). CTRW can account for non-Fickian transport as well as Fickian behaviour and the transition from non-Fickian to Fickian in geological formations (Cortis and Berkowits, 2004). In addition, CTRW is a general approach from which the ADE and other formulations, such as multirate mass transfer models (Carrera et al., 1998, Roth and Jury, 1993) can be derived as special cases. The CTRW framework describes transport in porous media based on a ψ function (Berkowitz et al., 2006). By definition $\psi(t)dt$ is the ensemble averaged probability of a particle just arrived a site first moving to an adjacent site in a time between t and $t+dt$. In this framework two characteristic times are defined, t_1 and t_2 . t_1 is the mean advective transit time and t_2 is a late time cut-off due to diffusion:

$$t_1 = \frac{L}{u_{av}} \quad 2.15$$

$$t_2 = \frac{L^2}{2D_m} \quad 2.16$$

where L is the characteristic length associated with a porous medium (average grain size for unconsolidated porous media), u_{av} is average velocity and D_m is molecular diffusion coefficient. t_1 can be interpreted as the time necessary for a particle located at a connected pore to displace over a characteristic length of L . On the other hand, t_2 is the time necessary for a particle trapped in a no-flow region to diffuse out and join faster streamlines and displace through the porous medium. In highly heterogeneous media, between appropriate physical limits, there appears to be no typical time scale and the transit time probability may, empirically, approximately fit a power-law form for $t_1 < t < t_2$:

$$\psi \sim \tau^{-(1+\beta)} \quad 2.17$$

where β is an exponent representing the heterogeneity associated with the porous medium and t_1 is the mean advective transit time and t_2 is a late time cut-off (Dentz et al., 2004). If β is greater than two, the dispersion is Fickian where the mean and variance of the particles location scales linearly with time. For β value between 1 and 2, the long tail exists and the dispersion is non-Fickian but the average movement of the plume is consistent with travel at an average speed v . For β smaller than 1, the dispersion will have

the most anomalous behaviour with an injected plume having a mean position and variance both of which scale non-linearly with time.

CTRW predicts that if $\psi \sim t^{-(1+\beta)}$ then $\sigma^2 \sim t^{2\beta}$, for $\beta < 1$; for $2 > \beta > 1$, $\sigma^2 \sim t^{3-\beta}$, while for $\beta > 2$ the behaviour is Fickian with $\sigma^2 \sim t$ (Dentz et al, 2004). As discussed earlier, there is a late-time cut-off to the power law at time t_2 . For low to moderate Peclet number this is controlled by diffusion across the characteristic length (a typical pore size) and $t_2 = L^2/2D_m$ (Bijeljic and Blunt, 2006). Then for $t > t_2$ we see a cross-over to asymptotic (Fickian) behaviour. We now define dimensionless parameters using the characteristic length L , advective time t_1 , and molecular diffusion coefficient D_m as scaling factors:

$$\tau = \frac{t}{t_1} \quad 2.18$$

$$D_d = \frac{D}{D_m} \quad 2.19$$

$$\sigma_d^2 = \frac{\sigma^2}{L^2} \quad 2.20$$

where τ is dimensionless time, D_d is dimensionless dispersion coefficient, σ_d^2 is dimensionless variance of displacement. Note that $t_2/t_1 = Pe/2$.

Using the dimensionless parameters, we obtain:

$$D_d = Pe \frac{d\sigma_d^2}{d\tau} \quad 2.21$$

from which we find $D_d \sim Pe \tau^{2\beta-1}$ for $\tau < Pe$ and $D_d \sim Pe^{2\beta}$ for $\tau \gg Pe$ if $\beta < 1$; and $D_d \sim Pe \tau^{2-\beta}$ for $\tau < Pe$ and $D_d \sim Pe^{3-\beta}$ for $\tau \gg Pe$ if $2 > \beta > 1$. If $\beta > 2$, the dispersion is considered Fickian where $d\sigma^2/dt$ is invariant in time and equal to $2D$.

A review on recent advances and mathematical development of CTRW can be found in (Dentz et al., 2004, Berkowitz et al., 2006).

2.3.5. Numerical modelling of dispersion in porous media

2.3.5.1. Network models for modelling dispersion

Dispersion in porous media has been modelled numerically by several previous researchers applying different methods. The most common approach has been to use network models, where the pore space is conceptualized as a lattice of wide pore spaces connected by narrower throats (Koplik et al, 1988, Sahimi and Imdakm, 1988, Bruderer and Bernabé, 2001, de Arcangelis et al., 1986, Sahimi et al., 1986, Sorbie and Clifford, 1991, Sahimi, 1995, Bijeljic et al., 2004, Bijeljic and Blunt, 2007, Acharya et al., 2007, Jha et al., 2011).

Sahimi and Imdakm (1988) employed a Monte-Carlo approach to simulate dispersion on a percolation network model. The network consists of capillary tubes with distributed effective radii. They studied dispersion coefficient as a function of Peclet number for $10 < Pe < 100$. They showed that dispersion coefficient in this range of Peclet number can be treated as a power-law with power-law coefficient of 1.2 ± 0.1 .

Bijeljic et al. (2004) also studied the longitudinal dispersion coefficient on a two-dimensional lattice network model. The network model was extracted from a Berea micro-CT image of a linear size of 3 mm. They used a random walk method to account for diffusion and modelled the dispersion coefficient for different regimes of Peclet number. They showed that the power-law dispersion coefficient for Berea sandstone is 1.2 and compared their results with experiments on sandstones including Berea sandstone and showed a good agreement. In a later study, Bijeljic and Blunt (2006) showed that the power-law regime of dispersion can be interpreted by the variation in average velocity between throats of the network model as will be discussed in more detail in chapter 4.

Acharya et al. (2007a) also modelled dispersion on three dimensional network models with randomly distributed pore aspect ratio. The intersection of the elementary tubes was assumed to be volumeless. They calculated the longitudinal dispersion coefficient based on spatial positions particle, first-arrival times of particles, and fitting of the cumulative

first-arrival times distribution to the analytical solution of the advection diffusion equation and showed that different methods produce very similar results and in good agreement with experiments.

Acharya et al. (2007b) obtained dispersivity from the mixing cell method (MCM) on network models with random distribution of pore aspect ratio. They compared breakthrough curves obtained from MCM with the random walk technique and showed that MCM is a flexible method to model dispersion numerically.

Jha et al. (2011) also modelled dispersion on computer-generated network model of sphere packing. They used random walks to model diffusion and mapped particle position from an in-flowing bond to a point on an out-flowing bond in network models to track solute particles. This mapping of particle position yields the cancellation of convective spreading if the flow direction is reversed. They simulated dispersion and observed the power-law coefficient of 1.2.

Network models have been able to capture different regimes of dispersion and predict the scaling of dispersion coefficients. However, the ambiguities involved to extract networks from micro-CT image are still a challenge to model dispersion on network models. In addition, capturing hold-up dispersion and effects of particles trapped in dead pores on network models is not straightforward (Bijeljic et al., 2004).

2.3.5.2. Direct simulation of dispersion

A more direct approach is to simulate transport directly on a pore-space image that removes the need to extract an equivalent network with its inherent limitations and approximations (Maier et al., 2003, Coelho et al., 1997, Maier et al., 1998, Yao et al., 1997, Salles et al., 1993). Coelho et al. (1997) used a finite difference technique in conjunction with artificial compressibility method to solve for flow and simulated dispersion through packings of grains of arbitrary shape and found a good agreement with experimental results on unconsolidated bead packs and sandstones. They showed that dispersion coefficients for packings of grains with similar porosities regardless of

grain shape have similar values - see Figure 2.9. They suggested the existence of a very general class of random unconsolidated granular media where transport coefficients are only a function of porosity and equivalent grain size.

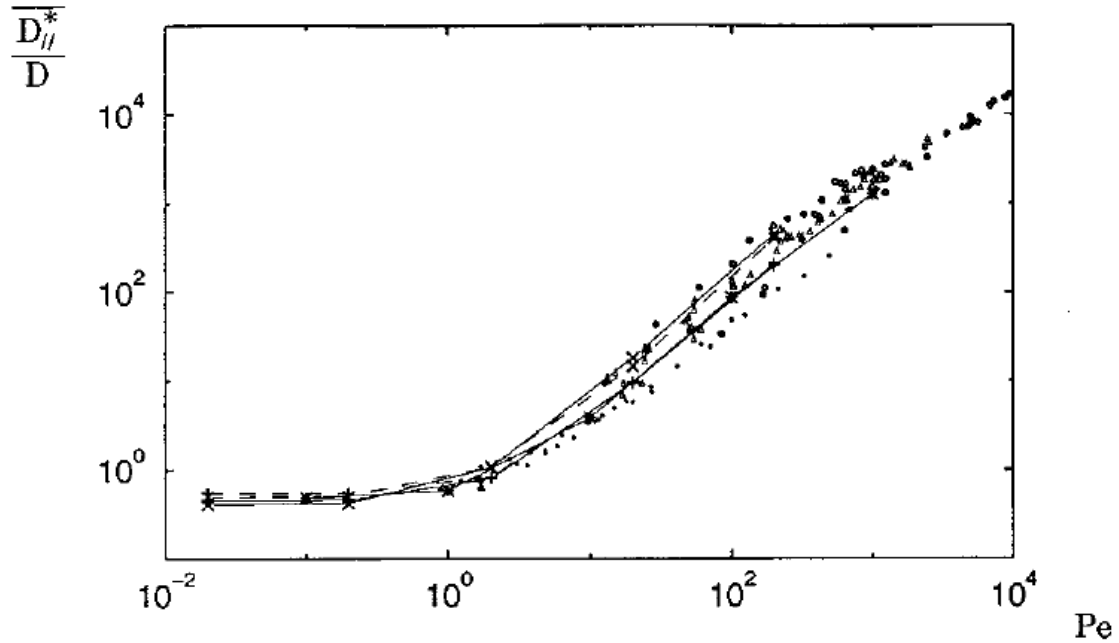
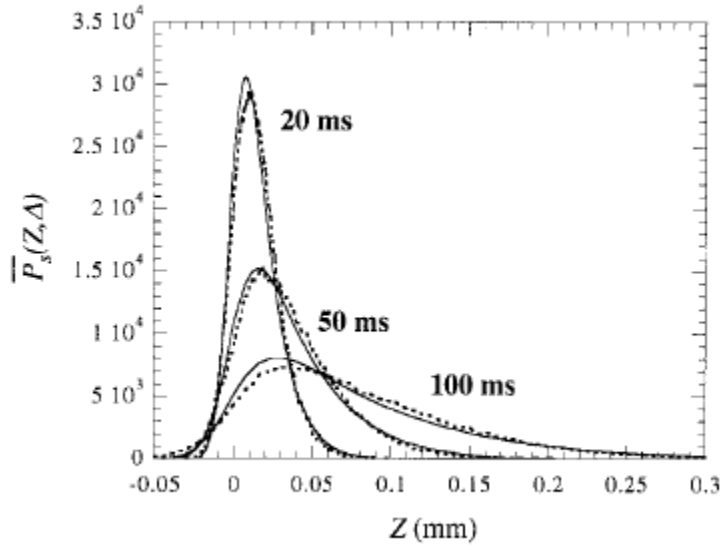


Figure 2.9: Longitudinal dispersion coefficient versus Peclet number for packings of spheres (solid line with *), ellipsoids with aspect ratio of 0.5 (short dashed line with +), 2 (long dashed line with +), 0.2 (dashed line with x), and 5 (solid line with x). Experimental data for bead packing (Quintard and Whitaker, 1993) and sands (Brenner, 1980) are also shown by solid circles and triangles respectively - reprinted from Coelho et al. (1997).

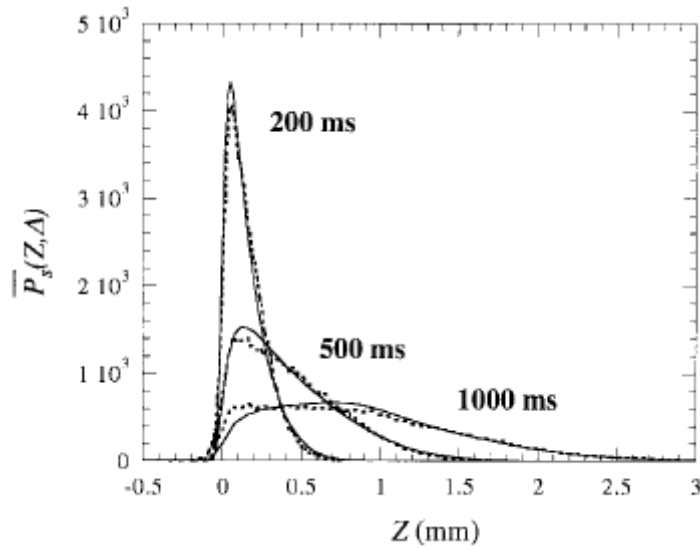
Yao et al. (1997) also used a similar method for modelling flow and dispersion on a statistically reconstructed geometry of Vosges sandstone. The geometry was obtained based on porosity and correlation function measured from serial thin sections. They generated three dimensional images with average size of $33 \times 33 \times 33$ grid blocks. The agreement of the model prediction with experimental measurements for dispersion coefficient was not satisfactory (Adler and Thovert, 1998). This was probably due to small size of images studied which is not capable of presenting the sandstone geometry.

Manz et al. (1999), studied dispersion and compared NMR velocimetry and propagator measurement with a lattice Boltzmann simulation on the same packing of spheres with

diameter of 1 mm. In literature, the propagator is defined as the probability distribution of molecular displacements measured as a function of time. Figure 2.10 shows their numerical results in comparison with NMR measurement at different times from 0.02 s to 1 s. A good quantitative agreement can be observed between numerical prediction and NMR measurement where $Pe = 350$.



(a)



(b)

Figure 2.10: Comparison of experimental NMR propagator (solid line) with simulated numerical results on a sphere packing (dashed line) after (a) $t=0.02$ s, 0.05 s, 0.1 s, (b) $t=0.2$ s, 0.5 s, 1 s - reprinted from Manz et al. (1999).

Maier et al. (2000) compared dispersion coefficient results obtained from lattice Boltzmann simulation on sphere packing with Seymour and Callaghan (1997), Lebon et

al. (1997) and Stapf et al. (1998) experimental NMR measurements. The experiments have been performed on spheres packed in cylinders where the ratio of cylinder diameter to sphere diameter was fifty or more. The simulated packing had dimension of $10d \times 10d \times 20d$ where d is diameter of spheres which conforms to experimental bead diameters. Some of the numerical simulations used the same diameter as Seymour and Callaghan where $d = 90.7 \mu\text{m}$, others used a larger diameter, $d = 3 \text{ mm}$. In all cases simulations used the same value of porosity and elapsed time as in experiments. Figure 2.11 compares dispersion coefficient from three NMR studies by Seymour and Callaghan (1997) and Lebon et al. (1997) and Stapf et al. (1998) and numerical results. The agreement is within 15% and for some cases they differ by a factor of two or more. It should be mentioned that for some cases the results are pre-asymptotic and inferring the scaling of dispersion coefficient with Peclet number is difficult.

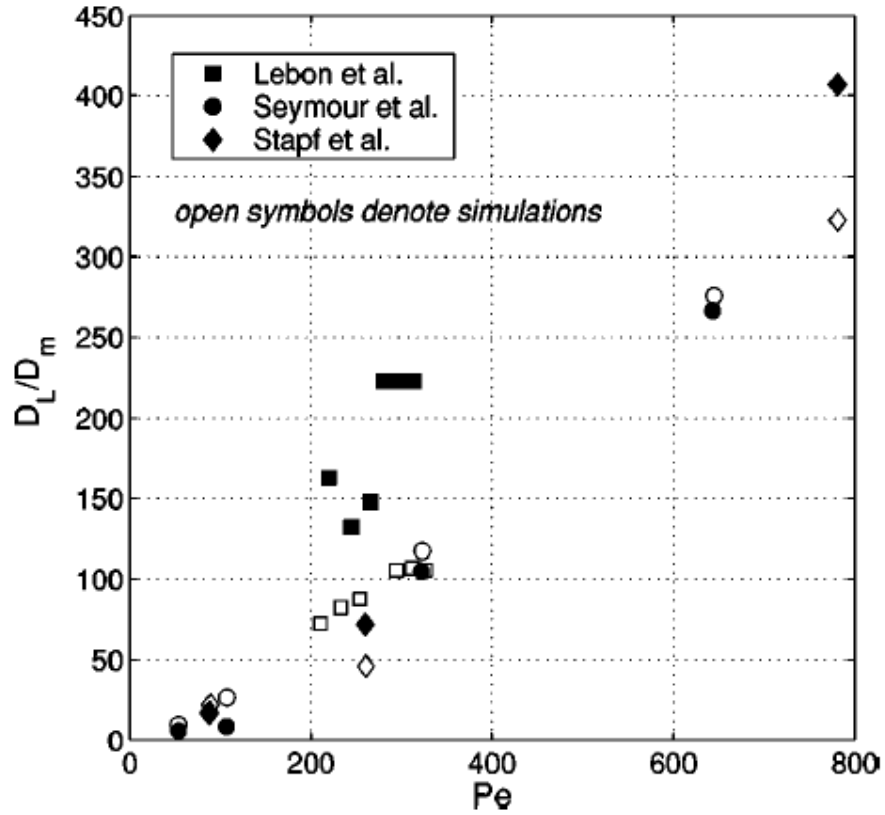


Figure 2.11: Numerical results for longitudinal dispersion coefficient in comparison with NMR studies by Seymour and Callaghan's (1997) and Lebon et al. (1997) and Stapf et al. (1998) on sphere packing with the same porosities, sphere diameters and elapsed time - reprinted from Maier et al. (2000).

Zhang and Kang (2004) applied lattice Boltzmann simulation on porous media with a single fracture - as shown in Figure 2.12 - and studied the effects of porosity of constructed fractured porous media on non-Fickian transport. The fracture is embedded in a porous medium with a specified porosity and the width of the fracture is 1mm equivalent to 32 lattice units. Figure 2.13 shows the concentration distribution for three porous media with porosities of 0, 0.308, and 0.601 for two different times. The Peclet number is 51.35. The long tails are obvious which shows that in fractured porous media the dispersion is highly anomalous. They demonstrated that the ADE is an inadequate framework to study dispersion in fractured porous media and the transport between the

matrix and fractures cannot be neglected in modelling transport even for low porosity matrix.

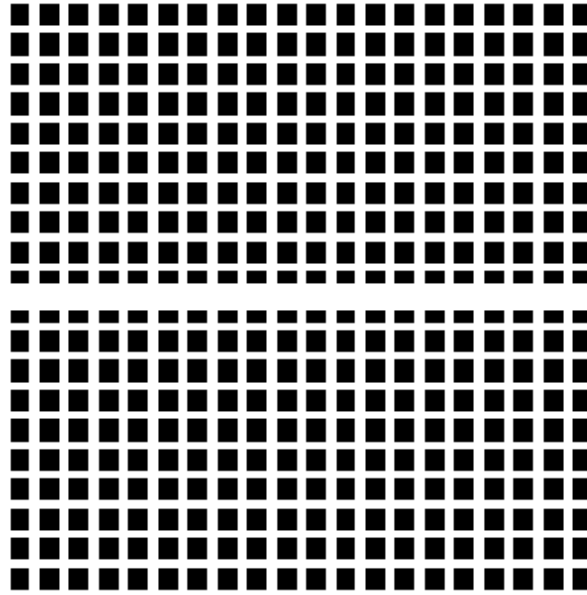


Figure 2.12: A two-dimensional porous media with a single fracture used by Zhang and Kang (2004) to study non-Fickian transport in fractured porous media.

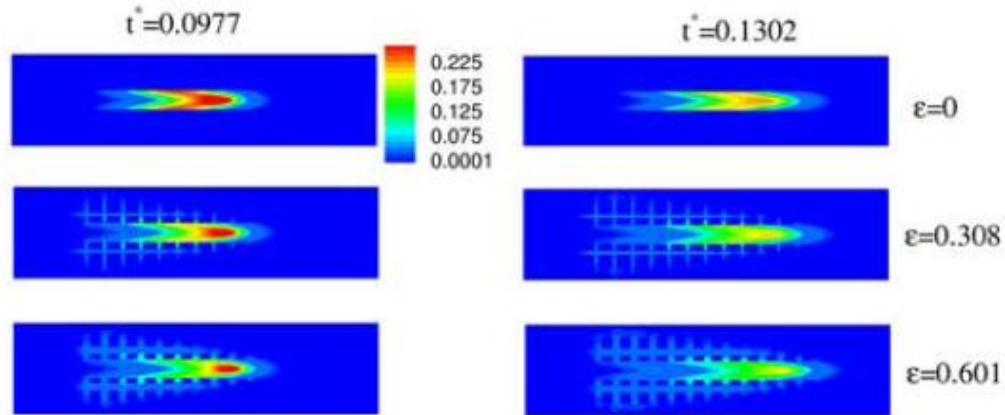


Figure 2.13: Concentration distribution for three matrix porosity at two dimensionless times - reprinted from Zhang and Kang (2004).

Harris et al. (2005) also simulated propagators using the lattice Boltzmann method on an image of a sphere packing of size of $256 \times 256 \times 126$ voxels with resolution of $3.6 \mu\text{m}$ obtained from laser scanning microscopy and compared them with NMR experimental results. They showed a good qualitative conformity between the propagator simulation

and experiments on the same packing – see Figure 2.14 - considering that the image represents less than 1% of the packing used for NMR measurement.

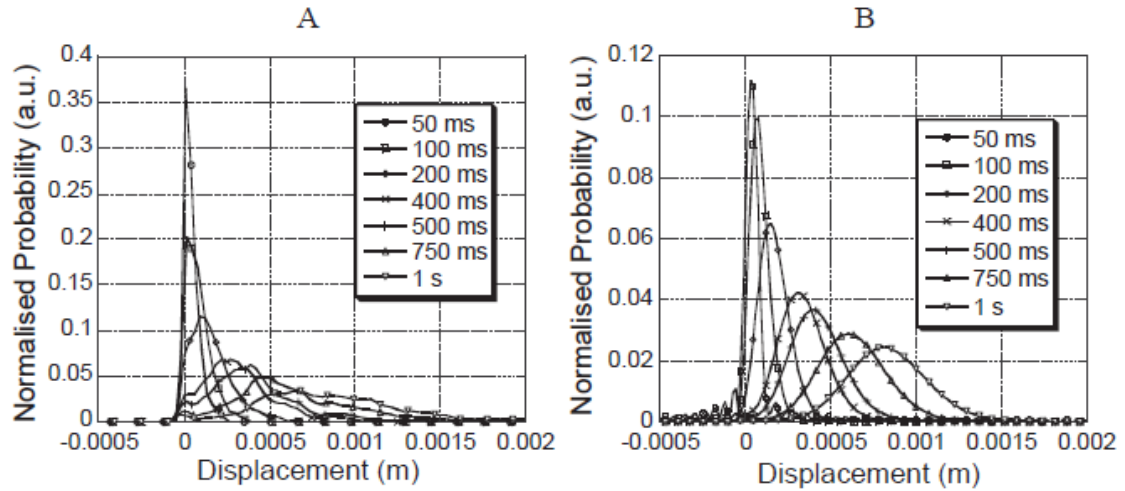


Figure 2.14: Numerical simulation of propagators in a sphere packing (A) in comparison with NMR measurements (B) for elapsed time from 0.05 s to 1 s - reprinted from Harris et al. (2005).

Zhang and Lv (2007) used the lattice Boltzmann method to simulate flow and dispersion on a two-dimensional column packed with discs – as shown in Figure 2.15. Discs have the diameter of 34 or 40 pixels. They modelled the spatial distribution and breakthrough curve of the averaged concentration and showed that even in a homogeneous two dimensional disk packing, anomalous transport effects cannot be neglected. In addition, they fitted their numerical results for spatial concentration profiles with ADE and CTRW predictions – see Figure 2.16. ADE captures the main feature of plume, however underestimates the tail and overestimates the front as more obvious in semilog plot. In contrast, CTRW is able to capture the tailing and front of plume as well as its main feature as shown in Figure 2.16. They demonstrated that the ADE cannot capture the transport details and CTRW is a more accurate framework for transport simulation.

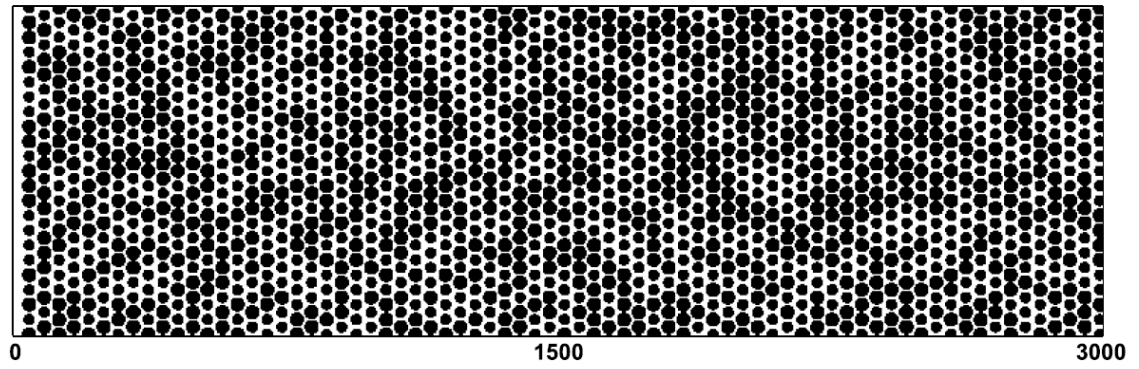
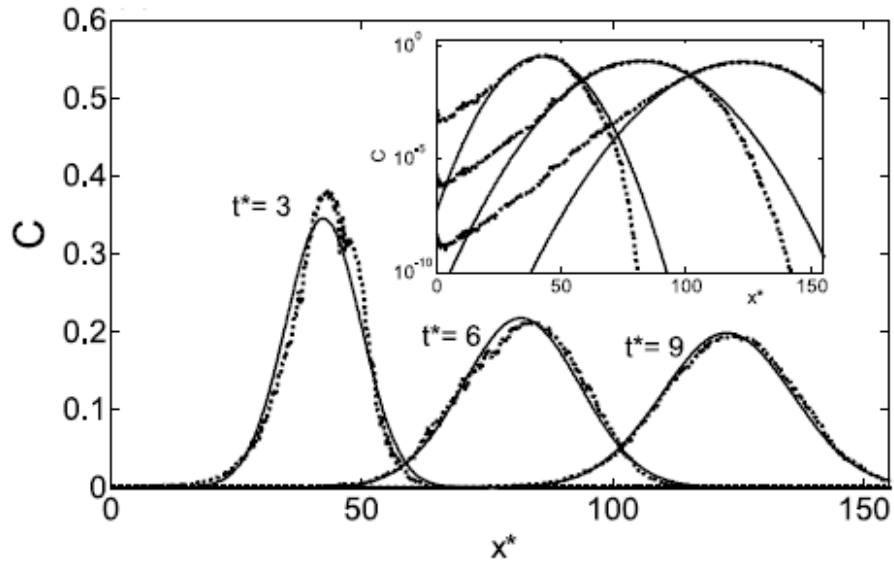
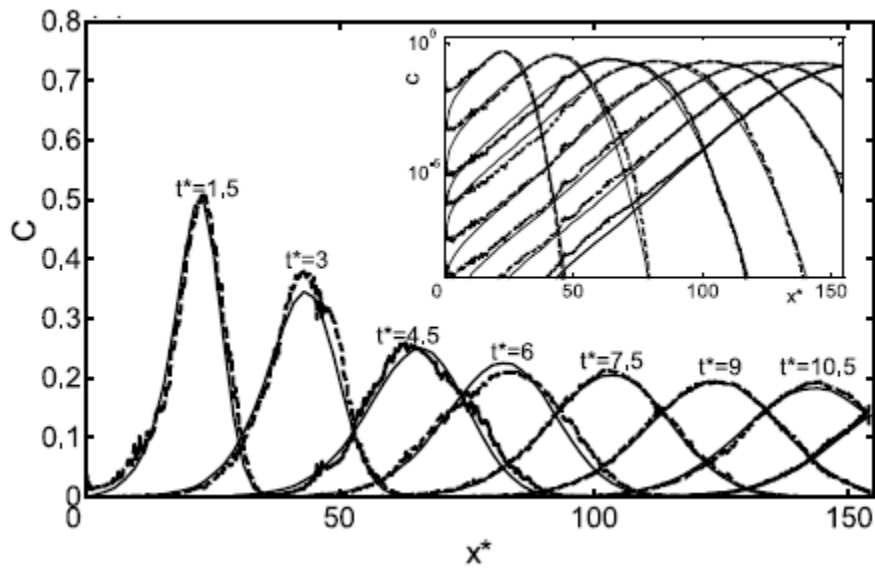


Figure 2.15: Half of the two-dimensional disc packing with discs of diameter 34 or 40 pixels - reprinted from Zhang and Lv (2007).



(a)



(b)

Figure 2.16: Numerical simulation of concentration profile for $Pe=19.61$ (dashed lines) in comparison with (a) the best fitting of ADE (solid lines), and (b) the best fitting of CTRW (solid lines). The main features of concentration profiles can be captured by both ADE and CTRW in the homogeneous porous media. However, CTRW is able to capture the tailing and front of the plume with a more elaboration - reprinted from Zhang and Lv (2007).

Maier et al. (2008) modelled propagators applying lattice Boltzmann method on random bead packs constructed by Monte-Carlo simulation and compared their numerical prediction on $10 \times 10 \times 40$ number of beads by experimental NMR data by Gage et al. (2005) for elapsed times of 0.02 s, 0.1 s, and 0.3 s. Their comparison showed a good agreement for propagator simulation even though the experimental results are flatter and more dispersed than numerical results – see Figure 2.17. This is probably due to packing density and random packing between simulation and NMR measurement.

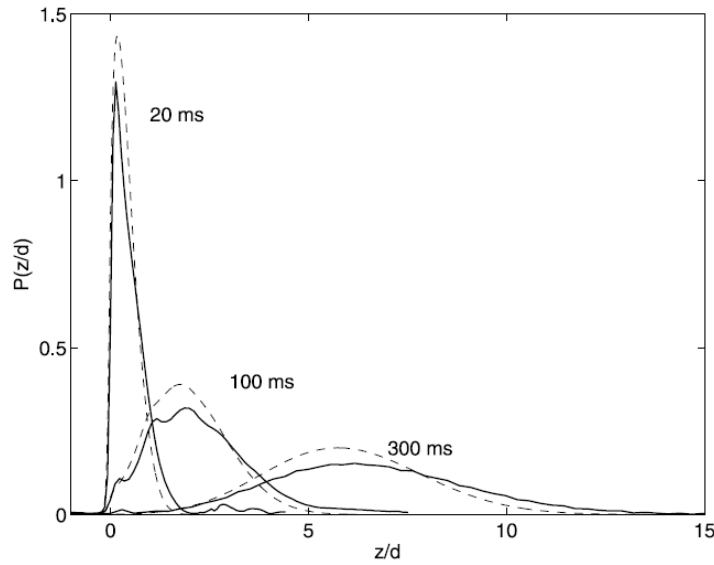


Figure 2.17: Comparison of numerical simulated propagators (dashed line) with measured NMR propagator (solid line) by Gage et al. (2005). Displacement is rescaled by the bead diameter, $Pe = 95$ - reprinted from Maier et al. (2008).

Cardenas (2009) applied the finite element method to solve for Navier-Stokes equation and ADE to model transport and flow on sphere packings and studied the transition from non-Fickian to Fickian transport. They showed that transport after around 10 pores can be considered Fickian and that ADE can be applicable to govern the transport on this homogeneous geometry.

Garmeh et al. (2009) also used a finite-element scheme to solve for fluid flow and after velocities were calculated they solved the ADE to model dispersion in two dimensional

packings of discs with porosity of 61%. Figure 2.18 shows longitudinal dispersion coefficient against Peclet number based on their simulation on the uniform disc packing. They showed that the dispersion coefficient power-law coefficient for a homogeneous uniform disc packing is 1.89. This large value in comparison with previous studies could be due to high porosity of the porous media and also due to two dimensional periodic flow.

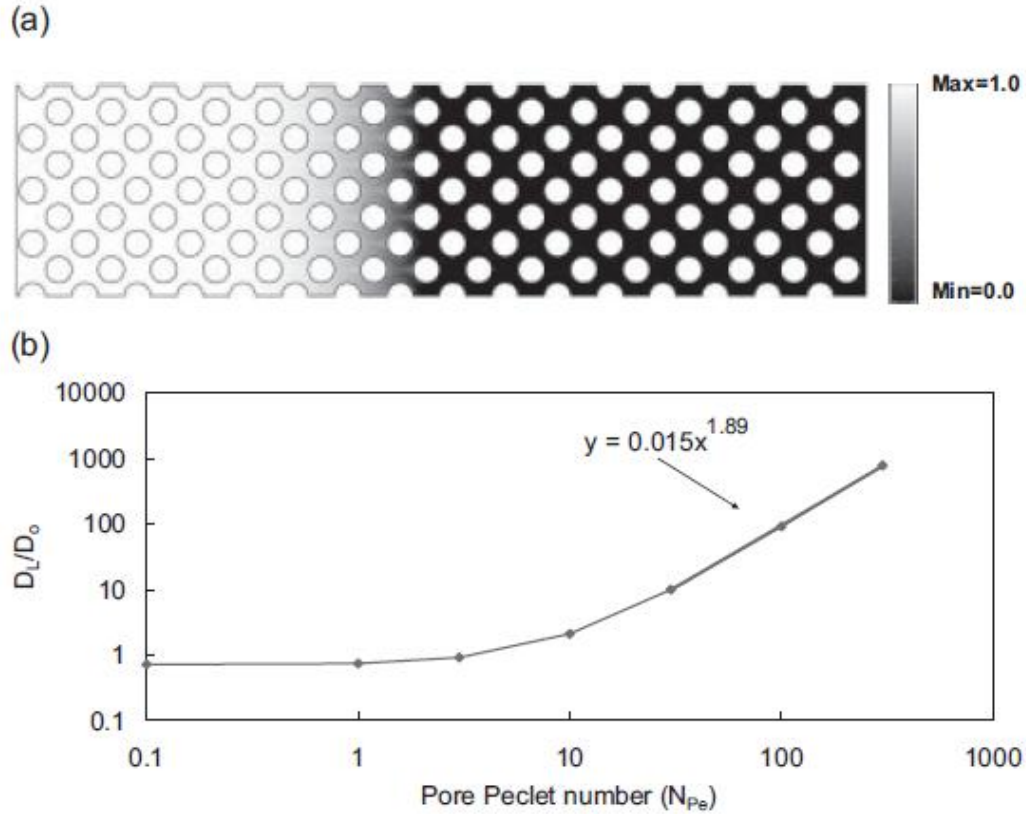


Figure 2.18: Concentration distribution at 0.4 of pore volume injected ($Pe=3$) on two-dimensional uniform disc packing of porosity 61% (a), longitudinal dispersion coefficient versus Peclet number on the disc packing (b) - reprinted from Garmeh et al. (2009).

Ovaysi and Piri (2011) applied a modified moving particle semi-implicit (MMPS) method to solve for flow and transport on Berea sandstone and two reservoir sandstones. The image size studied for Berea and the other two sandstones were $42 \times 42 \times 190$, $66 \times 66 \times 298$, and $52 \times 52 \times 234$ respectively. The image resolutions were $10.69 \mu\text{m}$ for the Berea and $6.796 \mu\text{m}$ and $8.683 \mu\text{m}$ for the other sandstones. They calculated dispersion

coefficient of Berea for a range of Peclet number and for $Pe=50$ they calculated dispersion coefficient for the other sandstones as shown in Figure 2.19. The values of dispersion coefficient for the other sandstones are also in the range of the experimental data. They also investigated the inclusion of inertial effect on predicted dispersion coefficient. They showed neglecting inertial effect in modelling flow in porous media leads to overestimation of dispersion coefficient at very high Peclet number – see Figure 2.19.

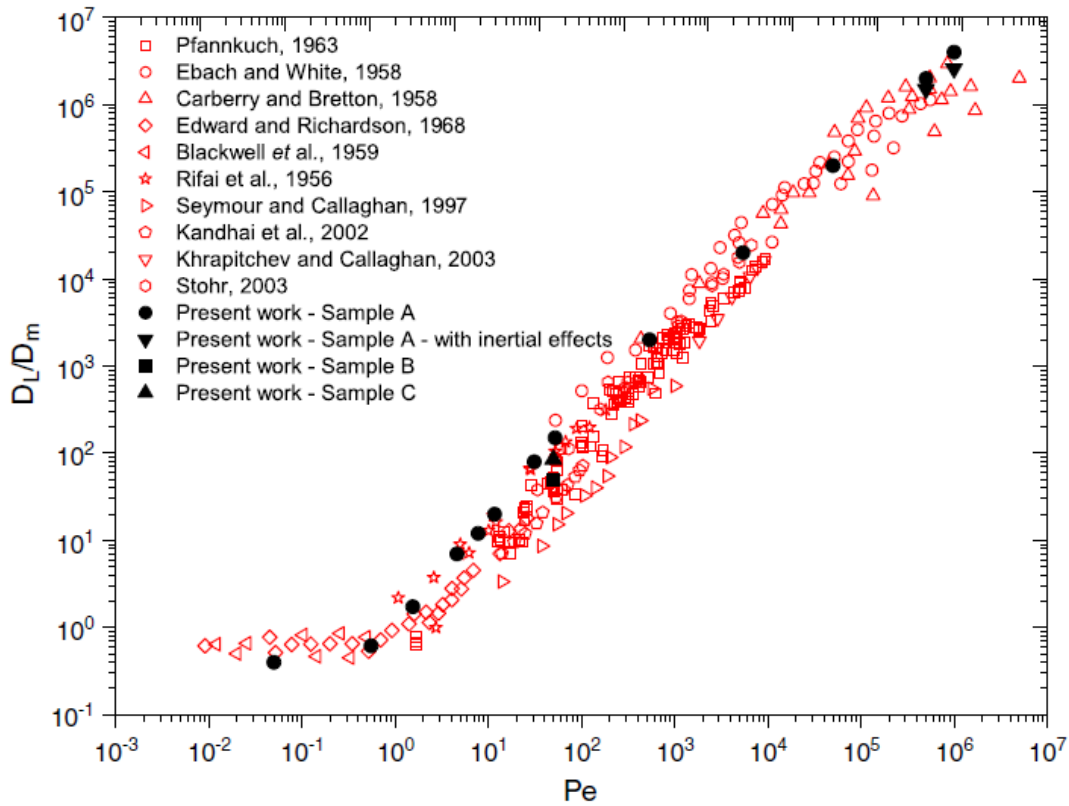


Figure 2.19: Longitudinal dispersion coefficient versus Peclet number for Berea sandstone along with published experimental data. For $Pe=50$, the dispersion coefficient of two other sandstones are also calculated which are again in the range of experimental data. For very high Peclet number, the results of calculating dispersion coefficient with and without inertial effect are shown. Neglecting inertial effect in this regime of Peclet number leads to over estimation of dispersion coefficient - reprinted from Ovaysi and Piri (2011).

These previous studies have been able to reproduce the behaviour of the dispersion coefficient as a function of Peclet number, demonstrating how the subtle interplay of advection and diffusion in a disordered pore space affects transport. However, the effect of heterogeneity on the dispersion coefficient and its scaling with Peclet number for different rock types is still a challenge due to complex interplay between structure, flow and diffusion. In addition, studying and direct modelling of propagators have been confined to relatively simple porous media: the effects of pore-space heterogeneity in combination with Peclet regime on propagator profiles have not been fully investigated for more complex systems, such as consolidated sandstones and carbonates.

In this research we apply a finite difference method to solve for the flow field in three-dimensional pore-space images. Then, we employ a random-walk technique for modelling diffusion and to calculate advection, a novel streamline-based method is used. For voxels with no solid boundary, the method is identical to the Pollock (1988) algorithm that is now standard in field-scale streamline-based reservoir simulators. Where a solid boundary is present, zero tangential and normal velocity is strictly imposed, resulting in a bilinear variation of tangential velocity and quadratic normal velocity away from the boundary. We study transport in geological media of increasing pore-scale complexity: bead pack, sandpacks, sandstones and carbonates. We separate our study for dispersion to asymptotic and pre-asymptotic regimes. In chapter 4, we study the asymptotic dispersion coefficient in bead pack, sandpacks, sandstones, and carbonates. We show that not only the value of dispersion coefficient, but also the scaling of dispersion coefficient versus Peclet number varies with pore-space heterogeneity. We interpret the scaling of dispersion coefficient based on the transit-time probability ψ from the CTRW framework defined on a grid-block basis. We then show that power-law regime of dispersion is controlled by the distribution of velocity at the pore scale.

In chapter 5, we investigate the pre-asymptotic dispersion on micro-CT images. We present the propagator profiles for different porous media for three regimes of Peclet number. In each rock sample, the Peclet regime influences the spreading of particles and we show that the profiles of propagator indicate an inherently different transport in

complex heterogeneous porous media such as carbonates in comparison with homogenous ones. We also compare our numerical results for Bentheimer sandstone and Portland carbonate with published NMR measurement on the same rock samples and demonstrate a quantitative and qualitative agreement. In addition, we study the time-dependent dispersion coefficient and transition from non-Fickian to Fickian transport based on the dispersion coefficient and interpret the results with CTRW predictions.

3. Flow simulation

3.1. Preparing the geometry

The main input for a flow simulator for porous media is the geometry of the void space within a core sample. As mentioned in chapter 2, micro-CT scanning technology is an accurate approach to capture the morphology a porous rock with a resolution of few microns. The micro-CT imaging of the samples used in this work has been performed in the micro-CT laboratory at Imperial College and at a synchrotron source at Trieste in Italy. In addition, some images have been obtained from colleagues around the world.

Micro-CT scanners employ X-rays to penetrate the core sample. The X-ray radiates from an X-ray source and passes through the core placed in the scanner – see Figure 3.1. The radiated X-ray is attenuated within the sample and the attenuated X-ray is received by the detector. The sample rotates 360 degrees and the imaging is performed step by step – at least every half degree. Then the received X-ray data by the detector is transferred to the processor of the scanner and two-dimensional projections are reconstructed to produce a three-dimensional image. To improve the contrast and remove the noise from the obtained image, filters are applied after imaging.

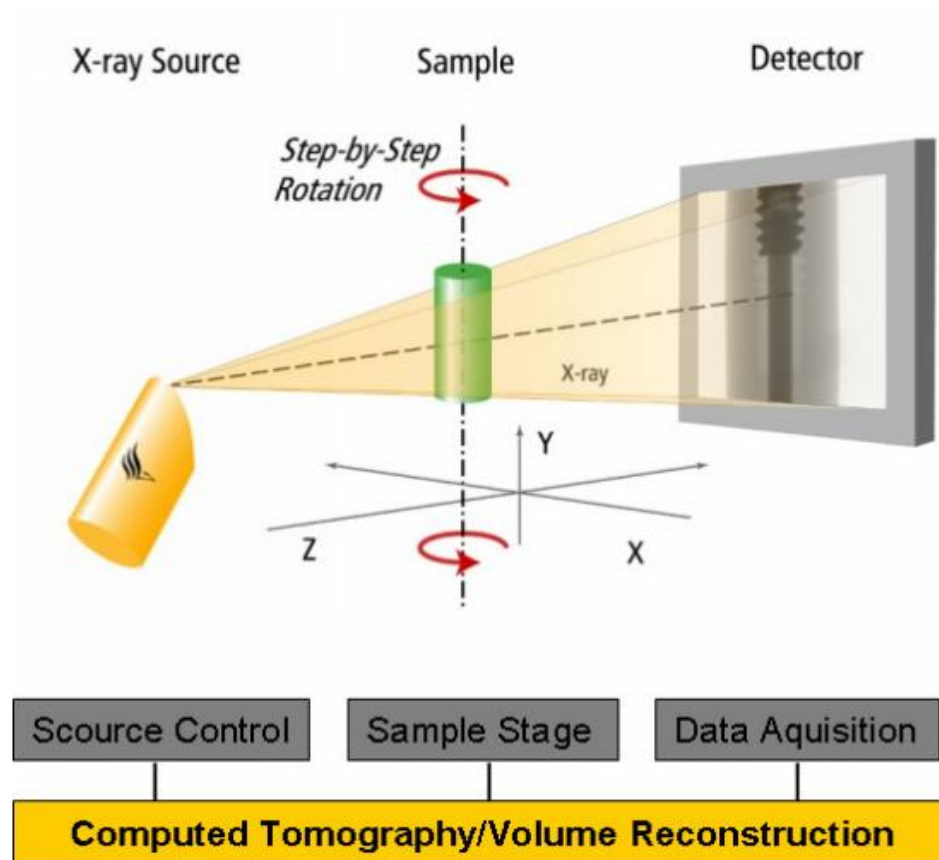


Figure 3.1: The three main parts of a micro-CT scanner: source control to generate X-rays; sample stage where the core is placed and rotates 360 degrees during the scanning; and the data acquisition part that receives the profile of X-ray attenuation and generates the reconstructed images - reprinted from the Manual of the v|tome|x system, Phoenix|x-ray.

At this stage, the output from a micro-CT scanner is a grey scale image that is post processed to be converted to a binarized image – 0 and 1 - which corresponds to a void or solid voxel respectively. A function threshold is used on the gray scale histograms to convert it to a binarized image. This function works in an iterative manner to find the thresholding value. More details regarding the micro-CT scanning, filtering, and binarizing of images can be found in Dong (2007) and Wildenschild et al. (2002). Figure 3.2 shows two-dimensional cross section of micro-CT images of a LV60 sand pack, Berea sandstone and C1 carbonate with resolution of 10, 5.3, and 2.85 μm respectively. More details regarding the rock samples will be presented later in this chapter.

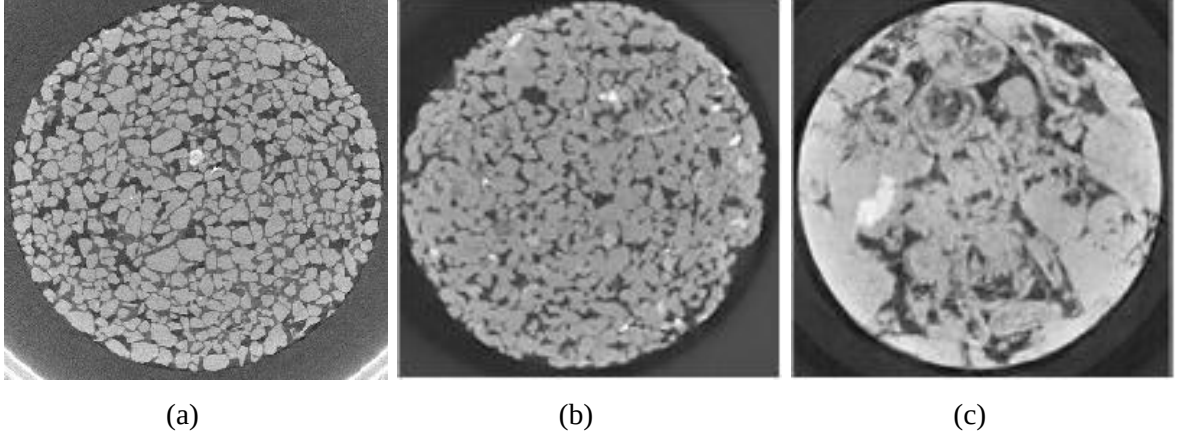


Figure 3.2: Cross section of micro-CT images of LV60 sandpack (a), Berea sandstone (b), and C1 carbonate (c) with resolution of 10, 5.3, and 2.85 μm respectively.

3.2. Modelling the flow

In this research, we simulate flow directly at the pore scale geometry obtained from micro-CT scanning of rocks. At the pore scale, fluids are considered continuous because the pore-scale is much larger than the mean free path of molecules in fluids (Adler, 1992). Therefore, at this scale local conservation laws are valid.

We solve the local governing equations for fluid flow, which are conservations of mass and momentum numerically on pore-space images.

The conservation of mass which is also known as the continuity equation is:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z} = 0 \quad 3.1$$

where ρ is density and u , v , and w are the velocity components in the x , y , and z directions respectively. For incompressible flow, with no change in density, this becomes:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad 3.2$$

The Navier-Stokes equation imposes conservation of momentum of a Newtonian fluid which is a balance between inertial, viscous and pressure forces (White, 1999).

$$\rho \left[\frac{\partial V}{\partial t} + V \cdot \nabla V \right] = -\nabla P + \mu \nabla^2 V \quad 3.3$$

where μ is viscosity, P is pressure and V is velocity vector. In equation 3.3, the left-hand side is the inertial term, first term on the right-hand side is responsible for flow caused by pressure gradients and the second term is the effect of viscosity. For steady state flow we have:

$$\rho V \cdot \nabla V = -\nabla P + \mu \nabla^2 V \quad 3.4$$

Now, we can define dimensionless variables and differential operators and then rewrite steady state Navier-Stokes equation in terms of dimensionless quantities which are defined below:

$$\tilde{V} = \frac{V}{V_0} \quad 3.5$$

$$\tilde{P} = \frac{P - P_0}{\mu V_0 / L} \quad 3.6$$

$$\tilde{\nabla} = L \nabla \quad 3.7$$

$$\tilde{\nabla}^2 = L^2 \nabla^2 \quad 3.8$$

where V_0 and L are characteristic velocity and length respectively.

Now, steady-state Navier-Stokes equation can be rewritten as:

$$\text{Re}(\tilde{V} \cdot \nabla \tilde{V}) = -\tilde{\nabla} \tilde{P} + \tilde{\nabla}^2 \tilde{V} \quad 3.9$$

where $\text{Re} = \frac{LV_0\rho}{\mu}$ is Reynolds number, a dimensionless number shows the importance of inertial force over viscous force.

For flow in porous media at the pore scale, the characteristic length can be considered as the average pore diameter which is in order of 10^{-5} m. The average velocity of fluid in sub-surface porous media is around 10^{-6} m/s or smaller, except near the wellbore. The

density and viscosity are in order of 10^3 kg/m^3 and 10^{-3} Pa.s respectively. Hence for flow through a pore:

$$\text{Re} \approx \frac{10^{-5} \text{ m} \times 10^{-6} \text{ m/s} \times 10^3 \text{ kg/m}^3}{10^{-3} \text{ Pa.s}} = 10^{-5} \ll 1 \quad 3.10$$

Since the Reynolds number for flow in porous media is in order of 10^{-5} , the inertial force is much less than viscous force and can be ignored in comparison with the viscous term. Therefore, the right hand side in equation 3.3 is ignored and in steady state, with no time dependence, the Navier-Stokes equation reduces to the Stokes equation:

$$0 = -\nabla P + \mu \nabla^2 V \quad 3.11$$

The main difficulty in solving the Stokes equation numerically is the weak coupling of pressure and velocity fields. This coupling has to be accomplished to ensure the divergence of velocity converges to zero.

The two most common techniques to deal with velocity-pressure coupling in numerical computations of the flow field are the Pressure-Based Method (PBM) and the Artificial Compressibility Method (ACM). In the ACM (Chorin, 1967), a virtual compressibility is introduced to the continuity equation and the unsteady terms in the momentum equation are retained. ACM is a common technique for solving the Stokes equation in porous media at the pore scale (Silin and Patzek, 2009, Mourzenko et al., 2008, Adler, 1992, Kainourgiakis et al., 2005). On the other hand, PBM decouples pressure and velocity by converting the continuity equation to a pressure-correction equation.

In a comparative study, Tamamidis et al. (1996) showed that ACM required sixteen times more memory than PBM on both parallel and series processing machines. They also showed that PBM is more accurate than ACM and its converged solutions have better mass conservation. Since we deal with large images, the memory requirement is an essential consideration for our simulations. Therefore, for flow simulations we use PBM in conjunction with an algebraic multigrid solver to solve for linear systems of equations (Stüben, 2001).

We use structured marker-and-cell (MAC) gridding (Peyret and Taylor, 1985, Harlow and Welch, 1965). MAC gridding means that the nodes where different variables are being estimated are not the same: pressures are determined at the centre of cells and normal velocities are defined at cell faces - see Figure 3.3.

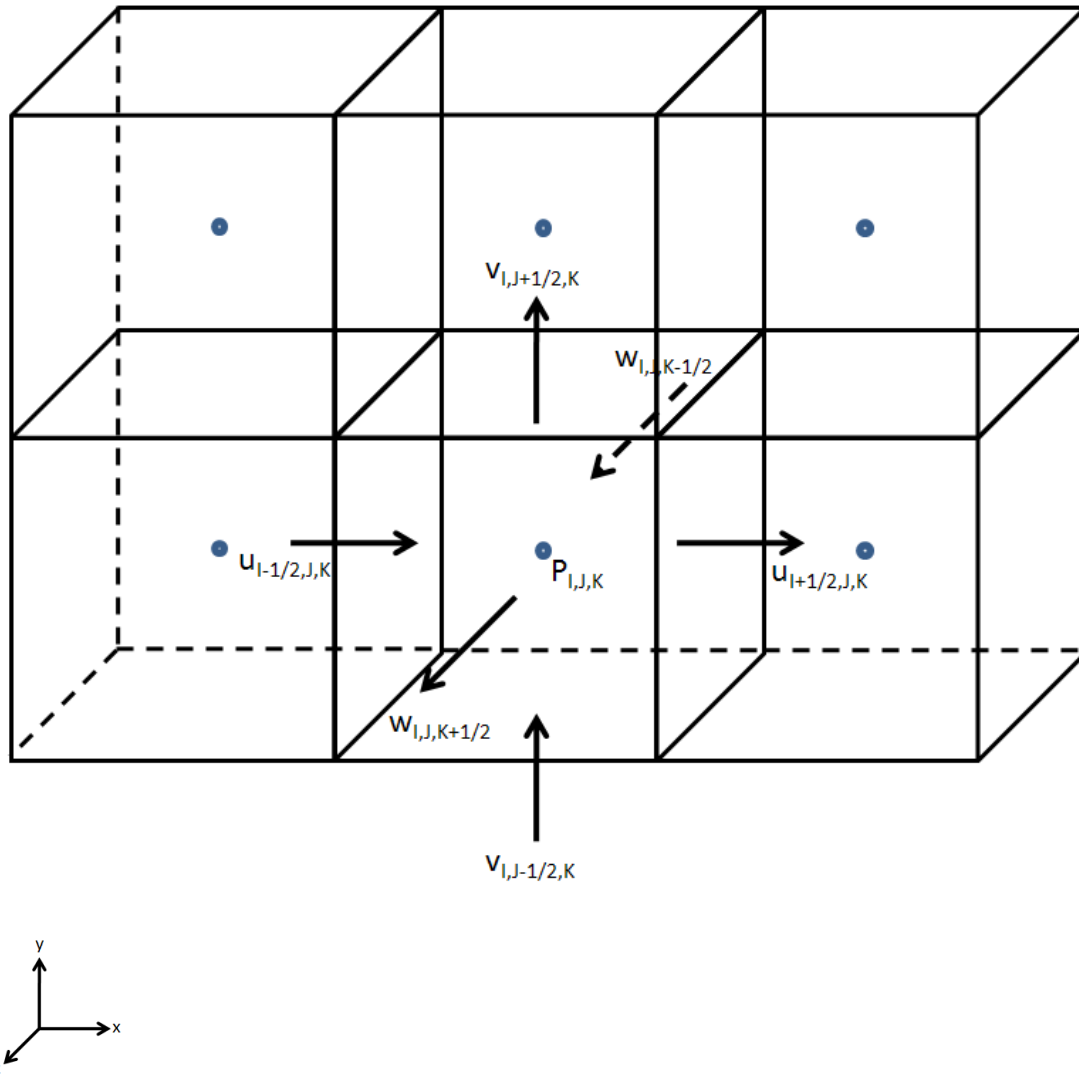


Figure 3.3: Marker-and-cell, MAC, gridding used for flow simulation. Pressures are determined at the centre of cells and normal velocities are defined at cell faces. u , v and w are components of the velocity in the x , y and z directions respectively.

Applying finite difference discretization on the MAC gridding to equations 3.11 and 3.2 leads to:

$$\begin{aligned} & \frac{u_{I+\frac{3}{2},J,K} - 2u_{I+\frac{1}{2},J,K} + u_{I-\frac{1}{2},J,K}}{(\Delta x)^2} + \frac{u_{I+\frac{1}{2},J+1,K} - 2u_{I+\frac{1}{2},J,K} + u_{I+\frac{1}{2},J-1,K}}{(\Delta y)^2} + \frac{u_{I+\frac{1}{2},J,K+1} - 2u_{I+\frac{1}{2},J,K} + u_{I+\frac{1}{2},J,K-1}}{(\Delta z)^2} \\ &= \frac{1}{\mu} \frac{P_{I,J,K} - P_{I-1,J,K}}{\Delta x} \end{aligned} \quad 3.12$$

$$\begin{aligned} & \frac{v_{I+1,J+\frac{1}{2},K} - 2v_{I,J+\frac{1}{2},K} + v_{I-1,J+\frac{1}{2},K}}{(\Delta x)^2} + \frac{v_{I,J+\frac{3}{2},K} - 2v_{I,J+\frac{1}{2},K} + v_{I,J-\frac{1}{2},K}}{(\Delta y)^2} + \frac{v_{I,J+\frac{1}{2},K+1} - 2v_{I,J+\frac{1}{2},K} + v_{I,J+\frac{1}{2},K-1}}{(\Delta z)^2} \\ &= \frac{1}{\mu} \frac{P_{I,J,K} - P_{I,J-1,K}}{\Delta y} \end{aligned} \quad 3.13$$

$$\begin{aligned} & \frac{w_{I+1,J,K+\frac{1}{2}} - 2w_{I,J,K+\frac{1}{2}} + w_{I-1,J,K+\frac{1}{2}}}{(\Delta x)^2} + \frac{w_{I,J,K+\frac{3}{2}} - 2w_{I,J,K+\frac{1}{2}} + w_{I,J-1,K+\frac{1}{2}}}{(\Delta y)^2} + \frac{w_{I,J,K+\frac{3}{2}} - 2w_{I,J,K+\frac{1}{2}} + w_{I,J,K-\frac{1}{2}}}{(\Delta z)^2} \\ &= \frac{1}{\mu} \frac{P_{I,J,K} - P_{I,J,K-1}}{\Delta z} \end{aligned} \quad 3.14$$

$$\frac{u_{I+\frac{1}{2},J,K} - u_{I-\frac{1}{2},J,K}}{\Delta x} + \frac{v_{I,J+\frac{1}{2},K} - v_{I,J-\frac{1}{2},K}}{\Delta y} + \frac{w_{I,J,K+\frac{1}{2}} - w_{I,J,K-\frac{1}{2}}}{\Delta z} = 0 \quad 3.15$$

It can be seen that in the momentum equation in the x-direction, $u_{I+\frac{1}{2},J,K}$ is a function of the pressure gradient in the x-direction and u at its neighbours and similarly $v_{I,J+\frac{1}{2},K}$ and $w_{I,J,K+\frac{1}{2}}$ are functions of pressure gradient, v and w of their neighbours. Therefore, the

discretized momentum equations can be rewritten:

$$A_p u_p = \sum A_n u_n - \Delta_x p \quad 3.16$$

$$A_p v_p = \sum A_n v_n - \Delta_y p \quad 3.17$$

$$A_p w_p = \sum A_n w_n - \Delta_z p \quad 3.18$$

where u_p is the location for which we are solving the velocity components, u_n denote the velocities at neighbouring cells and A_p and A_n are constant coefficients can be obtained from equations 3.12, 3.13 and 3.14.

For decoupling pressure and velocities the Semi-Implicit Method for Pressure-Linked Equations (SIMPLE) that belongs to the family of PBM (Patankar, 1980) is used. This method was pioneered by Patankar and Spalding (1972) and has been widely applied to the fields of computational fluid dynamics and numerical heat transfer. To start using this process we need to make an initial guess for pressure within the porous medium. Then the algorithm calculates the velocity distribution based on the pressure field and if the estimated flow was not divergent free, the pressure field is amended. Then the velocity field based on the pressure can be solved from equations 3.16, 3.17 and 3.18. We call these estimated velocity and pressure fields, $V^* = (u, v, w)$ and p^* respectively. The star superscripts indicate that the obtained velocities are not necessarily correct since they do not satisfy continuity and that the pressure field p^* which has been applied is not necessarily the correct pressure field. The corrected velocities and pressure are obtained by adding the correction values to them:

$$p = p^* + p' \quad 3.19$$

$$V = V^* + V' \quad 3.20$$

where p' and V' are pressure and velocity correction factors. The continuity equation can now be used as an equation to correct the used pressure field. Continuity can be converted to pressure correction by substituting the velocity components as function of pressure correction terms.

$$A_p p'_p = \sum A_n p'_n + b_p \quad 3.21$$

The source term b_p in this equation arises from the incorrect velocity fields which already have satisfied the momentum equations and is called the continuity imbalance. Now, we can amend the pressure and velocity fields and check the convergence criterion. The convergence criterion is defined as the average of continuity imbalance in one voxel over the average volume flux in a voxel. The average flux through a voxel is calculated from:

$$Q_v = \frac{Q}{A_x \phi} = \frac{Q}{N_y N_z R^2 \phi} \quad 3.22$$

where Q_v is average flux passing through a single pore voxel, Q is total flux (in x-direction), N_y and N_z are number of voxels in the y- and z-directions respectively, ϕ is porosity and R is the image resolution which is the size of each voxel.

The average continuity imbalance is:

$$b_{avg} = \frac{\sum_{p=1}^N |b_p|}{N} = \frac{\sum_{p=1}^N |b_p|}{N_x N_y N_z R^3 \phi} \quad 3.23$$

where b_{avg} is average continuity imbalance, b_p is continuity imbalance in each pore voxel, N is the total number of pore voxels, and N_x is the number of voxels in the x-direction.

Therefore, the convergence criterion is defined as:

$$CC = \frac{b_{avg}}{Q_v} = \frac{\sum_{p=1}^N |b_p|}{QN_x R} \quad 3.24$$

where CC is the convergence criterion.

If convergence is not reached, we iterate until we converge for velocity and pressure fields; in the cases we present we iterate until $|CC| < 10^{-4}$.

To reduce memory usage, coefficient matrices are saved in Compressed Row Storage format (Chung, 2002). In addition we process only pore voxels whereas solid voxels are excluded, thus further reducing the memory requirements. To solve the linear system of equations, we apply an algebraic multigrid solver (Stüben, 2001).

The macroscopic boundary conditions are no-flow at solid boundaries and fixed pressures on inlet ($X=0$) and outlet ($X=L$). In the MAC gridding system, the computed velocity component parallel to the solid surface is not located at the surface of solid voxels, but at

the centre of faces – see Figure 3.3. This means that care needs to be taken to apply no-flow condition directly at the solid.

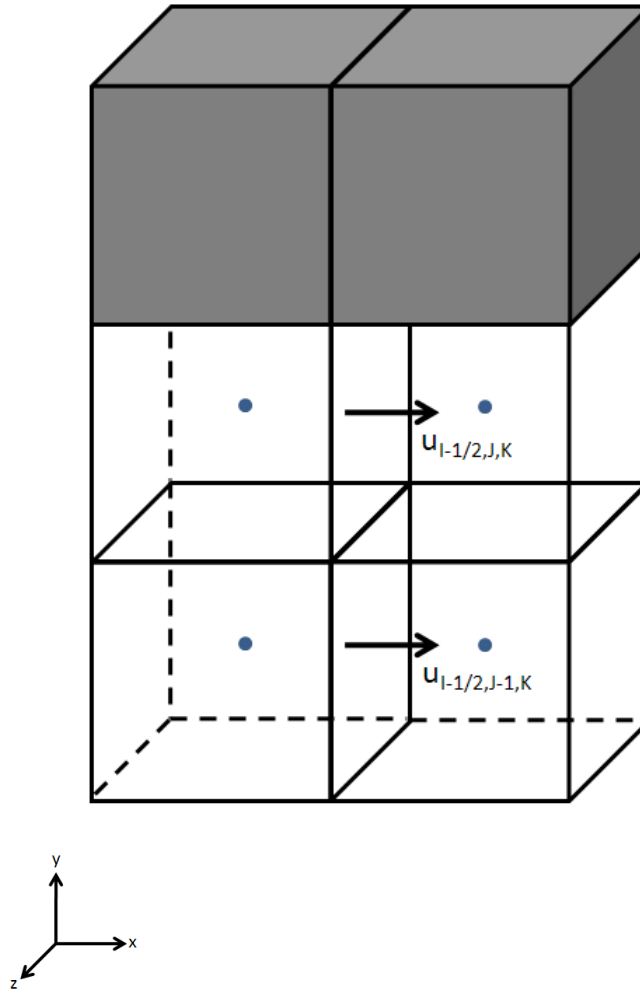


Figure 3.4: To apply a no-slip boundary condition for a pore voxel in the neighbourhood of a solid surface is difficult, since velocities parallel to the solid (shown in dark grey) are assigned at the centre of cell faces, not at the solid boundaries. Non-centred discretization has been applied and we rewrite the equations in blocks containing solid to impose strictly no-flow at the solid surface.

We apply non-centred finite-difference and rewrite the formulation for the cells in the neighbourhood of solid pixels. We place the no-slip condition exactly on the solid surface and write the finite difference equations with this condition. Rewriting a Taylor series for

the velocity parallel to the x-direction, u_s at the surface and at the other side of the cell, for the case illustrated in Figure 3.4, gives us:

$$u_s = u_{I-\frac{1}{2},J,K} + \frac{\partial u}{\partial y} \frac{\Delta y}{2} + \frac{\partial^2 u}{\partial y^2} \frac{(\Delta y)^2}{8} + O(\Delta y^3) \quad 3.25$$

$$u_{I+\frac{1}{2},J,K} = u_{I-\frac{1}{2},J,K} - \frac{\partial u}{\partial y} \Delta y + \frac{\partial^2 u}{\partial y^2} \frac{(\Delta y)^2}{2} + O(\Delta y^3) \quad 3.26$$

The second spatial derivative of velocity in the x-direction parallel to the cell in the neighbourhood of the solid voxels:

$$\frac{\partial^2 u}{\partial y^2} = \frac{-12u_{I-\frac{1}{2},J,K} + 4u_{I+\frac{1}{2},J-1,K}}{3\Delta y^2} \quad 3.27$$

with a similar expression for $\frac{\partial^2 u}{\partial z^2}$. We can also write expressions for derivatives of v and w for surfaces parallel to y and z respectively. These expressions are used to replace the second derivatives terms in equations 3.12, 3.13, and 3.14.

3.3. Storage of variables

In our numerical code, to overcome the memory limitations, all coefficient matrices are saved in a sparse format. In this work, the Compressed Row Storage (CRS) method is employed. CRS is an efficient manner with much lower memory cost to save sparse matrices in compressed form of three vectors (Saad, 1996). Furthermore, two of these matrices are in integer format indicating further reduction in memory. The three vectors to replace the matrix are:

A real vector, R , containing the real non-zero elements of the coefficient matrix stored row by row.

An integer vector, I , containing the column indices of the non-zero elements as stored in the vector R .

An integer vector, J , containing the pointers to the beginning of each row in I and R .

The example below illustrates this algorithm. M is a 7×7 matrix containing 15 non-zero elements. This matrix can be stored via three vectors, R , I , and J .

$$M = \begin{bmatrix} 1 & 2 & 0 & 0 & 0 & 0 \\ 3 & 4 & 0 & 0 & 5 & 0 \\ 0 & 0 & 6 & 7 & 8 & 9 \\ 0 & 0 & 0 & 10 & 11 & 0 \\ 0 & 0 & 0 & 0 & 12 & 13 \\ 14 & 0 & 0 & 0 & 0 & 15 \end{bmatrix}$$

$$R = [1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \ 11 \ 12 \ 13 \ 14 \ 15]$$

$$I = [1 \ 2 \ 1 \ 2 \ 5 \ 3 \ 4 \ 5 \ 6 \ 4 \ 5 \ 5 \ 6 \ 1 \ 6]$$

$$J = [1 \ 3 \ 6 \ 10 \ 12 \ 14 \ 16]$$

As it is obvious, length of R and I vectors equal to the number of non-zero elements while the length of J equal to row dimension of initial sparse matrix plus one.

In addition, the code is equipped with dynamic memory allocation. Memory is allocated to arrays after the dimensions are known and when the arrays are not needed the allocated memory are released.

3.4. Algebraic multigrid solver

Large matrices obtained for solving flow on micro-CT images cannot be solved with a direct method. We have applied an algebraic multigrid to solve the linear system of equations in an efficient manner. An algebraic multigrid solver is a non-direct solver which operates on a hierarchy of smaller matrices. Thanks to the algebraic multigrid solver without changing the geometry and using coarser gridding of the porous medium, we can coarsen just the coefficient matrices obtained from the governing flow equations.

In brief, a multigrid solver, transfers the system of equations to a coarser level. The coarse problem solution then is used as a starting guess on finer mesh and then the system of linear equation is solved in an iterative manner. More details regarding the algebraic multigrid solver can be found in Stüben (2001).

3.5. Validation

In order to validate our method we first consider a simple case of flow between two parallel plates. Figure 3.5 shows a comparison of the computed velocity for different numbers of grid blocks across the opening compared to the analytical solution (White, 1990). For two or more cells between the plates, we obtain the velocity semi-analytically within the machine error and we see the same for flow through a cylinder with a square cross-section.

We also modelled a simple three-dimensional flow around a cubic obstacle. The model contains $50 \times 50 \times 50$ voxels and the cubic obstacle is located at the centre of the opening with dimension of $15 \times 40 \times 40$ voxels. We compared our results against the free open source CFD toolbox, OpenFOAM (www.openfoam.com). The difference in the average velocity estimated is less than 0.1% between the two codes and the local velocities differ by no more than 0.5%.

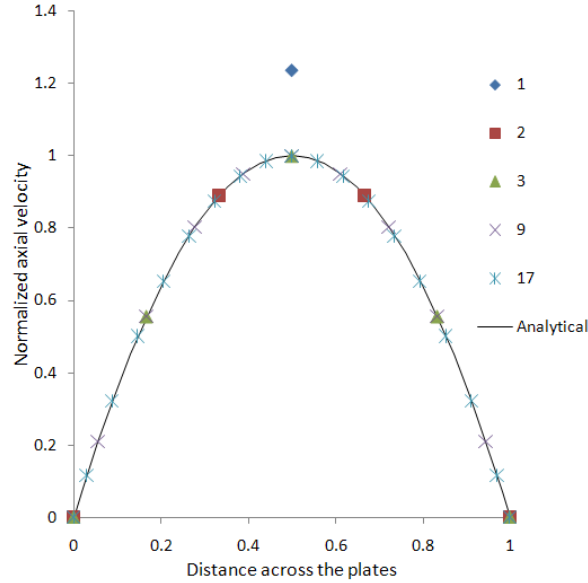


Figure 3.5: Numerical simulation of flow between two parallel plates. The numbers on the legends indicate the number of grid blocks between the plates. We obtain the analytical solution to within machine error if we have two or more blocks.

We then modelled flow through a tube with a circular cross-section. Applying a structured cubic mesh, we have errors in gridding the geometry as well as numerical

errors in the flow simulation. Figure 3.6 shows relative errors in the flow prediction in the tube as a function of the number of voxels (grid blocks) used across the diameter of the tube. Relative error is defined as:

$$E = \frac{|Q_A - Q|}{Q_A} \quad 3.28$$

where E is relative error, Q_A is the analytical flow, and Q is the numerically obtained flow.

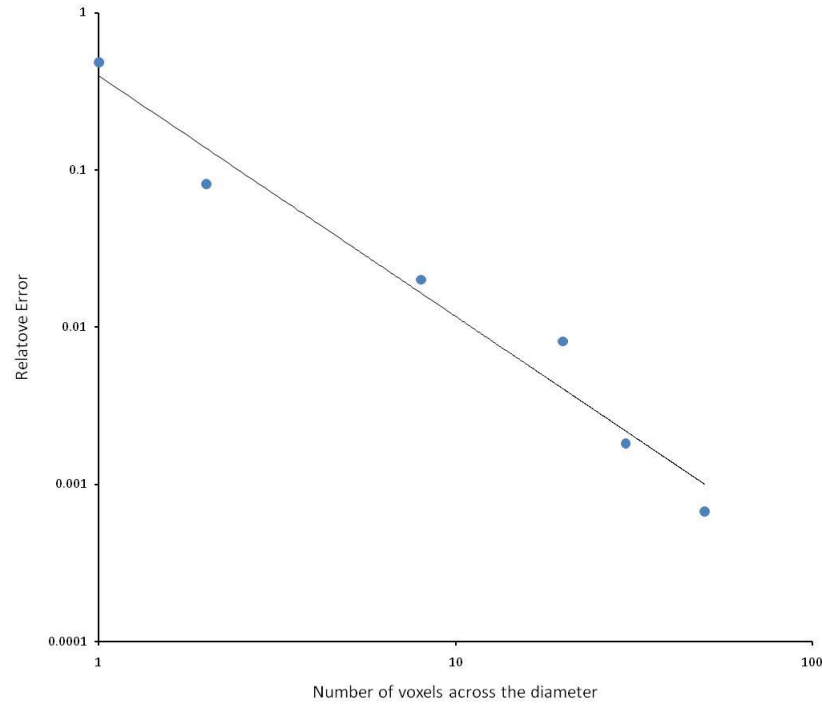


Figure 3.6: Relative error versus number of voxels across the diameter for flow through a tube of circular cross-section. The slope of line in log-log plot is -1.5.

It can be seen in Figure 3.6 that for just one square voxel across the diameter of a circular cross section, the relative error in flux is around 50% but this error is a consequence of the poor representation of the circular geometry. The error decreases approximately as the number of voxels across the circular cross-section to the power of -1.5, indicating approximately 1% error for a 10 voxel-representation.

The method can be applied on binarized-three-dimensional images to model flow within the pore structure. Post-processing data from a micro-CT scanner, the pore geometry of a rock sample can be converted to a binarized image where 0 shows a pore voxel and 1 represents solid phase. Figure 3.7 shows simulation CPU time as function of the number of voxels. The run time scales approximately linearly with the number of voxels. The CPU time has been computed for simulation of flow on subvolumes of a LV60 sandpack image (see Table 3.1). The simulation was performed on a PC with 3.0GHz CPU with no parallel processing. The memory requirement for the 300^3 image size is 3.5 GB, increasing to 40GB for the 700^3 image size. More details of the images themselves and the results of the flow simulations are provided later in this chapter.

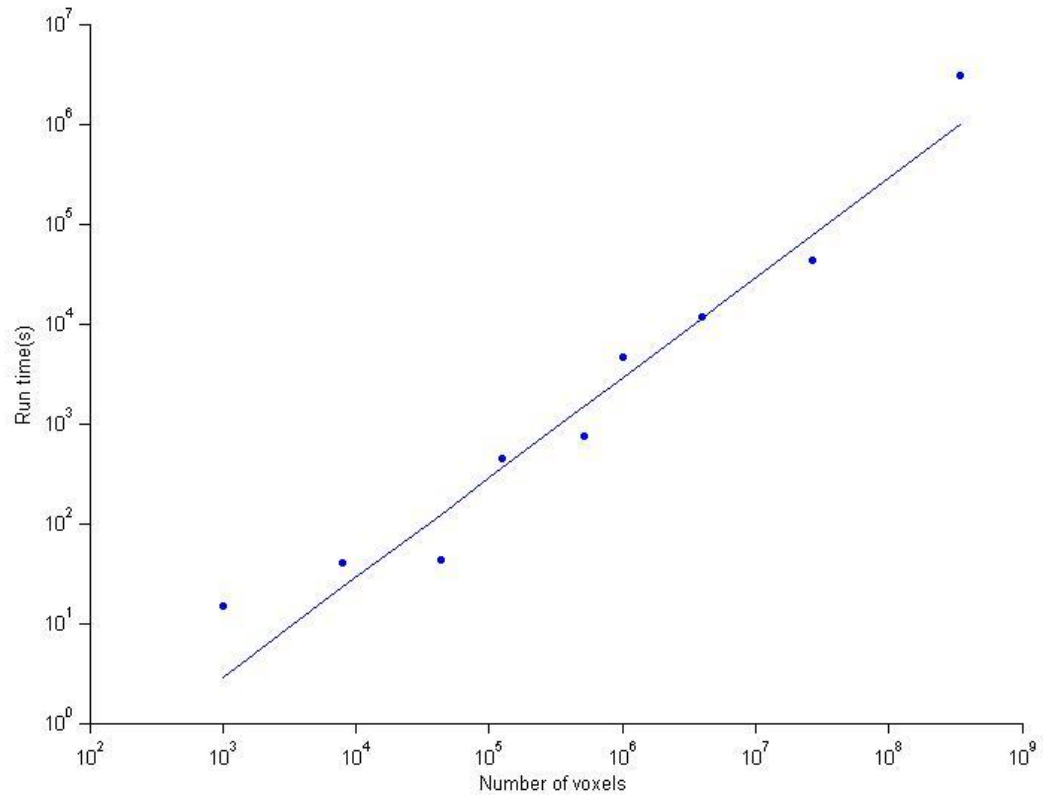


Figure 3.7: CPU time for simulation of images with different sizes on a three-dimensional micro-CT image of an LV60 sandpack along with a line with slope of 1. The run time scales approximately linearly with the number of voxels.

3.6. Results and Discussion

We present the results obtained by applying the flow simulation algorithm to estimate permeability on different rock geometries obtained from micro-CT imaging of core plugs. In addition we describe the heterogeneity of these rocks at the pore scale and discuss the applicability of the Carman-Kozeny equation in this context. Finally, in this section we study the possibility of existence and the size of representative elementary volume on the images studied.

3.6.1. Permeability prediction

We have modelled single-phase flow on a number of sandpack, sandstone and carbonate micro-CT images (Table 3.1). All the images have $300 \times 300 \times 300$ voxels. Having obtained the velocity distribution, the permeability can be calculated from the Darcy equation from the known flow rate Q , the pressure gradient applied ΔP , viscosity of the fluid, μ , the length of the system in the main direction of flow over which pressure gradient has been applied, L_x , and the area of the face normal to the main direction of flow, A_x :

$$K = \frac{L_x}{A_x} \frac{Q\mu}{\Delta P} \quad 3.29$$

If the number of voxels in the main direction of flow is called N_x and in the two other directions is N_y and N_z respectively, we can rewrite the equation for permeability:

$$K = \frac{N_x}{N_y N_z R} \frac{Q\mu}{\Delta P} \quad 3.30$$

where R is the resolution of the micro-CT images.

We simulate flow on two sandpacks with average porosity of 37% and 33%, named LV60 and F42 respectively. Sandpacks as synthetic high porosity porous media are used to study transport phenomena in homogeneous domain and to investigate the effect of heterogeneity when more simulations are performed on heterogeneous porous media like sandstones and carbonates. We also simulate flow on four reservoir sandstones, named S1, S2, S3, and S4 and Berea sandstone and two limestone carbonates named C1 and C2. The predicted permeabilities are in a good agreement with the results obtained by lattice-

Boltzmann method (Dong and Blunt, 2009), as shown in Table 3.1. The difference between our numerical simulations with the lattice Boltzmann results is, perhaps, due to imposed boundary conditions and the different approach to capture the no-slip condition on solid surfaces.

Table 3.1: Estimated permeabilities for the samples studied. For more details about the samples see EPAPS (<http://www.aip.org/pubservs/epaps.html>, Document No. E-PLLEE8-80-220908). $1 \text{ D} = 9.87 \times 10^{-13} \text{ m}^2$. The labels A, B, C indicate that three separate samples of the same material were imaged.

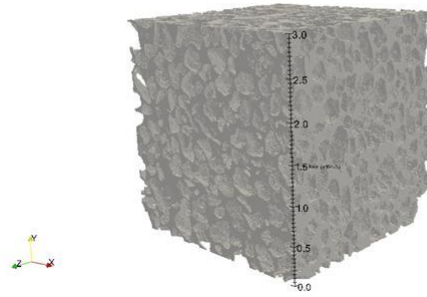
	Resolution (μm)	Porosity (%)	Predicted permeability (D)	Permeability by lattice Boltzmann simulation (D)
Sandpack LV60A	10.0	38	39	35
Sandpack LV60B	8.6	37	34	31
Sandpack LV60C	10.0	37	22	19
Sandpack F42A	10.0	33	62	59
Sandpack F42B	10.0	33	47	52
Sandpack F42C	10.0	33	54	50
Sandstone 1, S1	8.7	20	1.9	1.7
Sandstone 2, S2	5.0	25	2.9	3.9
Sandstone 3, S3	9.1	17	0.19	0.22
Sandstone 4, S4	9.0	17	0.31	0.26
Berea Sandstone	5.3	20	1.4	1.3
Carbonate 1, C1	2.85	23	1.1	1.1
Carbonate 2, C2	5.3	14	0.14	0.07

Experimental measurements of permeability, measured on larger core samples, are also available in some cases (Talabi and Blunt, 2010). The LV60 and F42 sandpacks have permeabilities of $32.2 \pm 0.3 \text{ D}$ and $42 \pm 4 \text{ D}$ respectively which are in reasonably good agreement with the average of our numerical predictions on the three different images. The core-measured permeability of Berea is 0.7 D , which is half the computed value. This is likely to be due to the difference in heterogeneity; the difference in size between

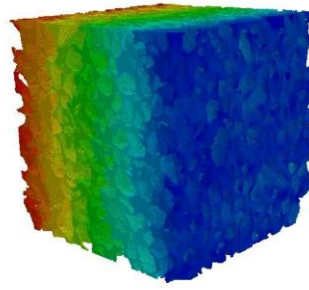
the micro-CT sample of 1.5 mm across and the core sample with a length of 7 cm is large.

We have also simulated flow on a Portland carbonate and a Bentheimer sandstone as they are exemplars for modelling propagator and we can compare our results with NMR measurement on the same rock samples. The Portland carbonate is scanned at Elettra Synchrotron Facility in Trieste, Italy, the Bentheimer sandstone is scanned at iRock Company in Beijing, China. More details will be shown in chapters 4 and 5.

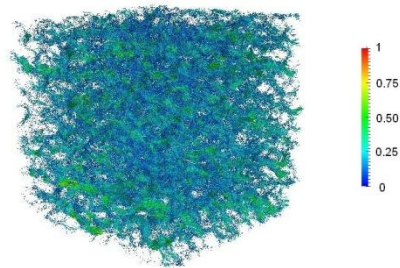
Figures 3.8 - 3.10 show the geometry, normalized pressure distribution and velocity for sandpack LV60, sandstone S1, and carbonate C1 respectively. From Figure 3.8 we observe flow in the sandpack that is well connected and evenly spread. For S1 sandstone in Figure 3.9 we see lower connectivity and more tortuous flow paths. This is even more pronounced for the flow distribution in carbonate C1 in Figure 3.10. This type of analysis offers a fast way of visualizing flow heterogeneity in different classes of porous media. A more quantitative analysis of the permeability variation dependent on flow heterogeneity is presented next.



(a)

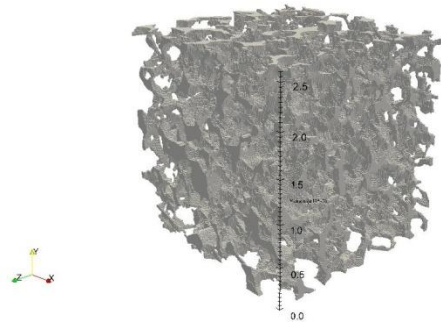


(b)

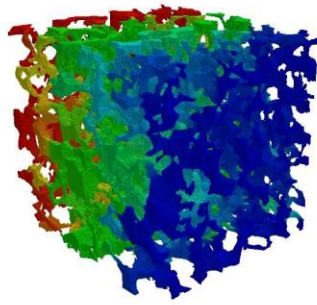


(c)

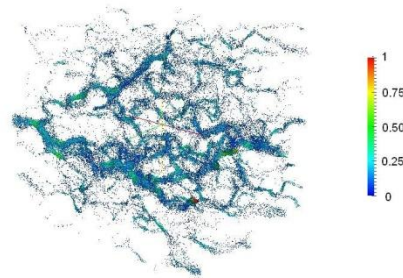
Figure 3.8: Pore structure (a), normalized pressure distribution (b), and normalized flow distribution in LV60A sandpack. The total system size is a cube 3 mm on each side.



(a)

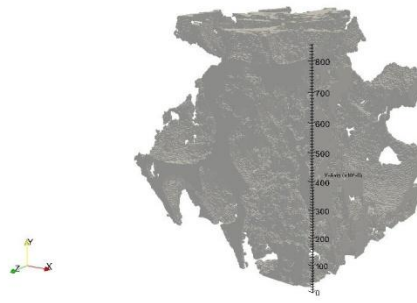


(b)

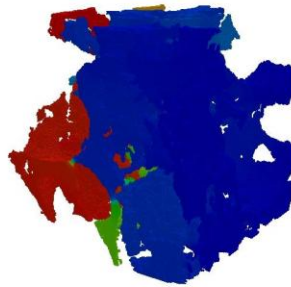


(c)

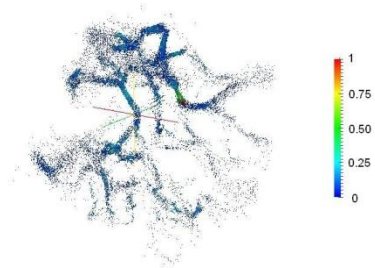
Figure 3.9: Pore structure (a), normalized pressure distribution (b), and normalized flow distribution in S1 sandstone. The total system size is a cube 2.6 mm on each side.



(a)



(b)



(c)

Figure 3.10: Pore structure (a), normalized pressure distribution (b), and normalized flow distribution in C1 carbonate. The total system size is a cube 0.86 mm on each side.

3.6.2. Permeability variation due to heterogeneity

In this section we present an analysis of permeability variation as a consequence of rock sample heterogeneity that can be calculated directly from pore-space images. For each rock image we study the variations in computed permeability on a slice of the original image, starting from the first six layers in the main direction of flow ($6 \times 300 \times 300$), and then expanding it to the image size $300 \times 300 \times 300$. In this way we increase the number of layers normal to main direction of flow from 6 to 300. Figure 3.11 shows the change in the image subsets permeability normalized by the permeability of the total images volume with increase of the number of layers in each subset. As it can be seen the slope changes considerably for different rock types. By adding each set of layers to the model, the flow is additionally dispersed thus reducing the flux in the flow direction for the same value of the pressure gradient.

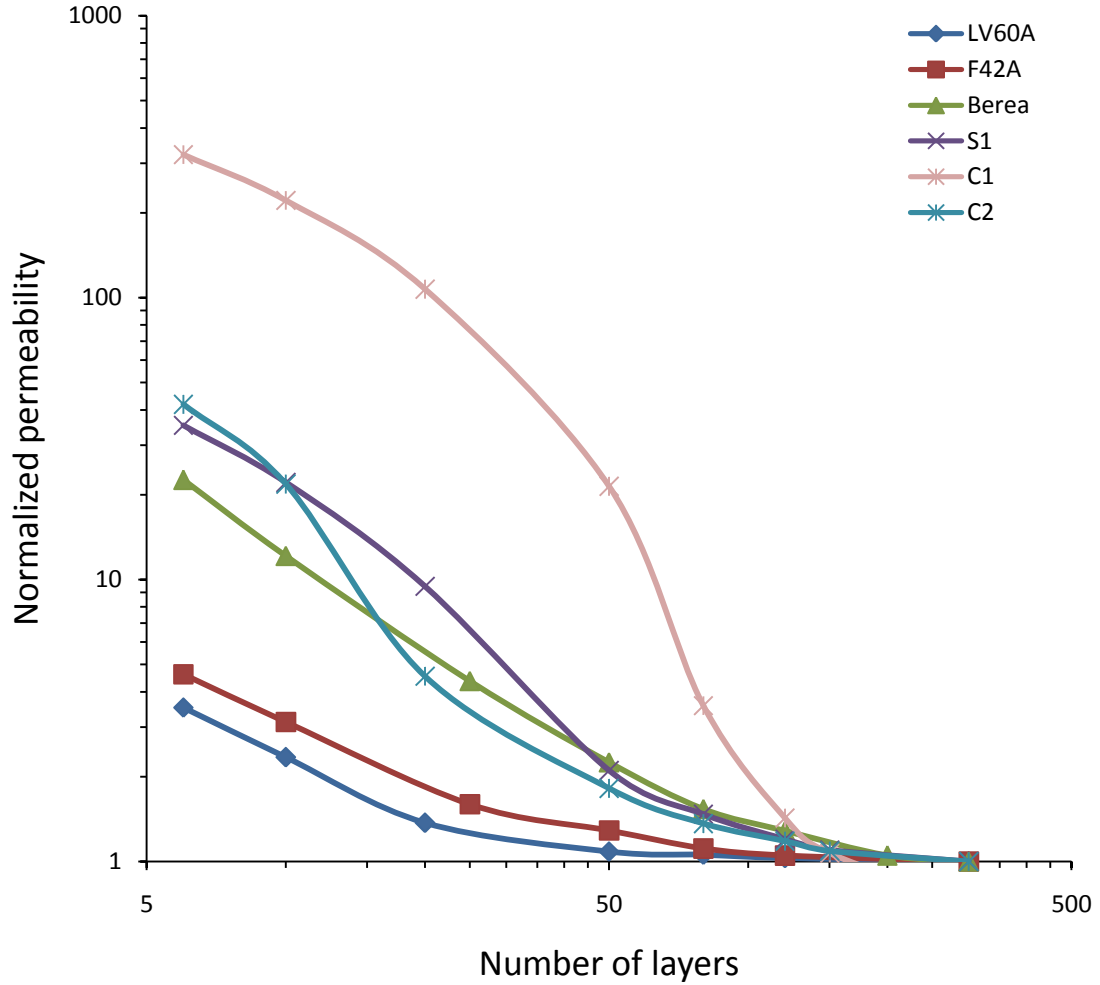


Figure 3.11: Normalized permeability (computed permeability divided by the permeability computed on the whole image) for images with different number of layers normal to the main direction of flow. The number of voxels in both y- and z-directions is 300. For instance, if the number of layers is 50, the image size is 50×300×300. The linear slope of these variations can be used as an index for heterogeneity. We start from the first layer in direction of flow and go to the whole image size.

The slope of the trend of $\log(K)/\log(N_L)$, where N_L is the number of layers is higher for sandstones and even more for carbonates when compared to unconsolidated porous media. This is a consequence of less connectedness and more tortuous geometry of sandstones and carbonates at the pore scale, as evident in Figures 3.9 and 3.10. Table 3.2 presents the average linear slope for each of the samples.

Table 3.2: The slope representing permeability variation as a function of the number of layers for the samples studied.

	Slope
Sandpack LV60	0.31
Sandpack F42	0.40
Berea	0.82
Sandstone 1	1.02
Carbonates 1	1.05
Carbonates 2	1.70

3.6.3. Carman-Kozeny equation

The most common approach to predict permeability of a porous medium is by using the Carman-Kozeny equation (Carman, 1937):

$$k = \frac{1}{c} \frac{\phi^3}{S^2 (1-\phi)^2} \quad 3.31$$

where ϕ is porosity, S is the specific surface area – the surface area between pore and grain per unit rock volume (m^{-1}) and c is constant generally given the value 5.0.

This equation relates permeability to porosity and specific surface area and is a convenient method to predict permeability without solving the governing equations on the extremely complex three-dimensional geometries of porous media, when a good image is available to find the specific surface area. However, this equation does not work accurately for all types of porous medium – indeed, as we show later, it gives very poor predictions for complex samples. It has been shown that this equation can estimate permeabilities of sphere packings (Philipse and Pathmamanoharan, 1993, Thies-Weesie and Philipse, 1994). Lemaitre and Adler (1990) have also shown that this equation is valid for high-porosity fractal porous media.

We calculate the values for the Kozeny constant to match the computed permeability; the results are shown in Table 3.3. The specific surface area is found by counting the number of faces between pore and grain in the image and dividing by the number of voxels and the image resolution. Our results for sandpacks, $c \approx 7$, are in reasonable agreement with the traditional constant from the Carman-Kozeny equation, which is not surprising, since the method was developed for simple grain packings.

However, the application of this simple equation for more heterogeneous media is less promising, Table 3.3. Carman-Kozeny equation significantly over-estimates permeability – in many cases by over a factor of 10 – since it does not account sufficiently for the complex, tortuous and poorly connected nature of the pore space. For sandstones and carbonates the constant can vary over a wide range depending on the complexity of the morphology of the rocks. This implies that direct computation is required for these types of sample.

Table 3.3: Porosity, specific surface area, and permeabilities for a set of sandpacks, sandstones and carbonates and estimated Kozeny constants.

	Porosity (%)	Specific Surface Area (mm^{-1})	Permeability (D)	Kozeny Constant
Sandpack LV60A	38	22.1	39	7.25
Sandpack LV60B	37	22.9	34	7.16
Sandpack LV60C	37	26.24	22	8.43
Sandpack F42A	33	14.7	62	5.98
Sandpack F42B	33	15.2	47	7.37
Sandpack F42C	33	15.4	54	6.25
Sandstone 1	20	9.9	1.9	20.22
Sandstone 2	25	27.3	2.9	12.19
Sandstone 3	17	19.7	0.19	93.97
Sandstone 4	17	20.3	0.31	57.28
Berea Sandstone	20	23.9	1.4	14.65
Carbonate 1	23	35.7	1.1	14.77
Carbonate 2	14	14.3	0.14	130.14

3.6.4. Representative Elementary Volume

When applying pore-scale modelling to predict macroscopic parameters, it is of great importance that the underlying model of the pore space is representative of the rock structure at a larger scale.

In this section we investigate the possible existence and the size of a representative elementary volume (REV) for two sandpacks, two sandstones, and two carbonates. The REV is defined as the smallest volume that can be assumed at the continuum scale for which the microscopic properties (e.g. porosity) do not change if its dimensions are incremented (Bear, 1972). In other words, the REV is the smallest subvolume of a rock capable of representing its physical properties. The discussion in relation to concept of REV can be found in many publications (Nordahl and Ringrose, 2008, Noetinger, 1994, Hurst, 1993, Hassanizadeh and Gray, 1979). It needs to be mentioned that REV can be considered on different geological length scales. Norris and Lewis (1991) introduced the notation of scale n for the REV. Based on their definition, there are three distinct scale where the concept of REV can be found, $n=1$, 2 , and 3 named lamina, lithofacies, and facies association respectively (Figure 3.12). In this work, we study the existence of an REV at the lamina scale $n=1$. However, studies on REV on larger scales corresponding to $n=2$ and $n=3$ can be found in the literature (Muller, 2010, Nordahl and Ringrose, 2008, Li et al., 2009). The existence and size of the REV at the pore scale has been studied for different porous media (Al-Raoush and Papadopoulos 2010, Okabe and Oseto, 2006, Zhang et al., 2000). We study and compare the size of the REV for a set of unconsolidated and consolidated porous media obtained from micro-CT scanning of core samples.

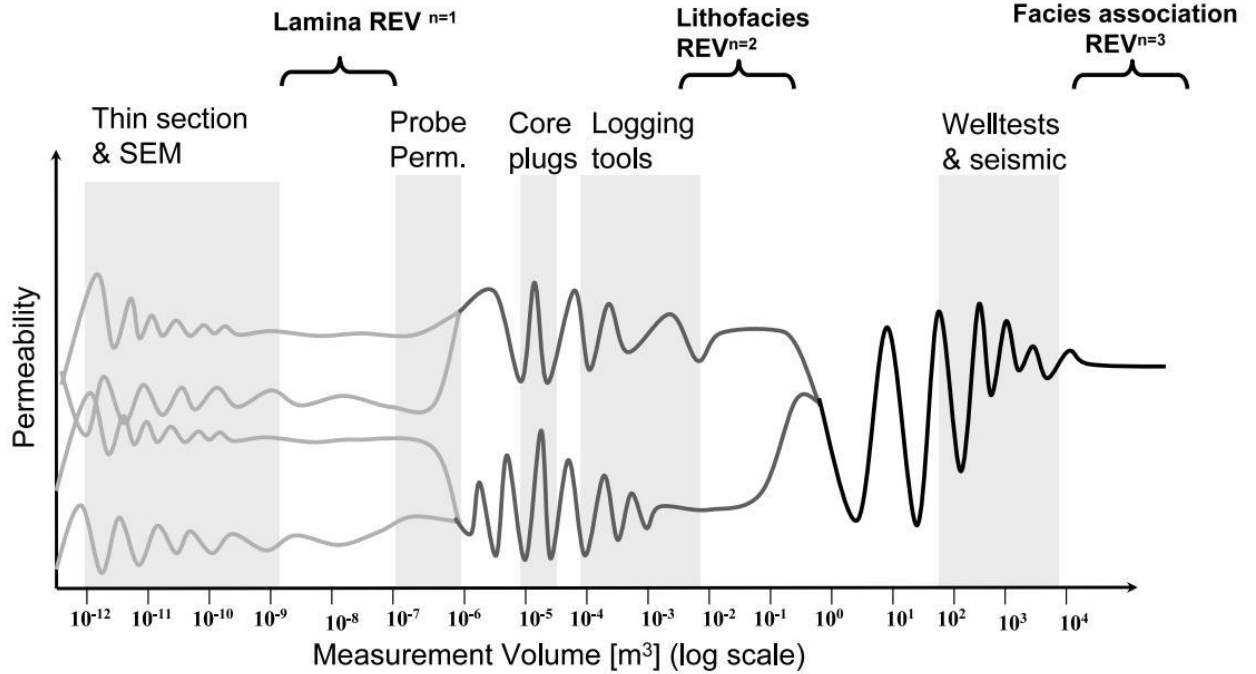


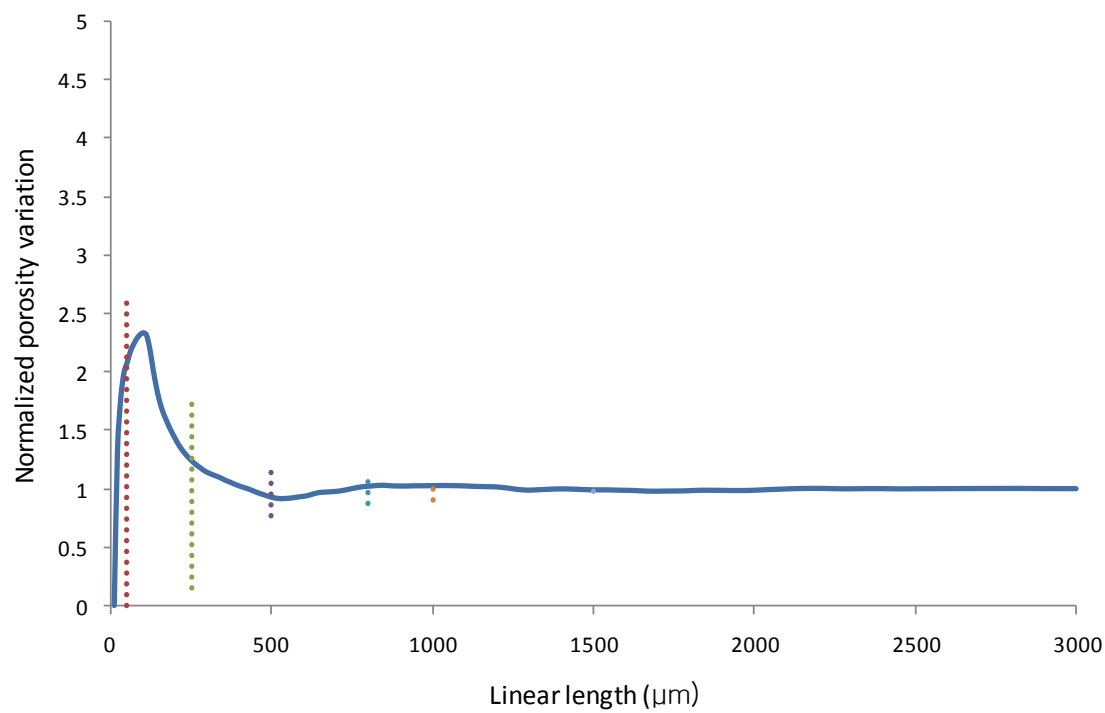
Figure 3.12: A schematic variation of permeability in different scale. This figure shows existing of REV at three scales, Lamina, Lithofacies and Facies association – reprinted from Nordahl and Ringrose (2008).

Figures 3.13 and 3.14 show the variation of porosity, specific surface area and permeability over sample length for two sandpacks (LV60A and F42A). Subvolumes of the original images, centred on the centre of the image, were considered. Dashed lines show the range of variation from lowest to highest calculated for porosity, specific surface area, and permeability for the independent subvolumes with the same size on the micro-CT image. The subvolumes cannot be independent for size bigger than about $150 \times 150 \times 150$. Therefore, the variation may be larger than that shown in the graphs. It can be seen that images with size of $50 \times 50 \times 50$ corresponding to a linear length of 0.5mm are sufficiently large to represent the porosity and specific surface area of the total sample volume. However, for permeability of both sandpacks, we see convergence to the REV for subvolumes larger than $110 \times 110 \times 110$ corresponding to a linear length 1.1mm; this larger REV is a consequence of having to capture the tortuosity and connectivity of the pore space. According to simulations on a crushed glass beads by Zhang et al. (2000) the REV based on porosity and permeability can be reached for linear dimensions of 1.71mm

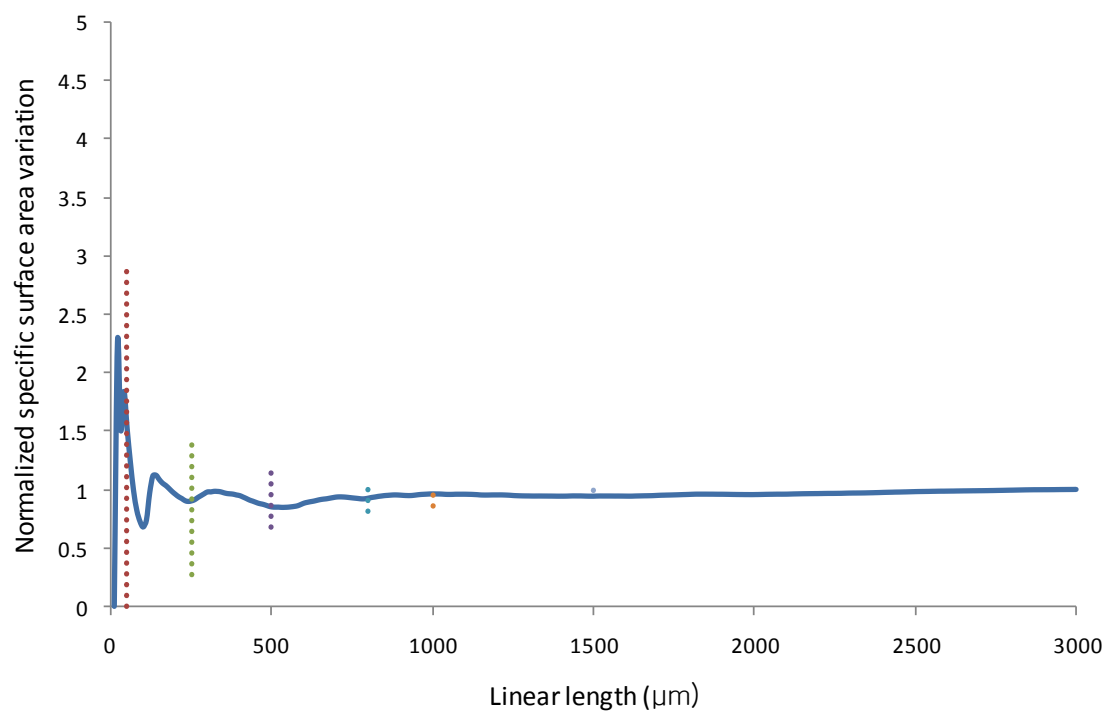
and 2.57mm which is larger than what we observe. This could be due to different grain size and higher heterogeneity of their sample.

Figures 3.15 and 3.16 show the trends of porosity, specific surface area and permeability for two sandstone samples (Berea and sandstone S1). The results indicate that for porosity and specific surface area, images larger than $120 \times 120 \times 120$ have constant properties. For the permeability variation the sizes larger than about $150 \times 150 \times 150$ corresponding to a linear length of about 1mm can be considered the REV. Okabe and Oseto (2006) applied a lattice Boltzmann simulation and showed that images larger than 1.2mm can be considered as REV for Berea sandstone in terms of porosity and permeability. Oveysi and Piri (2010) showed a linear size of 0.68mm as the REV for a reservoir sandstone which is in good agreement with our findings.

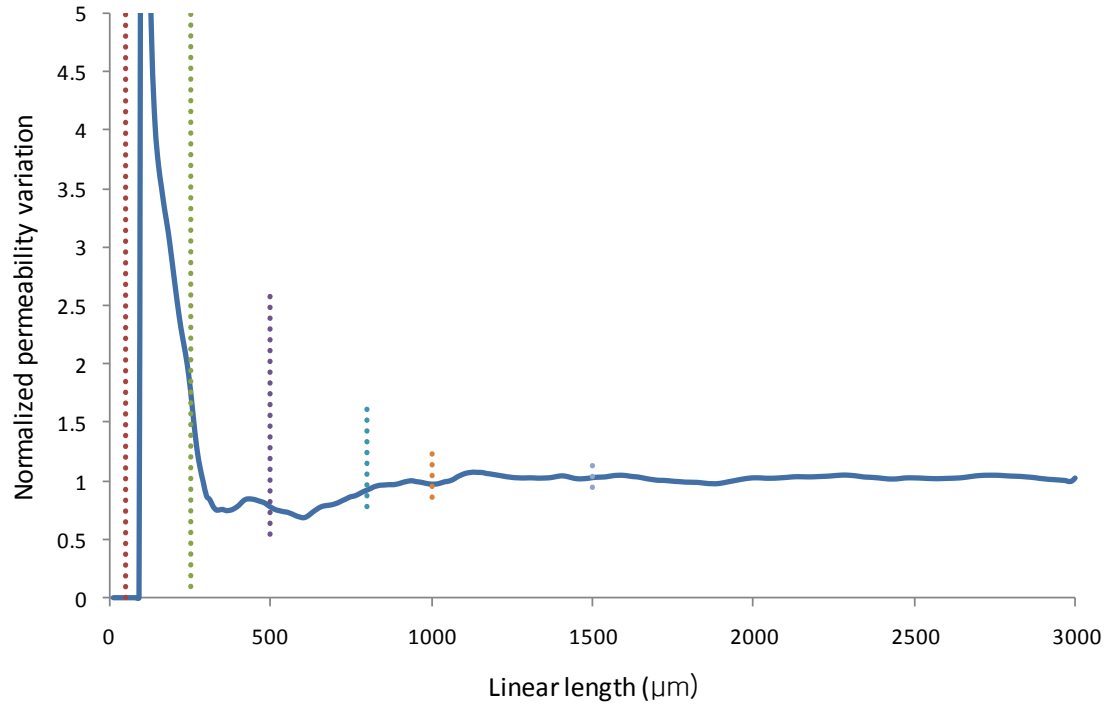
The REV of carbonate samples cannot be observed over the maximum image size shown ($300 \times 300 \times 300$ corresponding to a linear dimension of 0.86 and 1.6 mm for C1 and C2 respectively) for the porosity and specific surface area and the variation is even larger for permeability (Figures 3.17 and 3.18). This suggests that for the carbonates, the images are not sufficiently large to obtain reliable macroscopic estimates of permeability.



(a)

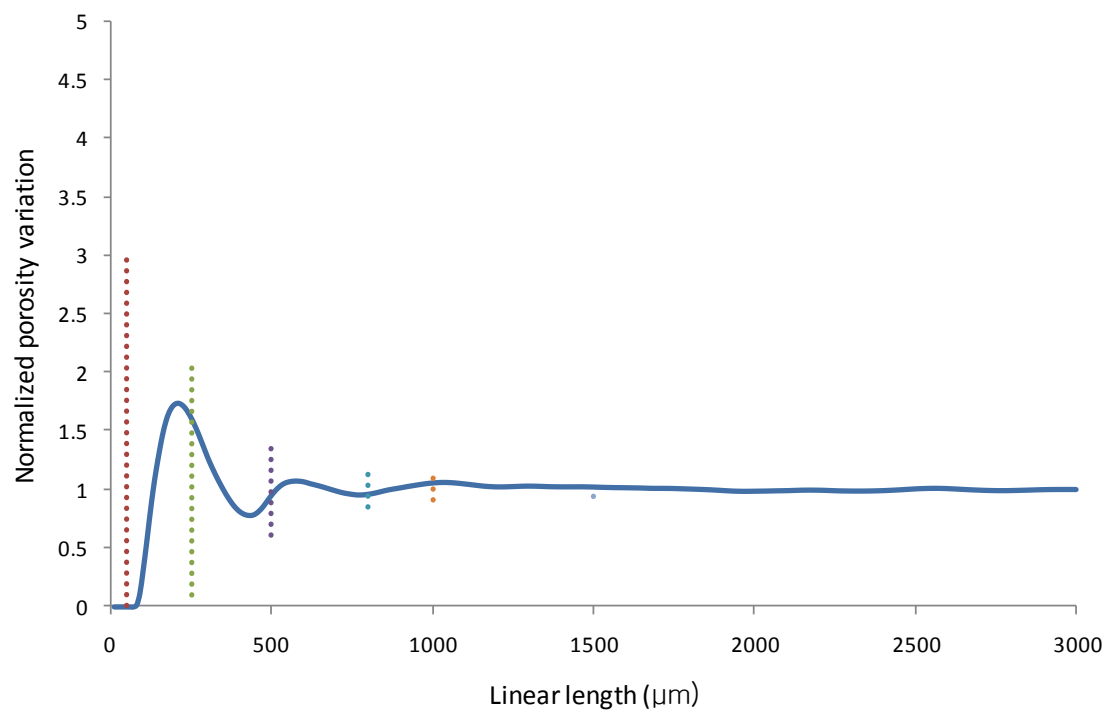


(b)

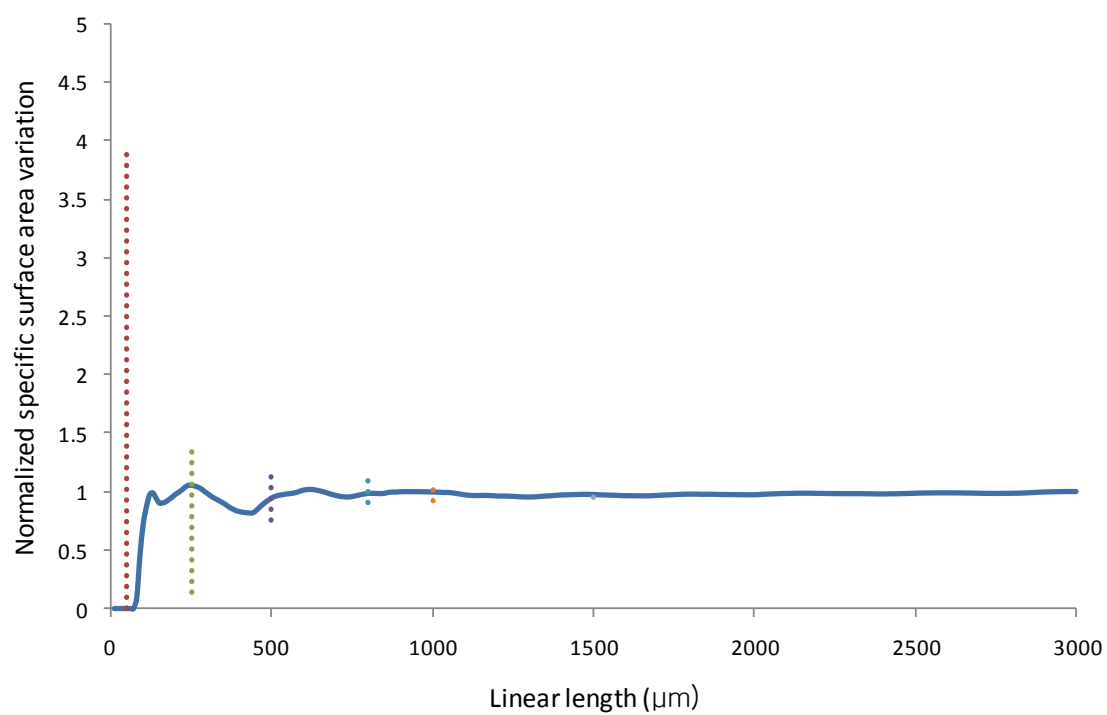


(c)

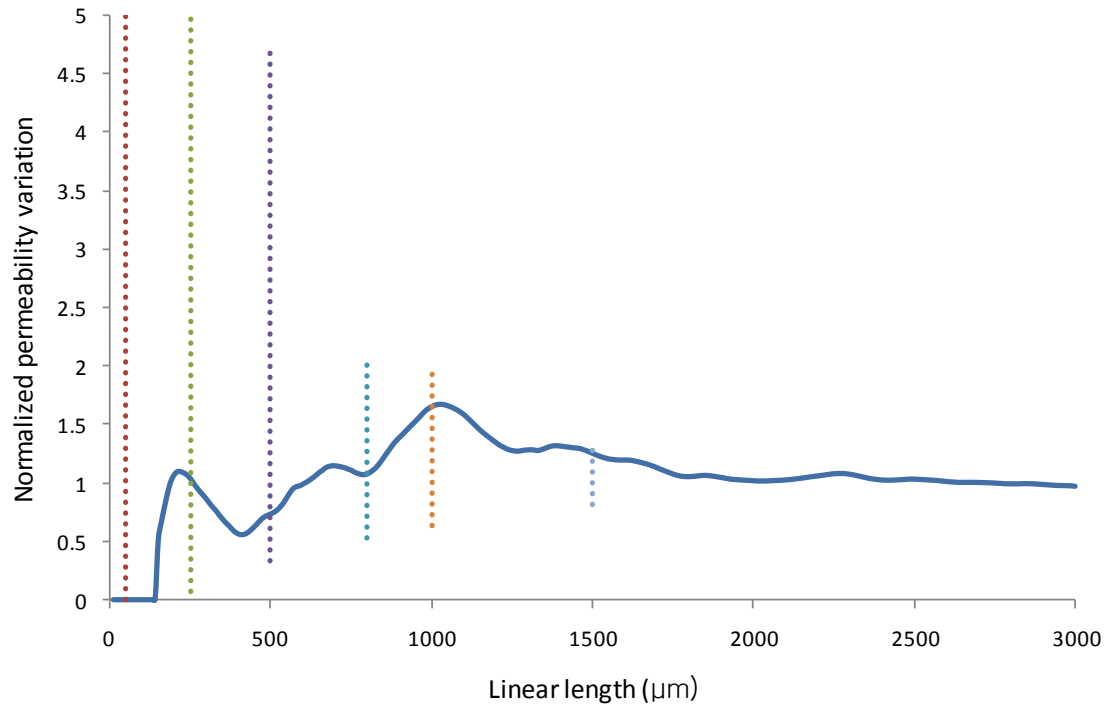
Figure 3.13: Porosity (a), specific surface area (b), and permeability (c) as a function of linear length (measured in number of voxels across each side of a cubic image multiplied by the image resolution) for sandpack LV60A. All values are normalized to the values obtained for the full image size (300 voxels). Dashed lines show the variation of properties of all subvolumes of the same size on the image.



(a)

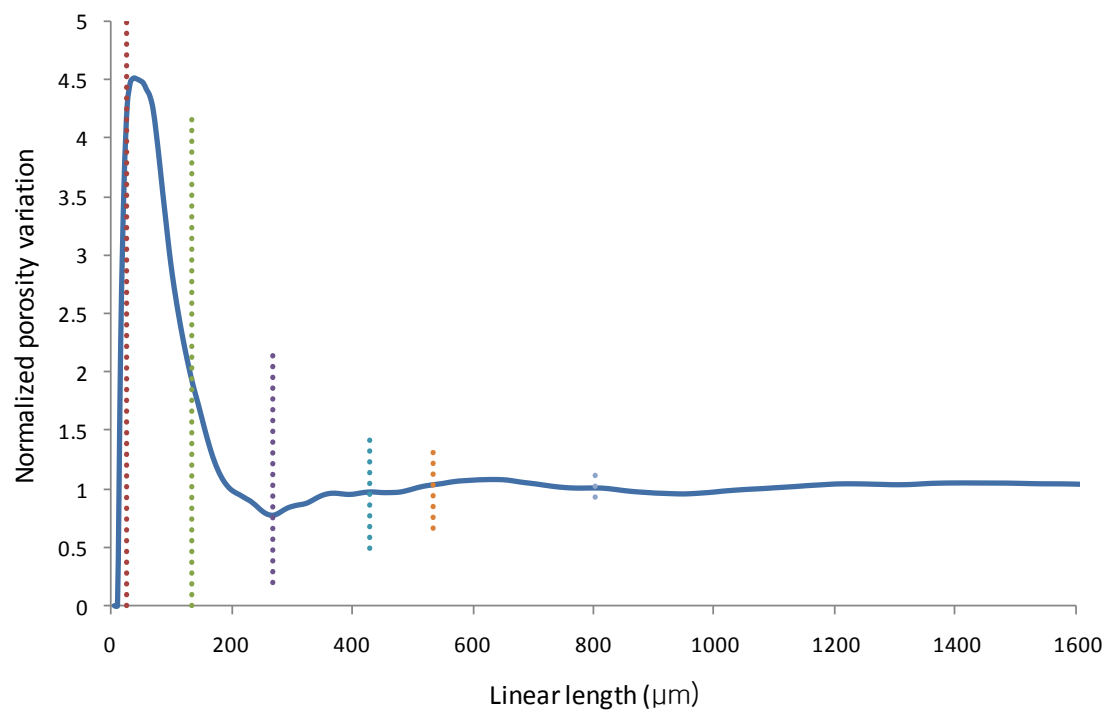


(b)

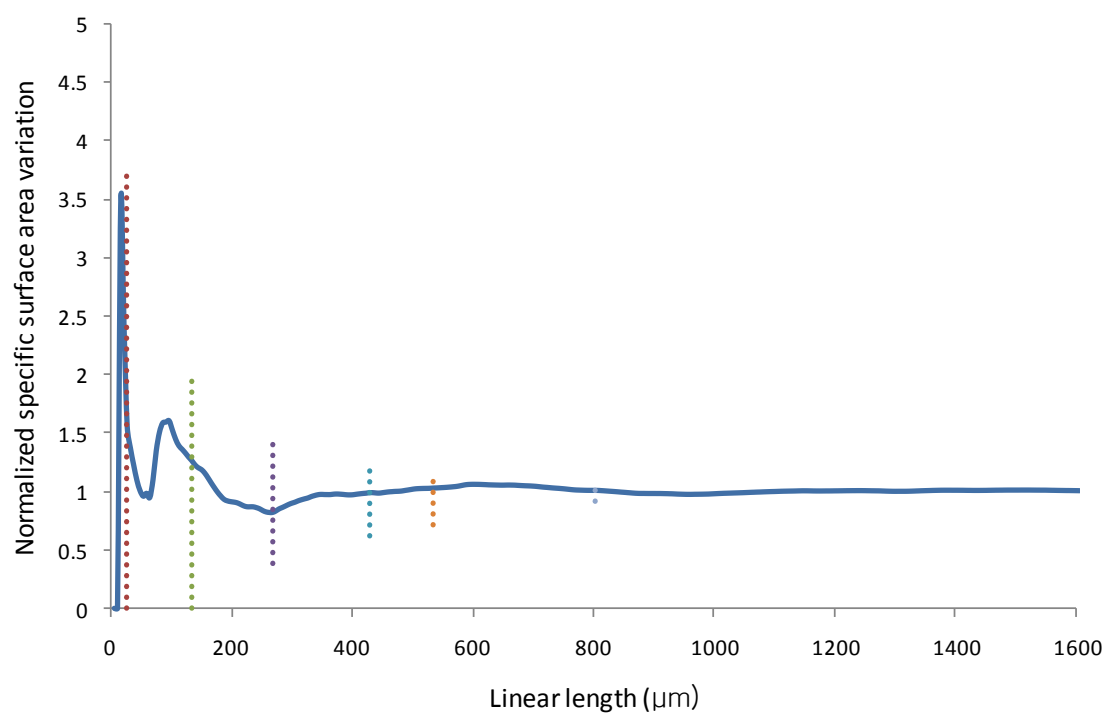


(c)

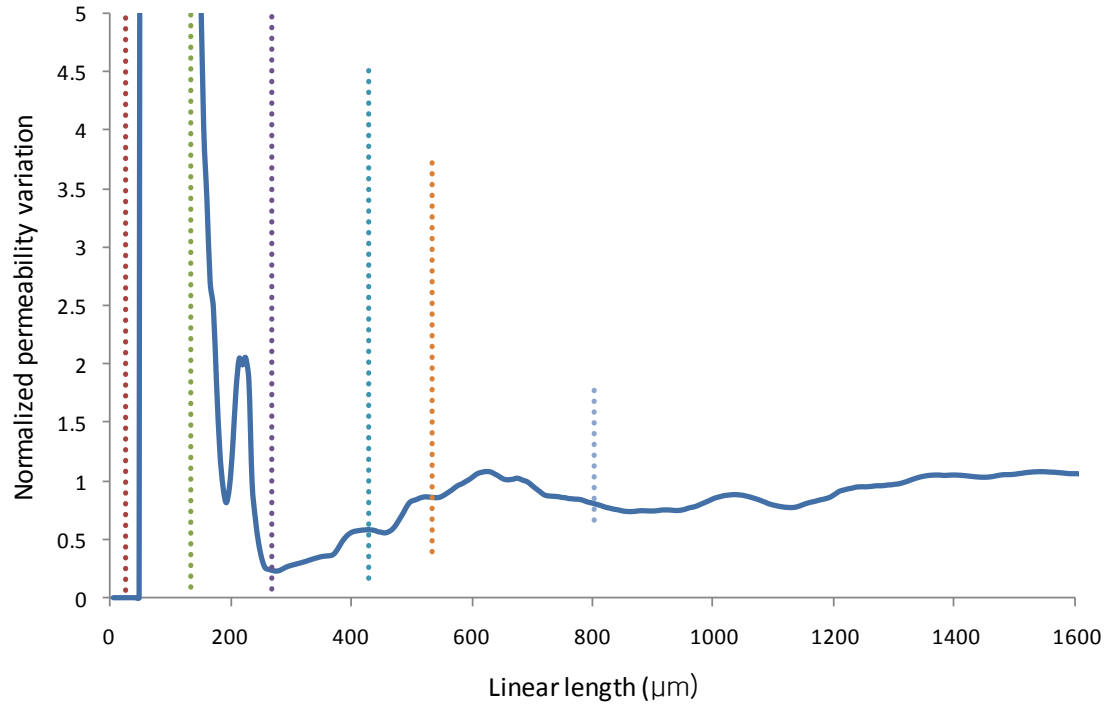
Figure 3.14: Porosity (a), specific surface area (b), and permeability (c) as a function of linear length (measured in number of voxels across each side of a cubic image multiplied by the image resolution) for sandpack F42A. Dashed lines show the variation of properties of all subvolumes of the same size on the image.



(a)

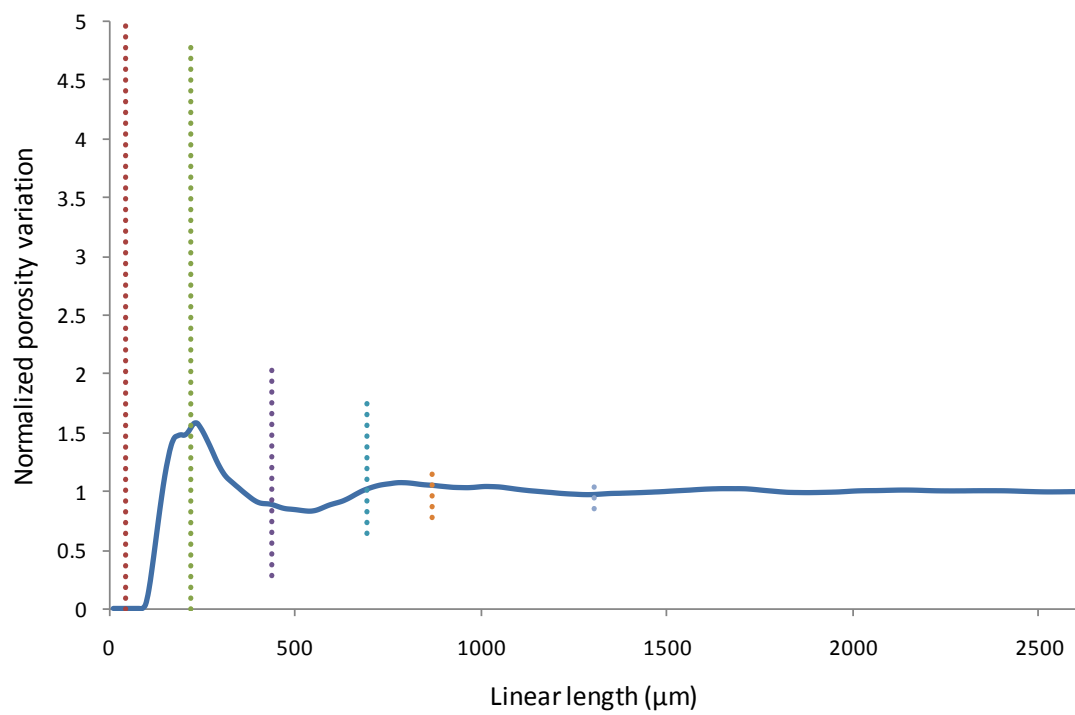


(b)

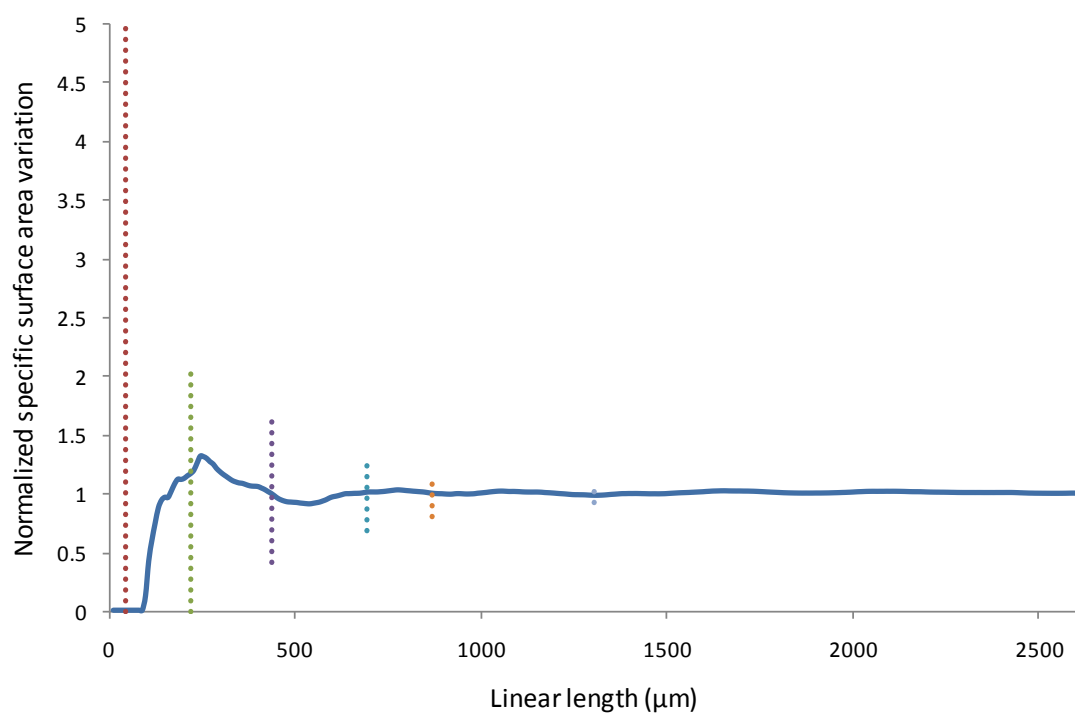


(c)

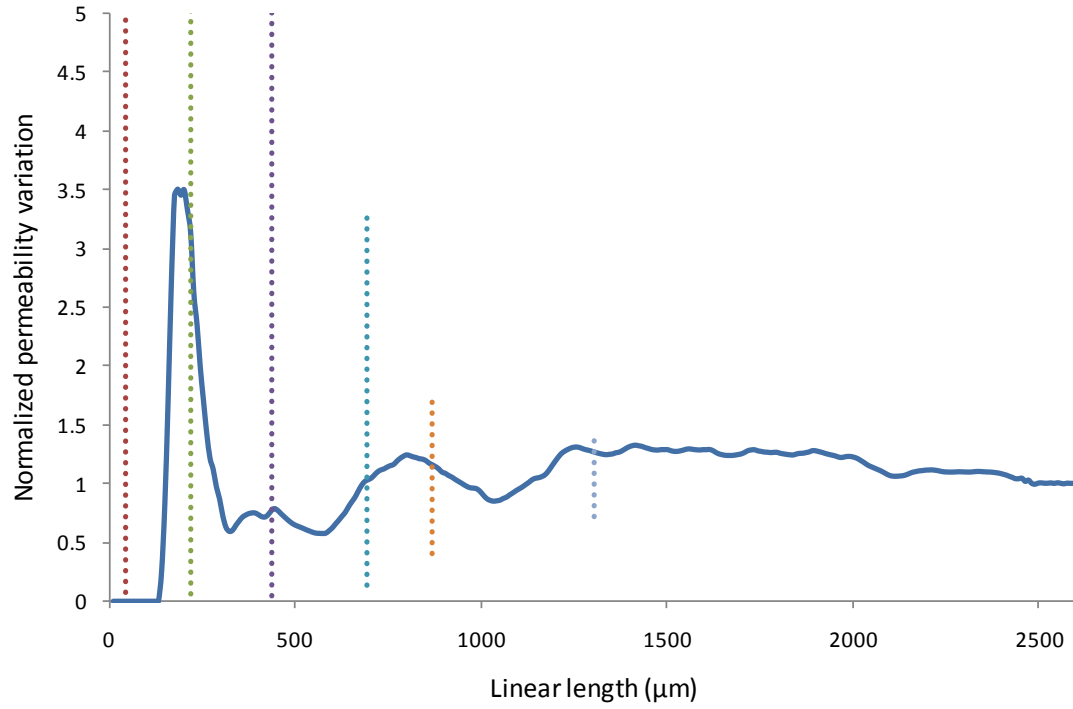
Figure 3.15: Porosity (a), specific surface area (b), and permeability (c) as a function of linear length (measured in number of voxels across each side of a cubic image multiplied by the image resolution) for Berea sandstone. Dashed lines show the variation of properties of all subvolumes of the same size on the image.



(a)

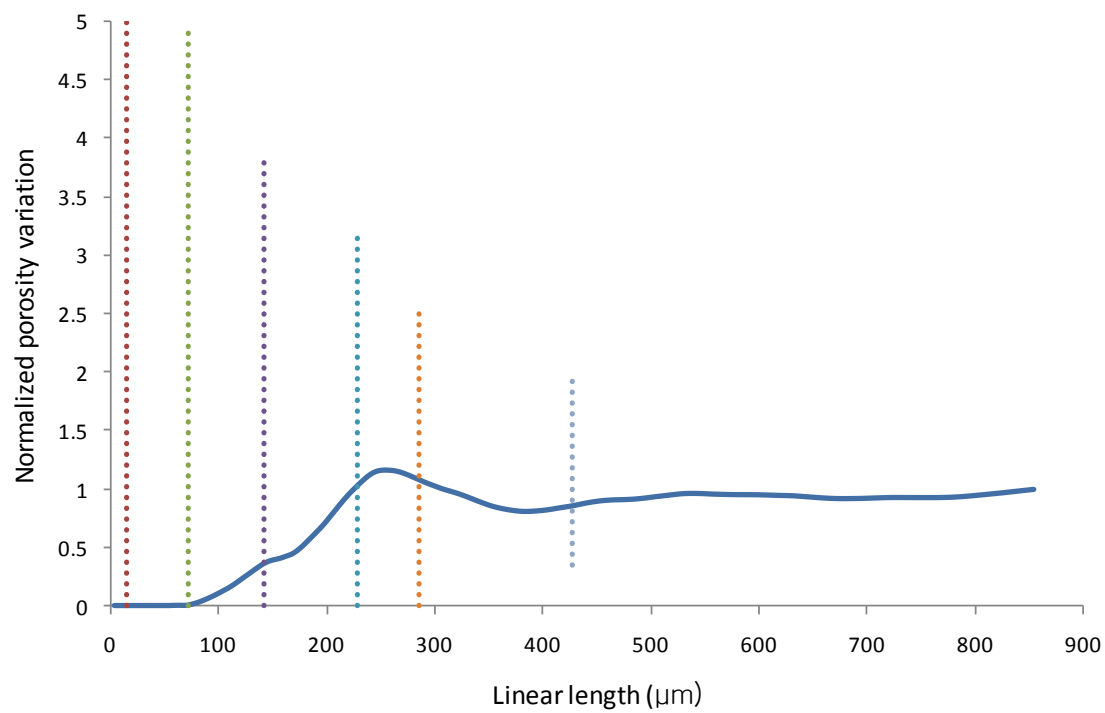


(b)

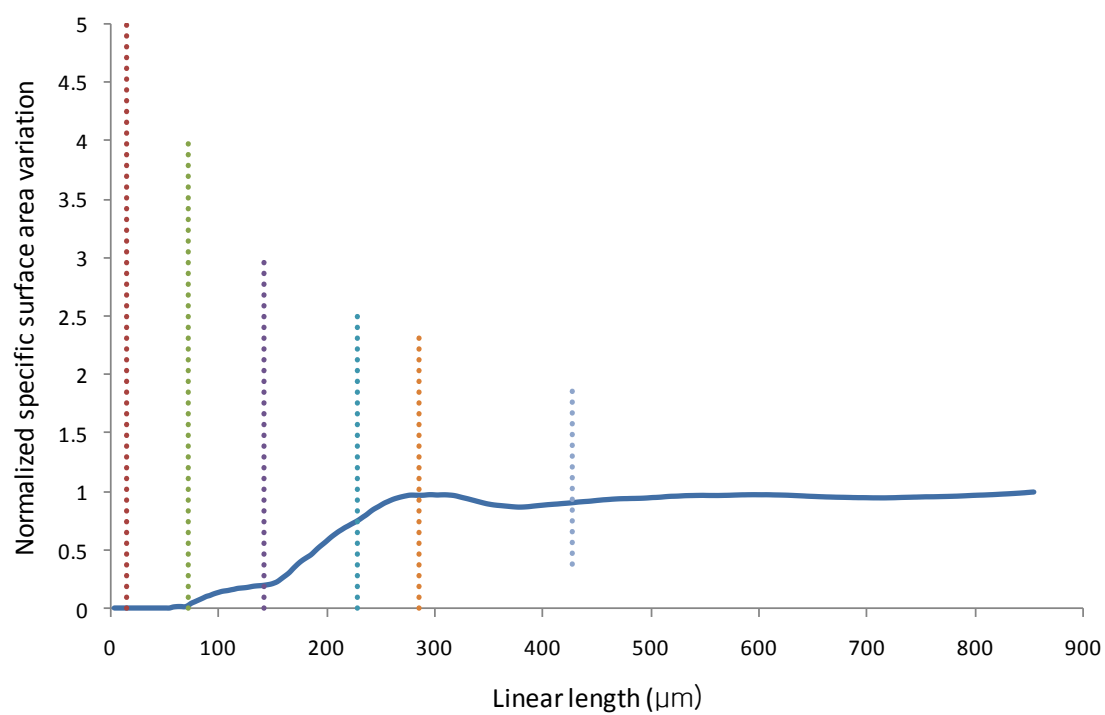


(c)

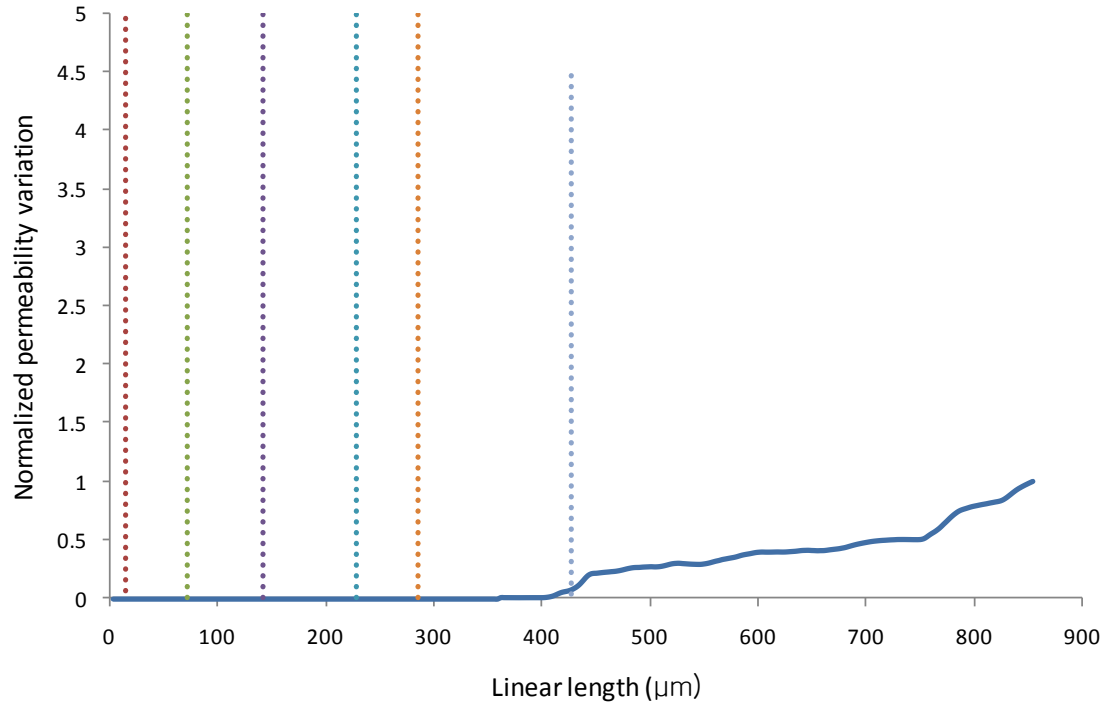
Figure 3.16: Porosity (a), specific surface area (b), and permeability (c) as a function of linear length (measured in number of voxels across each side of a cubic image multiplied by the image resolution) for sandstone S1. Dashed lines show the variation of properties of all subvolumes of the same size on the image.



(a)

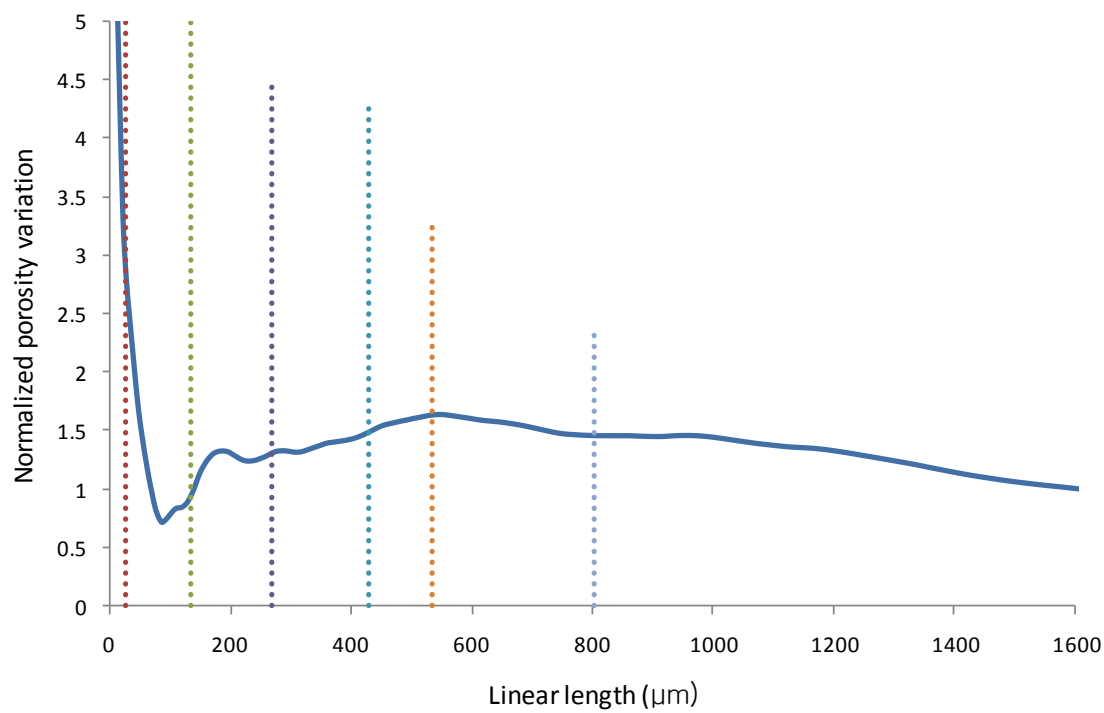


(b)

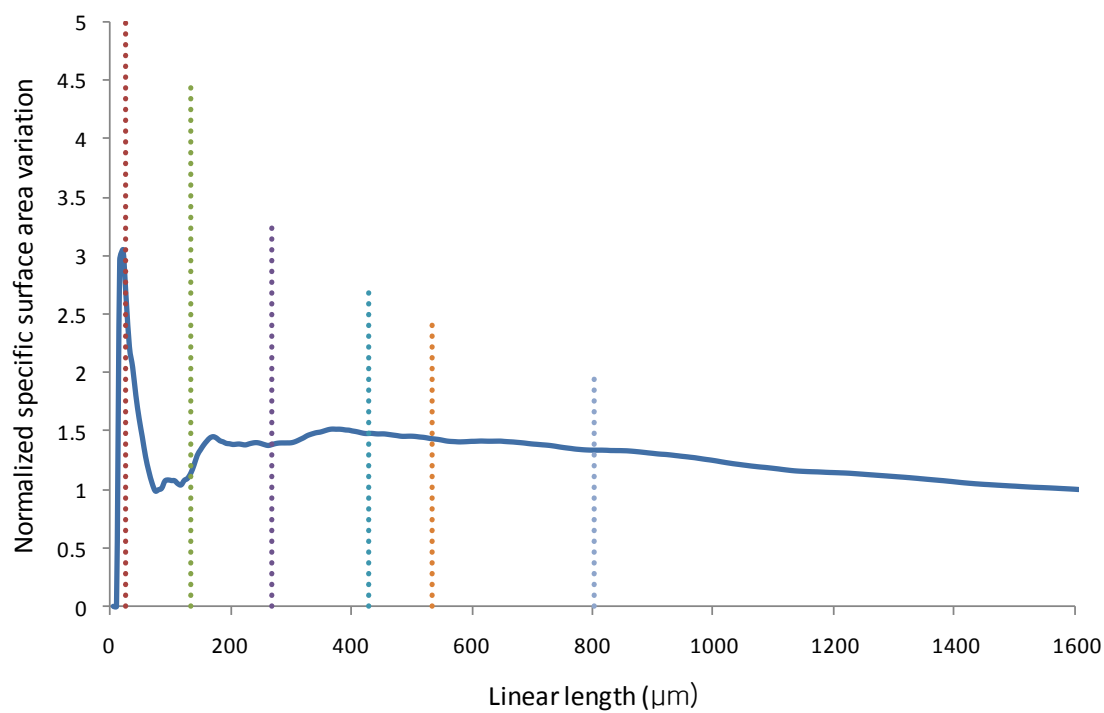


(c)

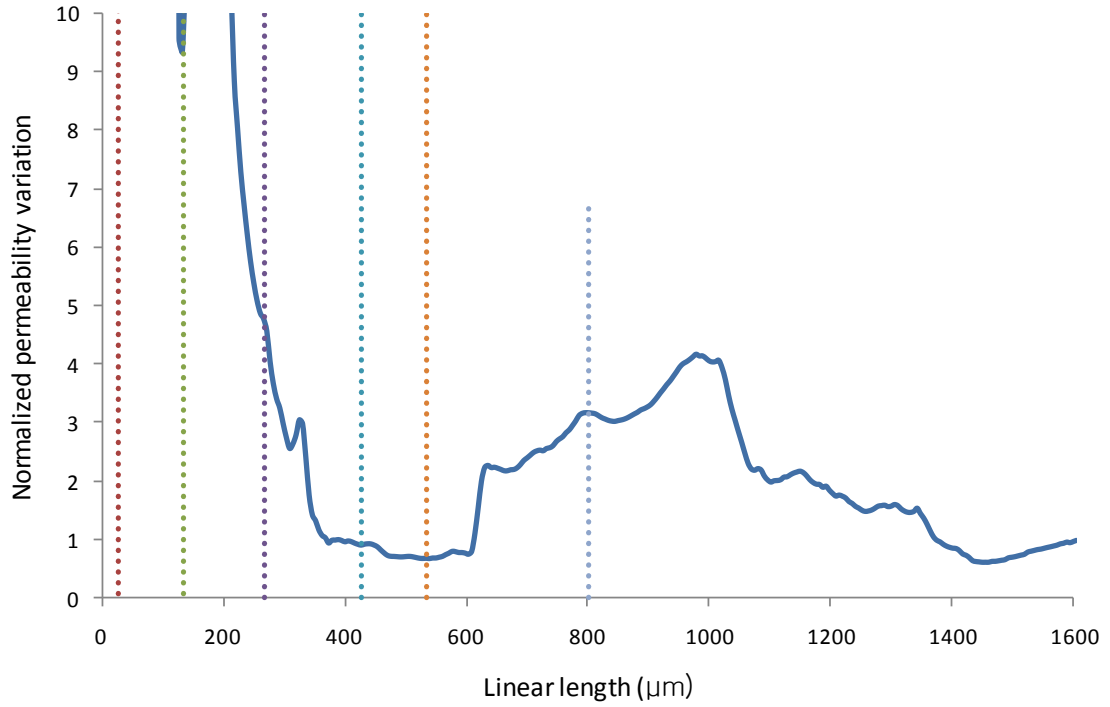
Figure 3.17: Porosity (a), specific surface area (b), and permeability (c) as a function of linear length (measured in number of voxels across each side of a cubic image multiplied by the image resolution) for carbonate C1. Dashed lines show the variation of properties of all subvolumes of the same size on the image.



(a)



(b)



(c)

Figure 3.18: Porosity (a), specific surface area (b), and permeability (c) as a function of linear length (measured in number of voxels across each side of a cubic image multiplied by the image resolution) for carbonate C2. Dashed lines show the variation of properties of all subvolumes of the same size on the image.

From this analysis it is evident that the size of REV is not the same for the geometry-based parameters (porosity and specific surface area) and the flow-based one (permeability): the size of REV based on permeability can be up to two times larger than size of REV based on porosity and specific surface are. The main reason is dependence of permeability on flow pattern, tortuosity and connectivity of pores in contrast to porosity and specific surface which are two geometry-based static properties of rocks.

4. Dispersion modelling

As discussed earlier, the transport of solute in the absence of reaction is due to two types of motion: advection and diffusion. Advection is dictated by the velocity distribution within the porous medium. The more heterogeneous the velocity distribution is, the more dispersion we will see in the particle distribution. On the other hand, diffusion is due to Brownian motion of particles in the void space and can be quantified with the diffusion coefficient.

We have developed a novel streamline-tracing technique to model advection. For voxels with no solid boundary, the method is identical to the Pollock's algorithm (Pollock, 1988) that is now standard in field-scale streamline-based reservoir simulators. Where a solid boundary is present, zero tangential and normal velocity is strictly imposed, resulting in a bilinear variation of tangential velocity away from the boundary. A semi-analytic description of the velocity field within a grid block is obtained for all combinations of solid boundaries

Afterwards, we model the diffusive motion of solute particles. A random walk method accounts for mixing by diffusion which is an established technique to model conservative and reactive transport in porous media (Ahlstrom et al., 1977, Tompson, 1993, Maier et

al., 2008). It can be shown that random walk is equivalent to solving the Fick's law describing diffusion based on concentration gradient (Risken, 1996).

In the following sections, we describe the details of the streamline tracing method and random walk technique for modelling advective and diffusive motions respectively. Then we describe how to calculate the dispersion coefficient as a generic property of porous media which describes the second moment spreading of solute particles. Employing Continuous Time Random Walk (CTRW) analysis, we interpret the scaling of dispersion in different types of porous media. We view transport as a series of movement between voxels on pore-space images and calculate the probability of transit between two neighbouring voxels. We then explain the scaling of power-law regime on D_L vs. Pe plot in porous media.

4.1. Streamline tracing

To capture the advective motion of a solute particle, a streamline-based technique has been developed. By solving Stokes flow on the micro-CT geometry, we obtain the velocity field based on voxelized geometry. In MAC gridding, we have six values of velocities for each voxel – see Figure 3.3. We need to calculate the variation of velocity within each voxel based on computed velocities on face of each voxel. Pollock (1988) suggested a linear interpolation between the normal velocities on opposite faces of a grid block. This is consistent with a divergence-free velocity field and the finite difference approximation used to compute pressure and flow, as well as ensuring continuity of normal velocity. This method is now standard in field-scale streamline-based reservoir simulation (Batycky et al., 1997). For voxels with no solid boundaries we use the same method here, which is, again, consistent with incompressible flow and the finite difference approximations used.

However, at a solid surface we need to impose a zero normal and tangential velocity, which is not consistent with the Pollock algorithm that would only ensure that the velocity normal to the solid is zero. To overcome this limitation and to impose a strictly vanishing velocity at the solid we have introduced a novel semi-analytic formulation for

the streamlines in voxels containing a solid boundary. The formulation for the velocity field and the time of flight in the voxel varies with number of solid voxels in the neighbourhood and their arrangement.

Afterwards, based on velocity distribution inside the voxel, we can calculate the time needed for a particle inside the voxel to exit, $\Delta\tau$. The time step is Δt . If $\Delta\tau > \Delta t$ the particle remains within the voxel, whereas for $\Delta\tau < \Delta t$ the particle enters a new block. We reduce the time step by $\Delta\tau$ and find the $\Delta\tau$ for the new grid block and repeat the previous procedure.

To recap, for voxels with no solid boundaries, we use the method of Pollock (1988). The velocity normal to a face varies linearly across the block – see Figure 4.1.

$$u = \frac{u_2 - u_1}{\Delta x} (x - x_1) + u_1 \quad 4.1$$

$$v = \frac{v_2 - v_1}{\Delta y} (y - y_1) + v_1 \quad 4.2$$

$$w = \frac{w_2 - w_1}{\Delta z} (z - z_1) + w_1 \quad 4.3$$

where u , v and w are the components of velocity in the x , y and z directions respectively. u_1 and u_2 are the computed velocities on the faces normal to the x direction, v_1 and v_2 are velocities on the faces normal to the y direction, while w_1 and w_2 are the velocities on the faces normal to the z -direction, Δx , Δy and Δz are the dimensions of the cell in the respective coordinate directions – see Figure 4.1 The time necessary for a particle to exit the x -face is $\Delta\tau_x$ and the time to exit y -face and z -face are $\Delta\tau_y$ and $\Delta\tau_z$ respectively.

$$\Delta\tau_x = \frac{\Delta x}{u_2 - u_1} \ln \frac{u_2 \Delta x}{u_1 \Delta x + (u_2 - u_1)(x_p - x_1)} \quad 4.4$$

$$\Delta\tau_y = \frac{\Delta y}{v_2 - v_1} \ln \frac{v_2 \Delta y}{v_1 \Delta y + (v_2 - v_1)(y_p - y_1)} \quad 4.5$$

$$\Delta\tau_z = \frac{\Delta z}{w_2 - w_1} \ln \frac{w_2 \Delta z}{w_1 \Delta z + (w_2 - w_1)(z_p - z_1)} \quad 4.6$$

where (x_p, y_p, z_p) are the initial coordinates of the particle. The particle leaves the grid block with the smallest value among the computed increments in time of flight.

$$\Delta\tau = \min(\Delta\tau_x, \Delta\tau_y, \Delta\tau_z) \quad 4.7$$

And the exit location can be obtained from equations below:

$$x_e = x_1 - \frac{u_1 \Delta x}{u_2 - u_1} + \left[\frac{u_1 \Delta x}{u_2 - u_1} + (x_p - x_1) \right] e^{\frac{u_2 - u_1}{\Delta x} \Delta\tau} \quad 4.8$$

$$y_e = y_1 - \frac{v_1 \Delta y}{v_2 - v_1} + \left[\frac{v_1 \Delta y}{v_2 - v_1} + (y_p - y_1) \right] e^{\frac{v_2 - v_1}{\Delta y} \Delta\tau} \quad 4.9$$

$$z_e = z_1 - \frac{w_1 \Delta z}{w_2 - w_1} + \left[\frac{w_1 \Delta z}{w_2 - w_1} + (z_p - z_1) \right] e^{\frac{w_2 - w_1}{\Delta z} \Delta\tau} \quad 4.10$$

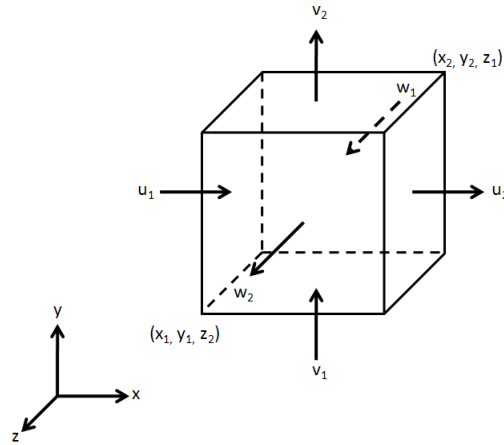


Figure 4.1: Velocity interpolation if there is no bounding solid voxel. This is the Pollock (1988) algorithm, standard in field-scale streamline-based reservoir simulation.

This method is used if no face is solid. For other cases we use a novel velocity distribution able to capture the no-slip boundary condition on solid surfaces. The novel velocity distribution introduces a quadratic normal velocity away from solid boundaries and a bi-linear tangential velocity. Here, we present the velocity distribution for the case where one of the neighbouring voxel is solid. Velocity formulation, time of flight and the exit location from the voxel for the other cases can be found in the Appendix.

The case where one of the adjacent voxel is solid can happen in six different ways depending on which face is solid. We show the formulation for one of the cases; the formulation for the others will be similar. If the solid voxel blocks the x_2 -face (Figure 4.2), the velocity distribution is:

$$u = \frac{u_1}{\Delta x^2} (x_2 - x)^2 \quad 4.11$$

$$v = \frac{2v_1}{\Delta x} (x_2 - x) + \frac{2(v_2 - v_1)}{\Delta x \Delta y} (x_2 - x)(y - y_1) \quad 4.12$$

$$w = \frac{2w_1}{\Delta x} (x_2 - x) + \frac{2(w_2 - w_1)}{\Delta x \Delta z} (x_2 - x)(z - z_1) \quad 4.13$$

The time of flight increment across the block is:

$$\Delta \tau_x = \frac{\Delta x^2}{u_1} \left(\frac{1}{\Delta x} - \frac{1}{x_2 - x_p} \right) \quad 4.14$$

$$\Delta \tau_y = \frac{\Delta x^2}{u_1 (x_2 - x_p)} \left(\frac{v_2 \Delta y}{v_1 \Delta y + (v_2 - v_1)(y_p - y_1)} \right)^{\frac{u_1 \Delta y}{2 \Delta x (v_2 - v_1)}} - \frac{\Delta x^2}{u_1 (x_2 - x_p)} \quad 4.15$$

$$\Delta \tau_z = \frac{\Delta x^2}{u_1 (x_2 - x_p)} \left(\frac{w_2 \Delta z}{w_1 \Delta z + (w_2 - w_1)(z_p - z_1)} \right)^{\frac{u_1 \Delta z}{2 \Delta x (w_2 - w_1)}} - \frac{\Delta x^2}{u_1 (x_2 - x_p)} \quad 4.16$$

$$\Delta \tau = \min(\Delta \tau_x, \Delta \tau_y, \Delta \tau_z) \quad 4.17$$

And the exit location is:

$$x_e = x_2 - \left(\frac{\Delta \tau}{\Delta x^2} u_1 + \frac{1}{x_2 - x_p} \right)^{-1} \quad 4.18$$

$$y_e = y_1 - \frac{v_1 \Delta y}{v_2 - v_1} + \frac{v_1 \Delta y + (v_2 - v_1)(y_p - y_1)}{(v_2 - v_1) \Delta y} \left(1 + \frac{u_1 (x_2 - x_p)}{\Delta x^2} \Delta \tau \right)^{\frac{2 \Delta x (v_2 - v_1)}{u_1 \Delta y}} \quad 4.19$$

$$z_e = z_1 - \frac{w_1 \Delta z}{w_2 - w_1} + \frac{w_1 \Delta z + (w_2 - w_1)(z_p - z_1)}{(w_2 - w_1) \Delta z} \left(1 + \frac{u_1 (x_2 - x_p)}{\Delta x^2} \Delta \tau \right)^{\frac{2 \Delta x (w_2 - w_1)}{u_1 \Delta z}} \quad 4.20$$

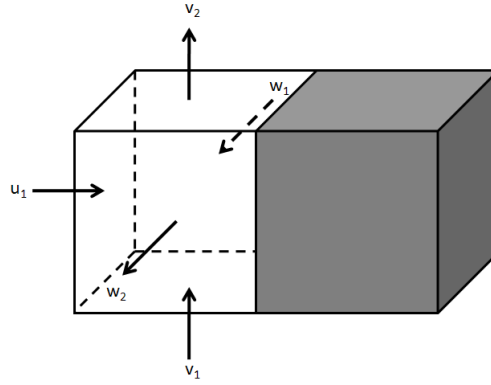


Figure 4.2: There is one solid nearest-neighbour voxel.

4.2. Random walk for diffusion

To capture the diffusive motion of a solute particle we have applied the random walk method. This method has been used for analysis of diffusion for a long time (Brandt, 1975, Ahlstrom et al., 1977, Tompson, 1993, Maier et al., 2008). Random walks are a Lagrangian approach for modelling diffusion by setting the mean free path and generating two random numbers. The mean free path of a solute particle then can be related to the diffusion coefficient of the fluid. Consider (x_p, y_p, z_p) is the coordinate of a particle before its diffusive motion. The coordinates of the particle after diffusion are:

$$x = x_p + \lambda \sin \varphi \cos \theta \quad 4.21$$

$$y = y_p + \lambda \sin \varphi \sin \theta \quad 4.22$$

$$z = z_p + \lambda \cos \varphi \quad 4.23$$

where θ is a random number between $(0, 2\pi)$ and φ is another random number between $(0, \pi)$ and λ is the mean free path of the solute particles. Einstein (1906) introduced an equation for Brownian motion of particle during a time interval of Δt in three dimensions:

$$\lambda = \sqrt{6D_m \Delta t} \quad 4.24$$

Figure 4.3 shows motion of solute particle by advection and diffusion schematically. Followed by each advective motion in which particle moves along a streamline, a diffusive motion occurs and the particle jumps to another streamline.

During a diffusive jump the solute particle may hit a solid surface. We use a reflecting boundary condition if the random jump places a particle in the solid. We allow multiple reflections if the particle encounters more than one solid surface.

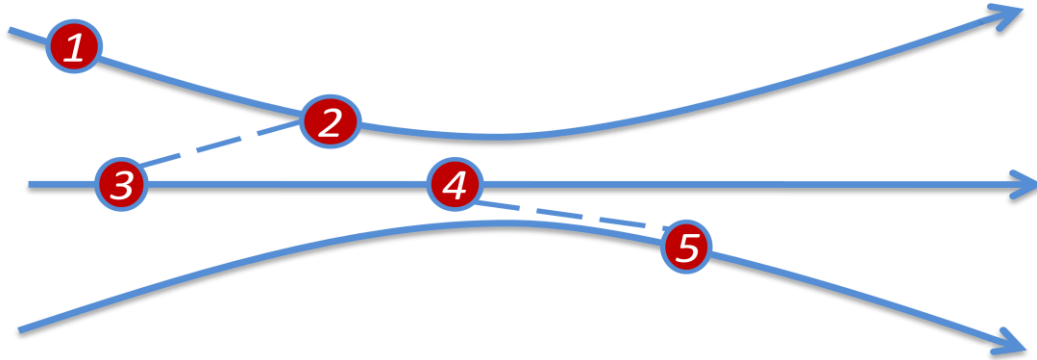


Figure 4.3: Motion of a particle due to advection and diffusion is illustrated. A particle is initially located at position number 1. Applying streamline tracing, the particle moves along the streamline passing through its initial position for a time interval of Δt . Then we see a random jump from position 2 to position 3. The length of this jump is equal to the mean free path of solute particles.

4.3. Periodic boundary condition

If a particle exits the system during its advection motion, it will be reinjected at the inlet face at a flow-weighted random location; if the particle leaves during the diffusive step, it will be re-injected by an area-weighted random position on the inlet face. In addition, if due to diffusion, a particle exits through the inlet, it will be injected on the outlet face, again assigning a random area-weighted position- see Figure 4.4.

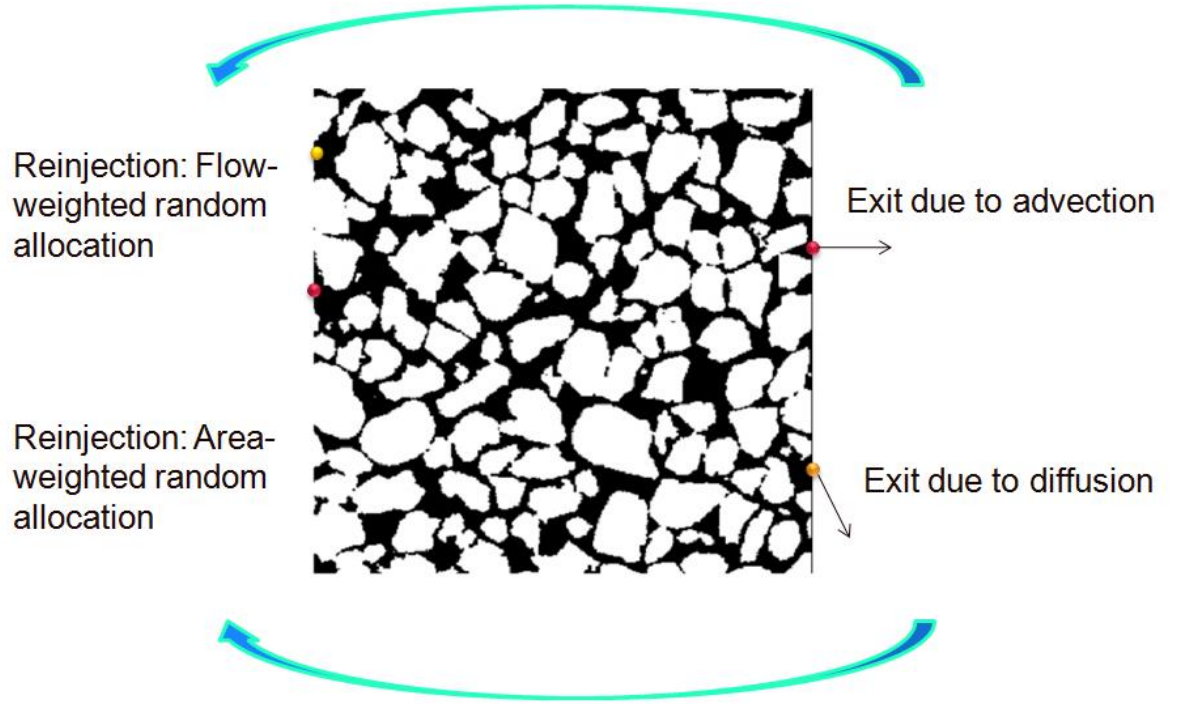


Figure 4.4: If a particle leaves the porous media during its advective motion, it will be reinjected by a flow-weighted random allocation. If the particle exits the porous media by diffusion the reinjection will be based upon an area-weighted allocation.

4.4. Dispersion coefficient

We record the location of particles in time and calculate the axial motion of ensemble of particles from the initial time. The dispersion coefficient then is estimated by calculating the second moment of the distance travelled by particles in the main direction of flow:

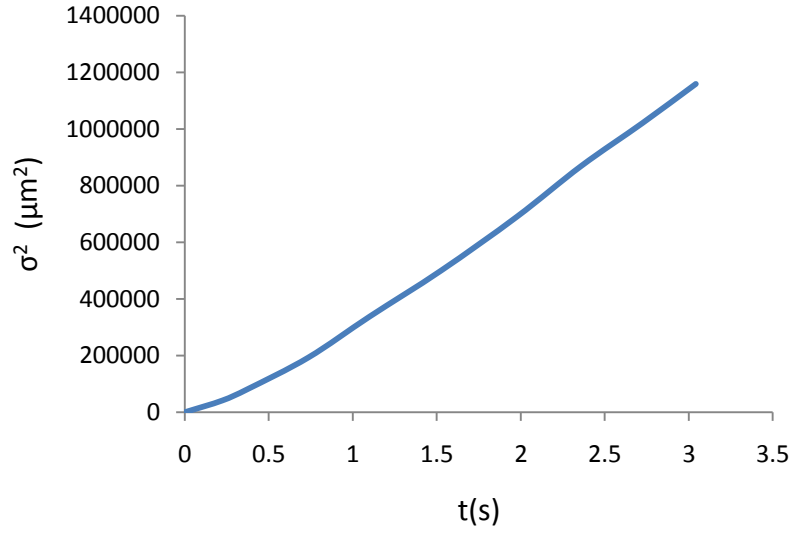
$$D_L = \frac{1}{2} \frac{d\sigma^2}{dt} \quad 4.25$$

where σ^2 is the second moment of the particle displacement:

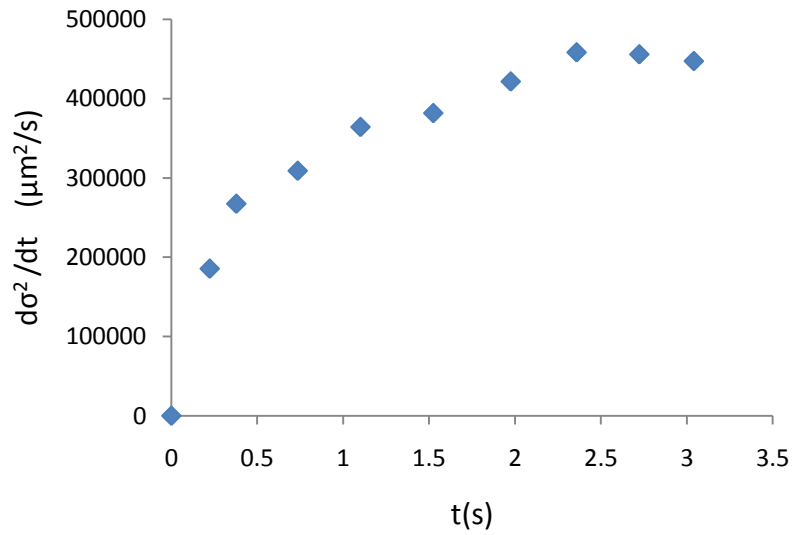
$$\sigma^2 = \langle [\zeta_i(t) - \langle \zeta_i(t) \rangle]^2 \rangle \quad 4.26$$

where ζ is the displacement of particles.

The time step for the simulation is 10^{-4} s. This value has been chosen to restrict the motion of particle at each time step be less than one voxel.



(a)



(b)

Figure 4.5. The variance of particles axial displacement (a) and its slope (b) in time for transport on an LV60 sandpack image, $Pe=40$. The variance starts from zero at the initial time. With progress of time, the variance increases linearly in time. The slope of the straight line is two times the dispersion coefficient.

Figure 4.5 shows the variance of location of particles - σ^2 - and its slope - $d\sigma^2/dt$ - for the LV sandpack with average velocity of 1.3 mm/s and molecular diffusion coefficient of $5 \times 10^{-9} \text{ m}^2/\text{s}$ corresponding to $Pe=40$. As it can be seen, the variance of location of

particles start from zero at $t=0$, increases with time, with its slope increasing. After a certain time – about 2 seconds - this increment in the slope of plot stops and the variance of locations of particles becomes a linear function of time. This is when the asymptotic region is reached. However, as it can be seen in chapter 5 the asymptotic behaviour occurs at different times for different types of porous media. The more heterogeneous porous media is, the later it converges to asymptotic dispersion. This is mainly due to heterogeneity and large variation in velocity field. Therefore, it takes a longer time for ensemble of particles to experience the full velocity field. In other words, after sampling the whole velocity field by ensemble of particles, the second moment of displacement increases linearly with time. This regime is called Fickian as the variance grows linearly with time and the ADE is valid.

4.5. Validation

To validate our particle tracking algorithm, we simulate dispersion in a single capillary with square cross section and compare it with the previous studies by Bruderer and Bernabé (2001) and Bijeljic et al. (2004). The square opening has 50×50 grid blocks across. The characteristic length used in calculating the Peclet number is the half-length of the side of the square. Aris (1956) showed that the longitudinal dispersion coefficient in a single capillary is proportional to the square of the Peclet number:

$$\frac{D_L}{D_m} = \kappa Pe^2 \quad 4.27$$

where κ is a constant coefficient that depends on the shape of the capillary. Bruderer and Bernabé (2001) found that for capillary with square cross section, $\frac{1}{\kappa} = 30.4 \pm 2.6$ and Bijeljic et al. (2004) obtained $\frac{1}{\kappa} = 29.24$.

The best fit to our results shows $\frac{1}{\kappa} = 28.9 \pm 1$ which is in a good agreement with the previous studies.

4.6. Characteristic length

To calculate Peclet number ($Pe = u_{av}L/D_m$), a characteristic length of the porous medium is needed. For the experiments on unconsolidated porous media, the average diameter of grains can be used as the characteristic length; however, this is not available directly from a micro-CT image of a consolidated rock. We define the characteristic length based on a cubic packing of regular spheres. For this idealized system, the grain diameter is $\pi V_b/S$, where V_b is the bulk volume of the porous medium (pore plus grain) and S is the area of the pore/grain interface. We use the same definition for our images, since the volume and pore/grain area are readily computed:

$$L = \frac{\pi V_b}{S} \quad 4.28$$

Table 4.1 shows the characteristic length of the samples we calculate the dispersion coefficient for.

Table 4.1: The characteristic lengths calculated based on mentioned definition for the bead pack, sandpacks, sandstones and carbonates.

	Characteristic Length (μm)
Bead pack	100
Sandpack LV60	160
Sandpack F42	214
Sandstone S1	313
Berea Sandstone	131
Bentheimer Sandstone	133
Portland Carbonate	290
Carbonate C2	158

4.7. Results and discussion

4.7.1. Asymptotic dispersion coefficient

In this section we present our numerical results for asymptotic dispersion coefficient in different types of porous media for different regimes of Peclet number. The image size

for the Benheimer sandstone and the glass bead pack is $500 \times 500 \times 500$ and for the rest is $300 \times 300 \times 300$. Figure 4.6 shows our simulated longitudinal dispersion coefficient as a function of Peclet number along with published experimental data on unconsolidated bead packs obtained from breakthrough curves (Pfannkuch, 1963), data on packs of plastic beads obtained by Pulsed-field-gradient NMR (Ding and Candela, 1996), data on bead packs obtained by magnetic resonance imaging (Seymour and Callaghan, 1997, Kandhai et al., 2002, Khrapitchev and Callaghan, 2003), data on a packed column of activated carbon grains with a bimodal pore size distribution based on radioactive dispersion (Drazer et al., 1999), data on bead packs obtained by planar laser-induced fluorescence method (Stöhr, 2003), data on a sandy soil column measured by electrical resistance between rod electrodes and fitting analytical models of advection-dispersion equation to concentration breakthrough curves at axial positions along the column (Aggelopoulos and Tsakiroglou, 2007), and data on a planar glass-etched pore network obtained by an experimental set-up detecting colour changes caused during the mixing (Theodoropoulou, 2007). Note that in all cases relatively simple unconsolidated media are considered.

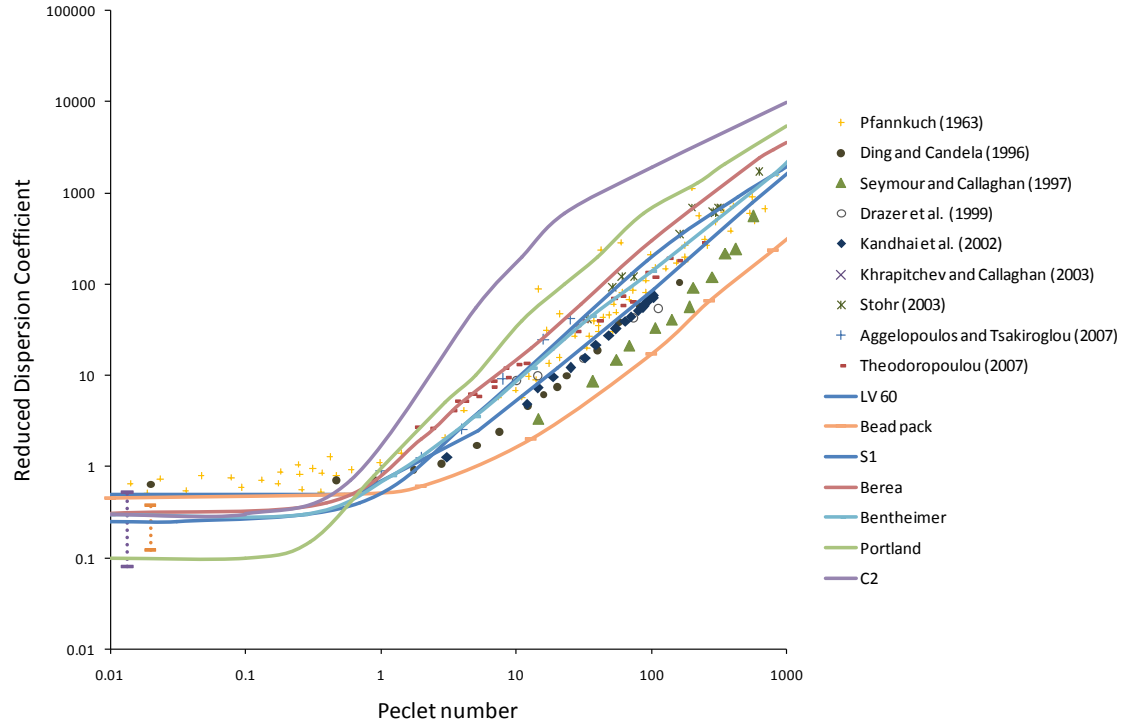


Figure 4.6: Reduced dispersion coefficient (ratio of longitudinal dispersion to molecular diffusion coefficient) against dimensionless Peclet number. Different characteristic lengths have been used for estimation of Peclet number in the numerical and experimental results. Error bars show results for sandstone samples in the restricted diffusion regime (Dullien, 1992, Frosch et al., 2000).

The agreement between experiment and the numerical results for unconsolidated porous media and sandstone is very good, although there is a tendency for the predicted curve to be shifted to slightly larger Pe , indicating, perhaps, the difference in definition of characteristic length, particularly at high Pe . All regimes of dispersion can be seen on the graph. The reduced dispersion coefficient is less than unity in low Peclet regime because of the presence of the solid, restricting diffusion. At low Peclet number, the reduced dispersion coefficient for unconsolidated porous media is larger than for more heterogeneous porous media. This is due to less tortuosity in unconsolidated porous media in comparison with sandstones and carbonates.

The transition regime begins at $Pe=0.8$ for unconsolidated porous media and sandstones and $Pe=0.3$ for carbonates; the existence of high velocity regions makes the transition from the diffusion restricted regime faster for the more heterogeneous media.

At higher Pe , the transition regime is followed by an approximate power-law regime with $D_L \sim Pe^\delta$. The power-law regime can be seen for $5 < Pe < 300$. In this regime, there is a strong interaction between diffusion and advection. In more heterogeneous porous media, like carbonates, there is a high fraction of slow velocity regions and dead-end pores and a low fraction of fast streamlines. Solute particles are trapped in slow regions and due to contribution of particles' retardation to plume spreading, dispersion increases. Therefore, in the power-law regime where diffusion and advection interplay, more heterogeneous porous media are more sensitive to Peclet number. For unconsolidated porous media and sandstones we observe an exponent $\delta = 1.2 \pm 0.05$, consistent with measurements and other analyses (Brigham et al., 1961, Salter and Mohanty, 1982, Kinzel and Hill, 1989, Bijeljic et al., 2004). For carbonates, δ is larger than in sandpacks and sandstones, having values of 1.4 ± 0.05 and 1.5 ± 0.05 for Portland and C2 respectively.

Following the power-law regime, mechanical dispersion is observed where the effects of molecular diffusion can be ignored and transport is dominated by advection only and where $D_L \sim Pe$. The magnitude of the dispersion coefficient is higher for the more heterogeneous samples – carbonates – and lowest for the most homogeneous media – sandpacks and bead pack.

Bijeljic and Blunt (2006) applied Continuous Time Random Walk (CTRW) analysis to interpret the slope of power-law regime and related it to transit time probability. In the CTRW framework, solute particles are considered to travel between discrete sites based on a transit time probability. Bijeljic and Blunt (2006) used this approach, where the sites are identified as pores in a network model. They showed that the power-law dispersion $D_L \sim Pe^\delta$ is governed by the distribution of velocity in the network model and $\delta = 3 - \beta$. β is an exponent used to characterize the amount of heterogeneity associated with the

porous medium (as discussed in chapter 2) and calculated based on the distribution of transit times between pores in the network model.

We will use the same approach but based on the probability of travelling between two neighbouring voxels directly on pore-space images and study the generic behaviour of transport in different types of porous media.

4.7.2. Transit Time Probability

In CTRW, transport of solute particles in geological formation can be described based on the $\psi(t)$ function. By definition, $\psi(t)dt$ is the ensemble averaged probability of a particle just arrived a site first moving to an adjacent site in a time between t and $t+dt$. The anomalous behaviour can be then treated as a power-law transit time distribution:

$$\psi \sim \tau^{-(1+\beta)} \quad 4.29$$

where τ is advective transit time and β is a constant to characterize the amount of heterogeneity associated with the porous medium.

In this work, we compute $\psi(t)$ on a grid-block basis by finding the time it takes for each particle to traverse each void cell. This approach has been used before using a pore-scale network model where the transitions are from pore to pore (Bijeljic and Blunt, 2006), and for grid blocks in field-scale simulation (Di Donato et al., 2003). We compute distribution of transit times that particles spend in grid blocks as a function of dimensionless time $\tau_b = t/t_{b1}$, where $t_{b1} = \frac{\Delta x}{u_{av}}$ is the mean advective transit time whose characteristic length is the grid block spacing Δx , indicated by the subscript b . The average velocity, u_{av} is defined as the total flow across the model divided by the cross-sectional area. The travel times are sampled for up to 10 seconds.

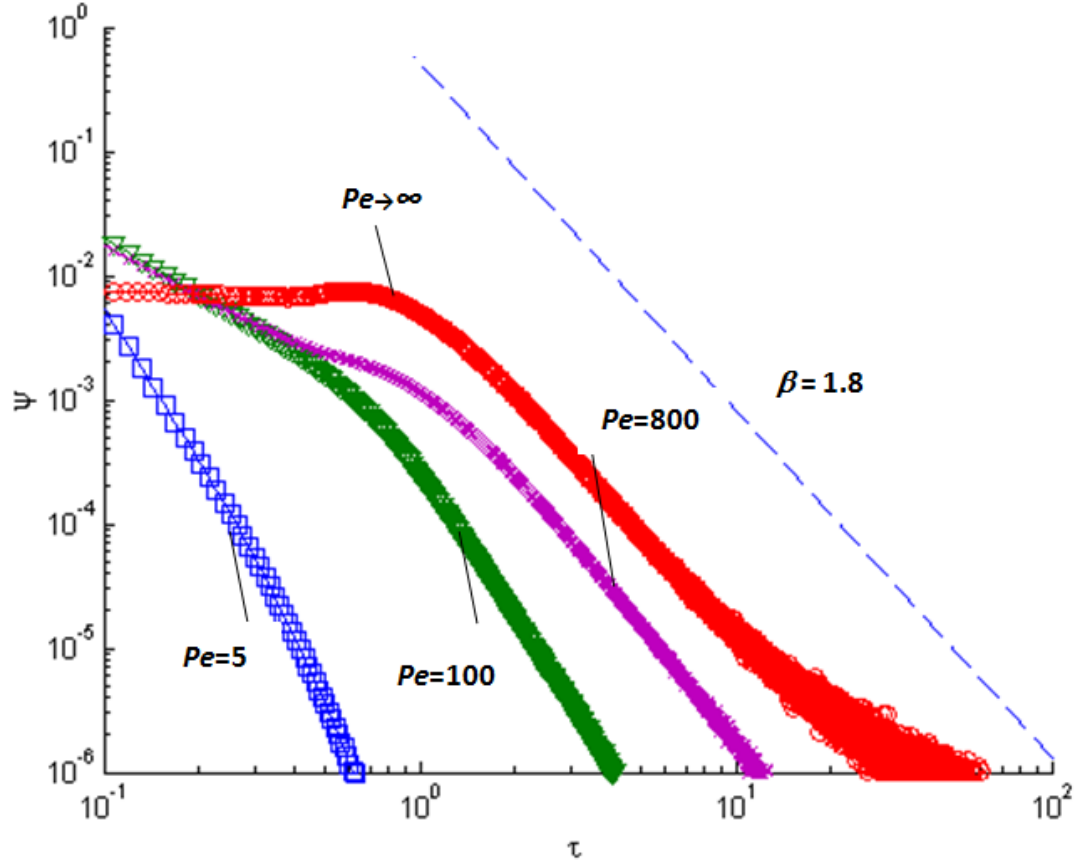


Figure 4.7: The probability $\psi(\tau_b)$ of traveling between two neighbouring voxels for the bead pack, for $Pe = 5, 100$, and 800 and for $Pe \rightarrow \infty$ presented by squares, triangles, plus signs, and circles respectively. The probabilities show a power-law trend with $\psi \sim \tau_b^{-(1+\beta)}$; a dashed line with slope corresponding to $\beta = 1.8$ is represented. The dimensionless time $\tau_b = t/t_{b1}$, where t_{b1} is the mean travel time through a grid block $\Delta x/u_{av}$.

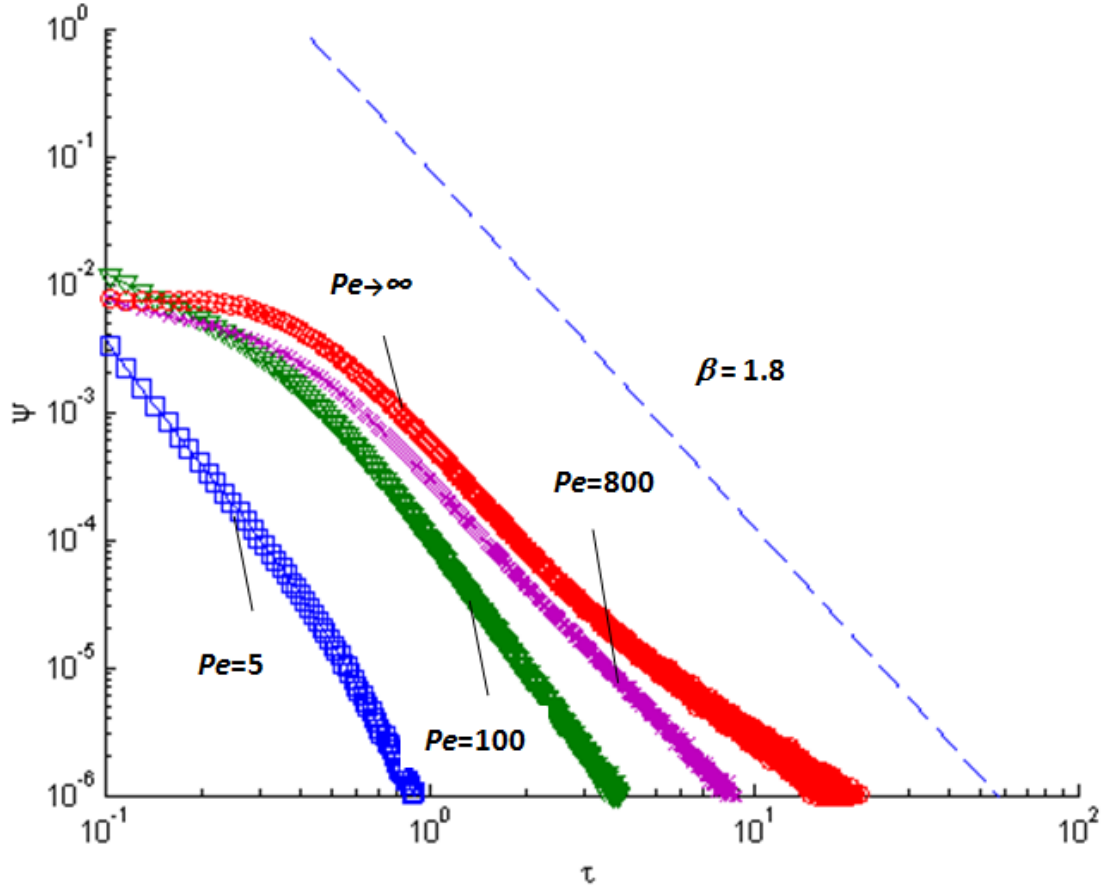


Figure 4.8: The probability $\psi(\tau_b)$ of traveling between two neighbouring voxels for sandpack LV60, for $Pe = 5, 100$, and 800 and for $Pe \rightarrow \infty$ presented by squares, triangles, plus signs, and circles respectively. The probabilities show a power-law trend with $\psi \sim \tau_b^{-(1+\beta)}$; a dashed line with slope corresponding to $\beta = 1.8$ is represented. The dimensionless time $\tau_b = t/t_{b1}$, where t_{b1} is the mean travel time through a grid block $\Delta x/u_{av}$.

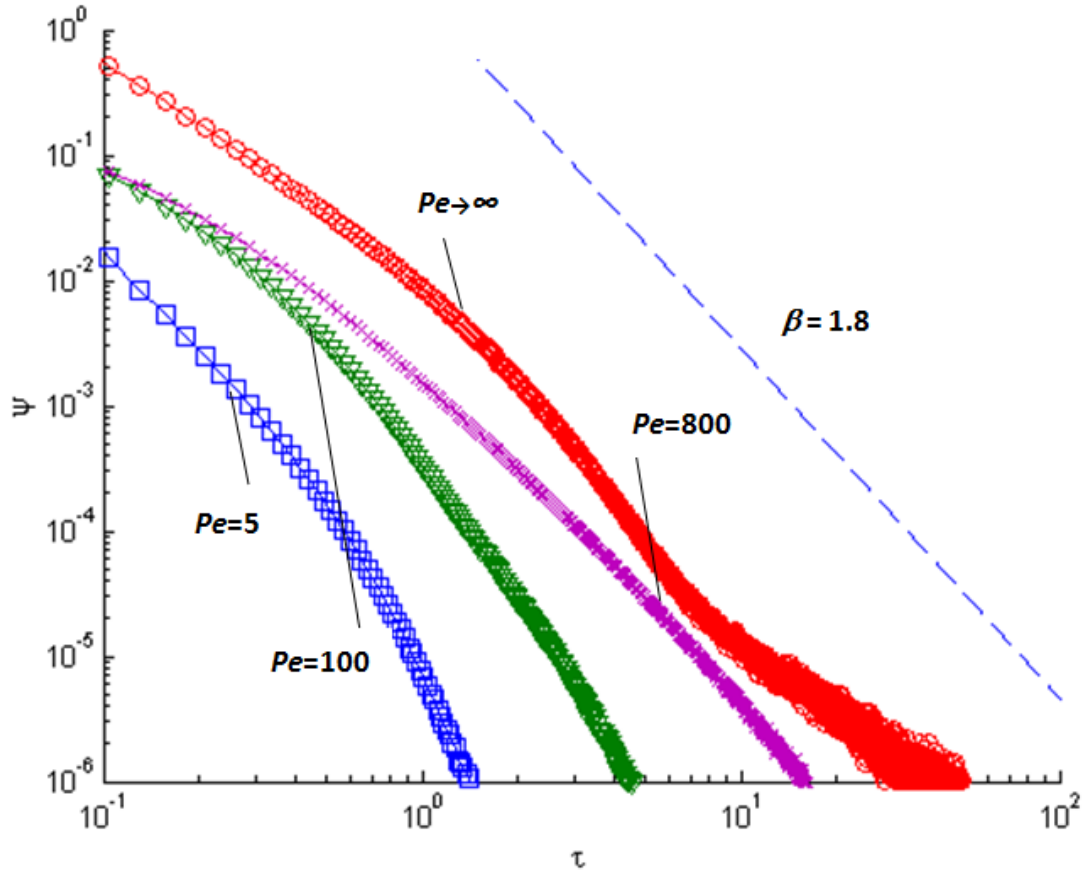


Figure 4.9: The probability $\psi(\tau_b)$ of traveling between two neighbouring voxels for Berea sandstone, for $Pe = 5, 100$, and 800 and for $Pe \rightarrow \infty$ presented by squares, triangles, plus signs, and circles respectively. The probabilities show a power-law trend with $\psi \sim \tau_b^{-(1+\beta)}$; a dashed line with slope corresponding to $\beta = 1.8$ is represented. The dimensionless time $\tau_b = t/t_{b1}$, where t_{b1} is the mean travel time through a grid block $\Delta x/u_{av}$.

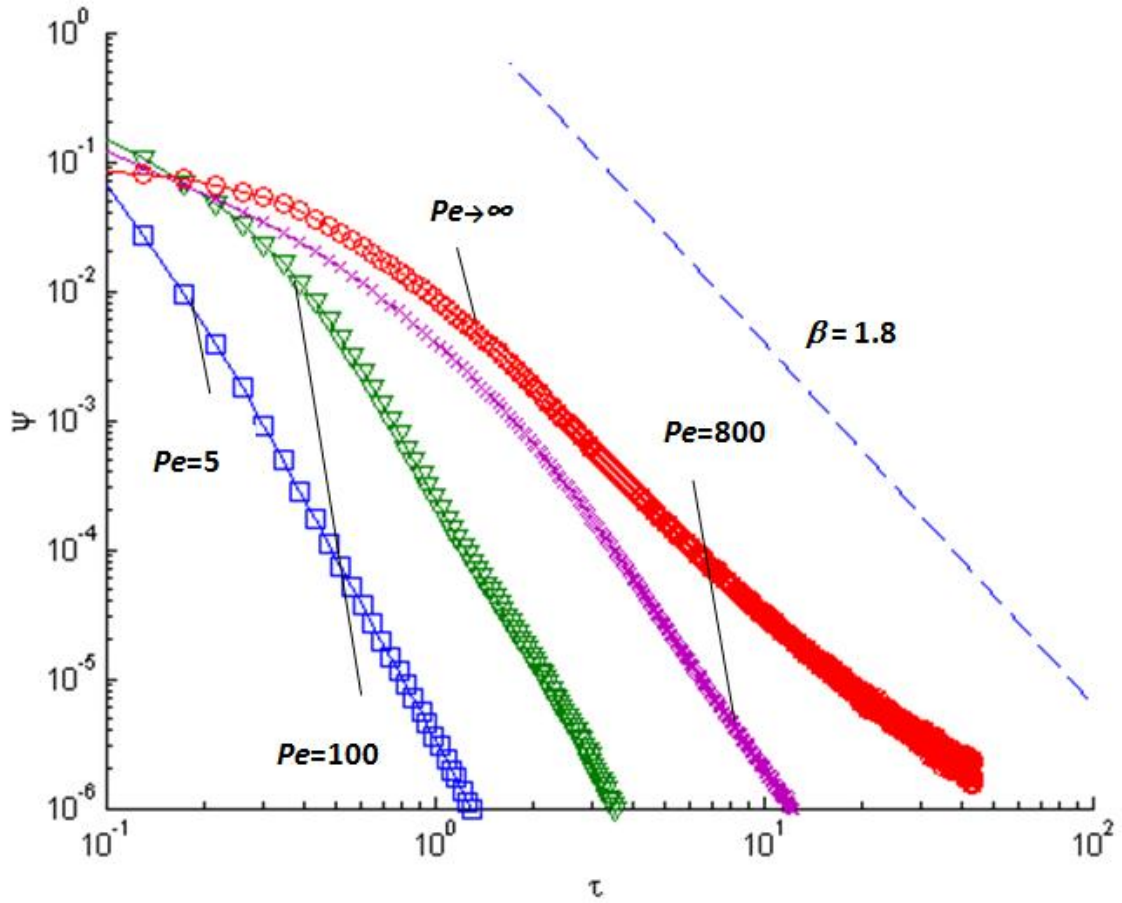


Figure 4.10: The probability $\psi(\tau_b)$ of traveling between two neighbouring voxels for Bentheimer sandstone, for $Pe = 5, 100$, and 800 and for $Pe \rightarrow \infty$ presented by squares, triangles, plus signs, and circles respectively. The probabilities show a power-law trend with $\psi \sim \tau_b^{-(1+\beta)}$; a dashed line with slope corresponding to $\beta = 1.8$ is represented. The dimensionless time $\tau_b = t/t_{b1}$, where t_{b1} is the mean travel time through a grid block $\Delta x/u_{av}$.

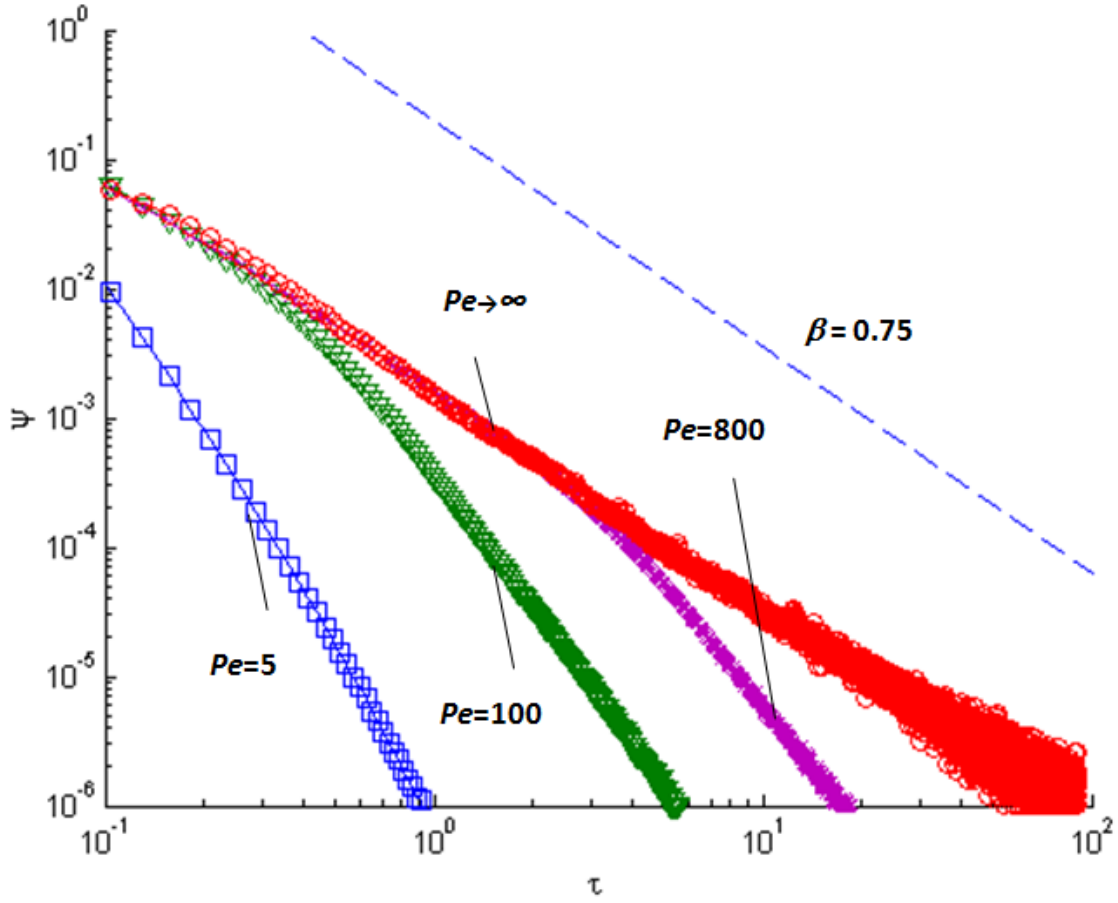


Figure 4.11: The probability $\psi(\tau_b)$ of traveling between two neighbouring voxels for C2 carbonate, for $Pe = 5, 100$, and 800 and for $Pe \rightarrow \infty$ presented by squares, triangles, plus signs, and circles respectively. The probabilities show a power-law trend with $\psi \sim \tau_b^{-(1+\beta)}$; a dashed line with slope corresponding to $\beta = 0.75$ is represented. The dimensionless time $\tau_b = t/t_{b1}$, where t_{b1} is the mean travel time through a grid block $\Delta x/u_{av}$.

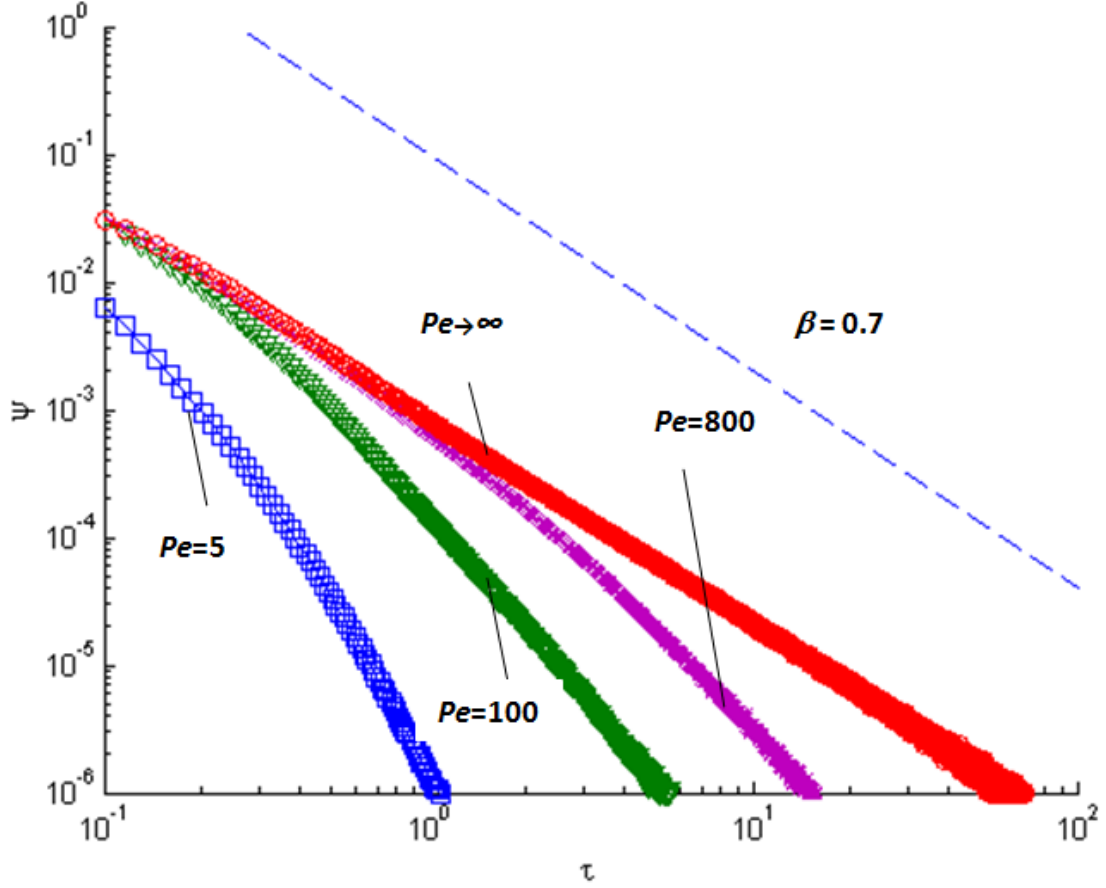


Figure 4.12: The probability $\psi(\tau_b)$ of traveling between two neighbouring voxels for Portland carbonate, for $Pe = 5, 100$, and 800 and for $Pe \rightarrow \infty$ presented by squares, triangles, plus signs, and circles respectively. The probabilities show a power-law trend with $\psi \sim \tau_b^{-(1+\beta)}$; a dashed line with slope corresponding to $\beta = 0.7$ is represented. The dimensionless time $\tau_b = t/t_{b1}$, where t_{b1} is the mean travel time through a grid block $\Delta x/u_{av}$.

In Figures 4.7 - 4.12, we plot $\psi(\tau_b)$ for a range of Pe (including $Pe \rightarrow \infty$ corresponding to $D_m = 0$) for the glass bead pack, LV60 sandpack, Berea and Bentheimer sandstones, and Portland and C2 carbonates. For the late time behaviour for $\psi(\tau_b)$ that is not affected by the minimum travel times, we observe an approximately power-law dependence of travel times $\psi \sim \tau_b^{-(1+\beta)}$ with $\beta = 1.8 \pm 0.05$ for the bead pack, sandpacks and sandstones in contrast to $\beta < 1$ for the carbonates. A lower value for β indicates greater heterogeneity of the porous medium, leading to more complex non-Fickian transport behaviour (Dentz et al., 2004). The power law is truncated at late times, representing the time to diffuse

across grid block (at low to intermediate Pe) or an advective cut-off for large Pe , representing the slowest flow speeds. This power-law dependence has been noted previously for a network model of Berea sandstone (Bijeljic and Blunt, 2006): we see a power-law dependence $\beta < 1$ for carbonates, indicating qualitatively different transport while for the sandstone, sandpack and bead pack where $2 > \beta > 1$. With increasing Peclet number the late time cut-off occurs at larger τ which results in increased dispersion.

Based on CTRW analysis the scaling of power-law regime in D_L/D_m vs. Pe plot, δ , can be related to β . For $\beta < 1$, CTRW predicts $\delta = 2\beta$ while for $1 < \beta < 2$ it predicts $\delta = 3 - \beta$ (as discussed in chapter 2).

This prediction is in a very good agreement with our observations for the scaling of dispersion coefficient with Peclet number. As it can be seen from Figure 4.6, in the power-law regime for the Portland and C2 carbonates we observe the scaling $D_L/D_m \sim Pe^{1.4}$ and $D_L/D_m \sim Pe^{1.5}$ respectively, while in the power-law regime for the bead pack, sandpacks and sandstones the scaling is $D_L/D_m \sim Pe^{1.2}$. This corresponds to the values of $\beta = 0.7$ and $\beta = 0.75$ for carbonates and $\beta = 1.8$ for the bead pack, sandpacks and sandstones (see also Bijeljic and Blunt, 2006, Rhodes et al., 2009). This suggests that power-law dispersion is controlled by the velocity distribution through the porous media. In addition, it confirms that transport in complex porous media ($\beta < 1$) is inherently different from unconsolidated porous media and sandstones where $\beta > 1$.

In the next chapter we explore this further by studying the approach to the asymptotic dispersion behaviour discussed here and comparing against *in situ* measurements of transport in porous media using NMR techniques.

5. Non-Fickian transport in porous media

Pre-asymptotic dispersion of solute particles in porous media and porous rock is of great importance in a broad range of scientific fields, notably in contaminant migration in subsurface hydrology, packed bed reactors and chromatography in chemical engineering and tracer studies in petroleum engineering,

Although driven by the interplay of simple physical processes i.e. advection and diffusion, the resulting macroscopic transport behaviour has been shown to be non-Fickian due to solute experiencing a wide spectrum of rate processes occurring between pore or larger scale geological features. In the asymptotic limit the dispersion coefficient is constant and can be used in an averaged advection-dispersion equation as studied in chapter 4. However, it is important to recognize that, until the velocity field is fully sampled, the particle transport is non-Fickian and dispersion coefficient possesses temporal or spatial variation. This variation is visually observed in varying plume shape and the corresponding description of the probability density function (PDF) of displacement or transit times of the solute particles.

In this chapter, we examine non-Fickian behaviour in solute transport simulated directly on micro-CT images of pore space. We study the impact of morphological structure of porous media as well as Peclet number on temporal and spatial concentration

distributions described by flow propagators. Flow propagator is a term used in the literature referring to the distribution of particle displacements due to diffusion and advection. It can be used to study pores' connectivity and quantify the fraction of fast streamlines and the fraction of non-connected and slow flow zones.

5.1. Results and discussion

We present the results obtained from numerical simulation of transport on sandpacks LV60 and F42, Berea sandstone, S1 sandstone which is a reservoir sandstone, Portland and C2 carbonates. For each sample, at time zero, particles are evenly distributed throughout the porous media similar to an NMR propagator experiment where molecules are initially distributed uniformly throughout the void space. Then we simulate the displacement of particles by advection and diffusion in porous media and study the PDF of displacement and time dependent dispersion coefficient.

To illustrate the contrast of the non-Fickian behaviour in heterogeneous porous media with a Fickian dispersion, we start by describing Fickian transport in porous media.

To recap from chapter 2, Fickian dispersion, obeys the advection-diffusion equation:

$$\frac{\partial C}{\partial t} + v \cdot \nabla C = D \nabla^2 C \quad 5.1$$

where C is the mean concentration, and D is the dispersion tensor. The ADE dictates a diffusional spreading of solute particles moving in the porous medium with the average motion equal to average velocity of flow in the porous media. In Fickian dispersion, the PDF of displacement with boundary conditions mentioned in chapter 2 (equations 2.6 to 2.8) can be written as a Gaussian distribution (Sahimi, 1995):

$$P(\zeta, t) = (8\pi Dt)^{-1/2} \exp\left(-\frac{(\zeta - vt)^2}{4Dt}\right) \quad 5.2$$

where ζ is displacement, and D is the dispersion coefficient.

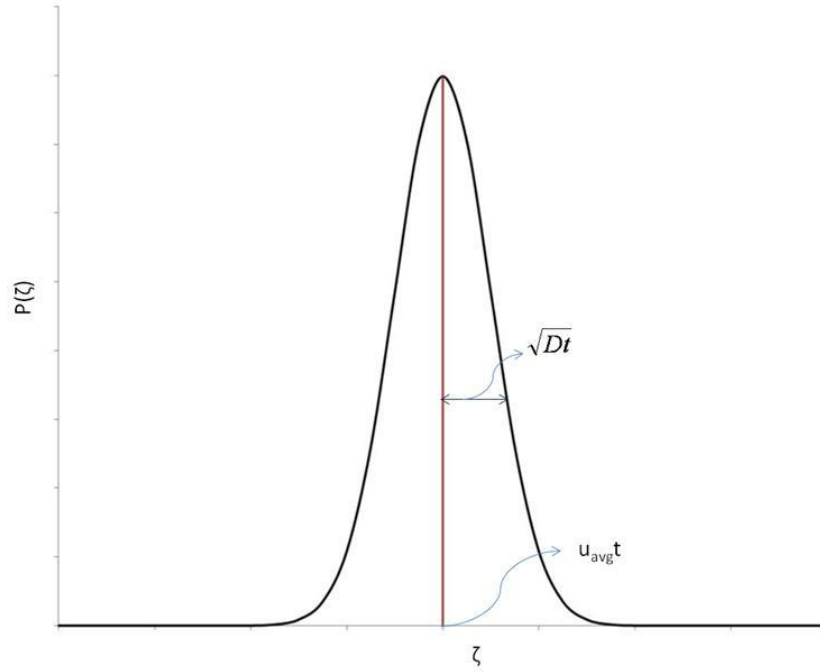


Figure 5.1: A Gaussian distribution of displacement in porous media governed by the ADE. The average displacement is $u_{avg}t$ and the variance of displacement of solute particles is Dt as predicted by equation 5.2.

Figure 5.1 shows the PDF of displacement in a Fickian transport. The variance of displacement is Dt and the average displacement occurs with $u_{avg}t$.

In addition, the ADE presumes that the dispersion coefficient is a constant value not varying in time. This is in contrast to experimental findings and our modelling predictions, as we show later.

ADE can solve for transport in homogeneous porous media with a reasonable accuracy. However, applying ADE for more heterogeneous porous media like reservoir sandstone and specially carbonate rocks is disappointing. In this chapter we will show the propagator results for different types of porous media – sandpacks, sandstones, and carbonates - and discuss effect of heterogeneity and Peclet regime on non-Fickian behaviour of transport in porous media.

5.1.1. Propagator simulation

We investigate the impact of heterogeneity and time on non-Fickian behaviour of probability displacements (propagators) for different dispersion regimes.

Figures 5.2 - 5.7 show the probability distribution function of displacement in LV 60 and F42 sandpacks, for $Pe = 5, 100$, and 800 after 0.1 s , 0.3 s , 1 s and 3 s . For $Pe = 5$, from very early time the displacement has a Gaussian distribution approximately. This demonstrates the simple geometry and high connectivity of pore spaces in the unconsolidated porous media. In the low Peclet regime, the main mechanism of spreading of particles is diffusion and the dispersion can be considered Fickian from the early time. The scales in propagator results are normalized by nominal average displacement of solvent fluid ($u_{av}=1.3\text{ mm/s}$). We can also see that the average displacement is equal to unity representing the plume is moving along with the solvent in the porous media. In higher Peclet regime in sandpacks (Figures 5.3, 5.4, 5.6, and 5.7), advection plays a more prominent role in dispersion. This shows that at early time, i.e. $t = 0.1\text{ s}$, some particles are moving along with high velocity streamlines and go forward while the others are retarded and do not move with the same velocity as the average velocity of the solvent. However with time the retarded particles and fast particles mix and the plume starts to move with the average velocity of solvent.

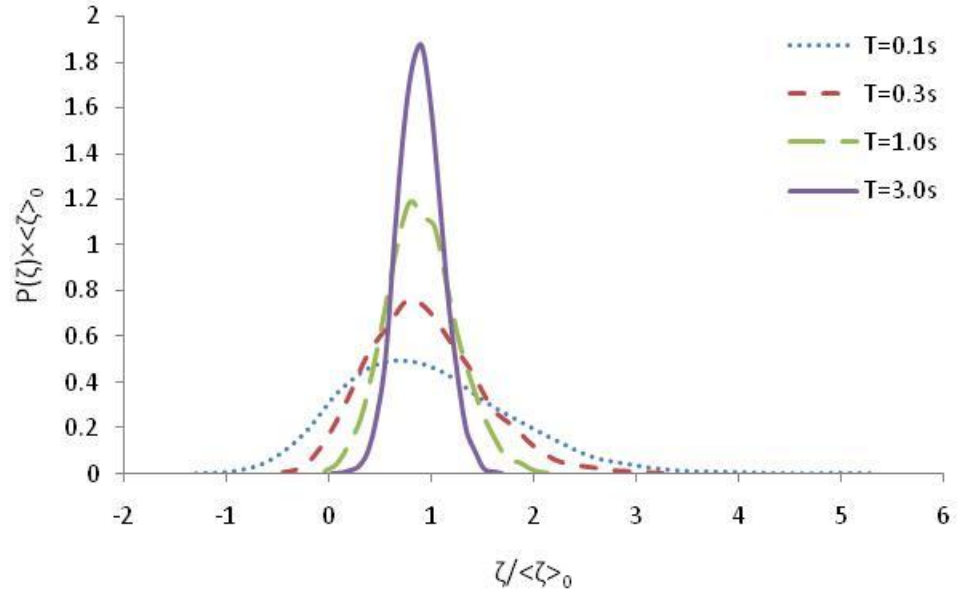


Figure 5.2: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=5$ in LV60.

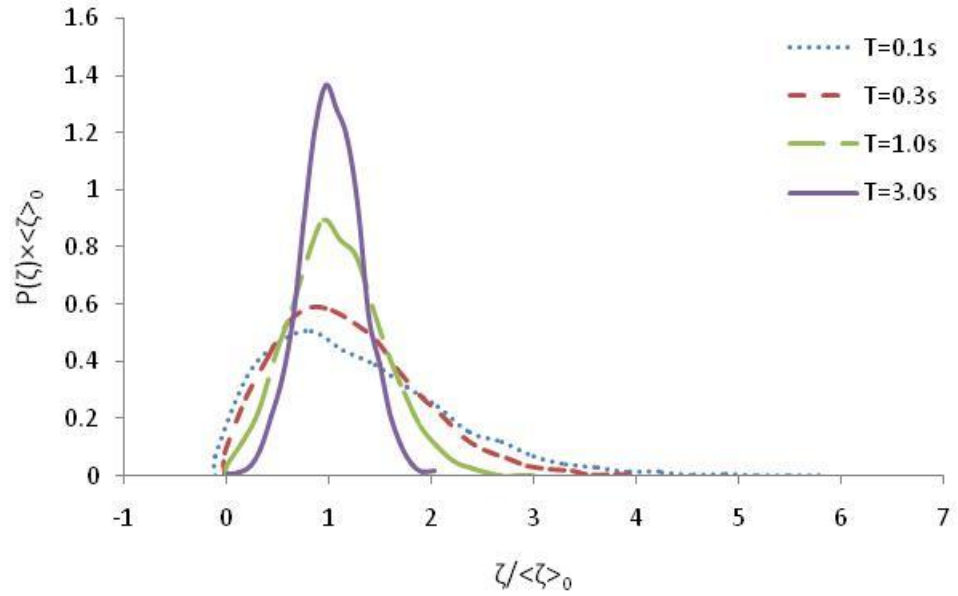


Figure 5.3: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=100$ in LV60.

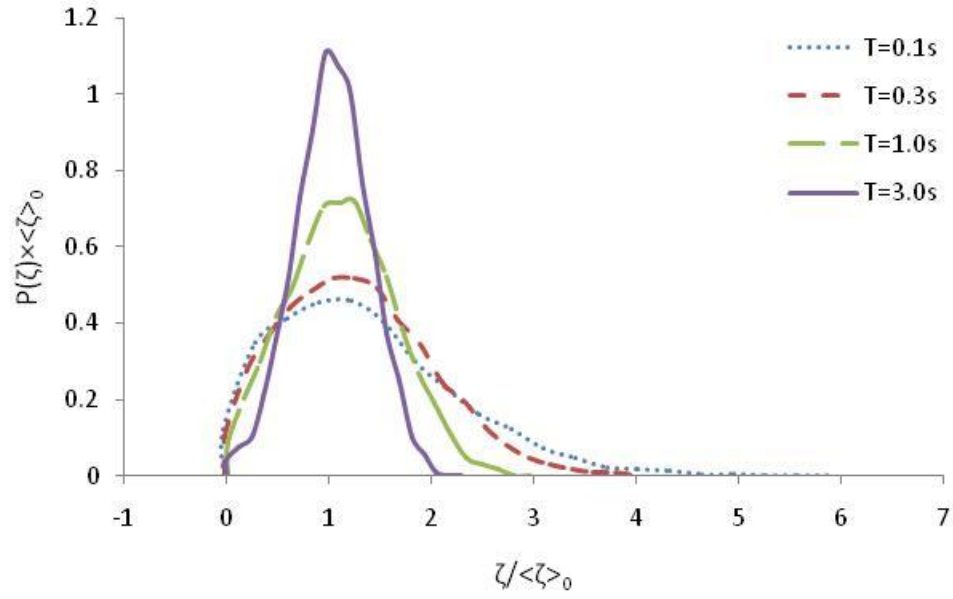


Figure 5.4: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=800$ in LV60.

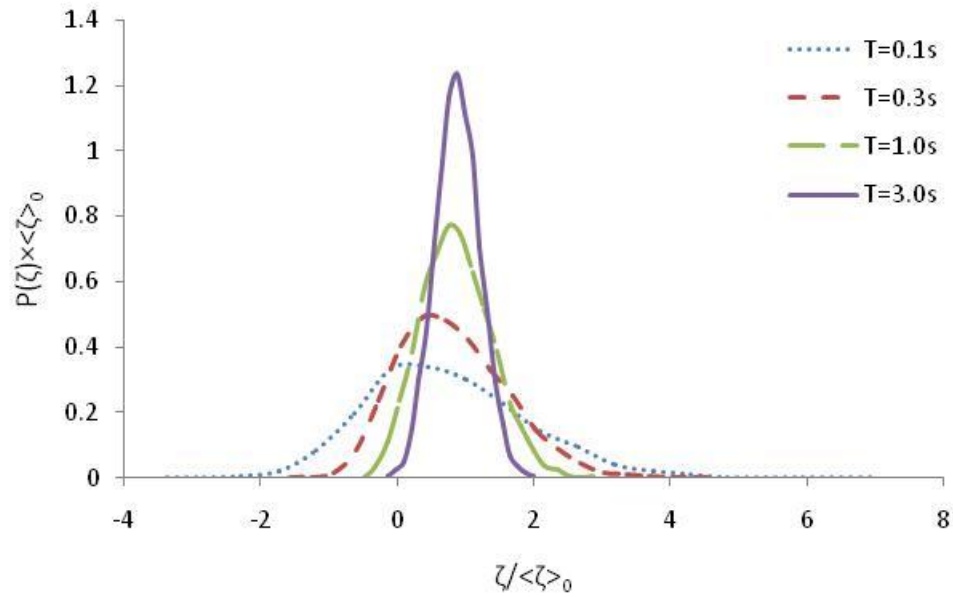


Figure 5.5: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=5$ in F42.

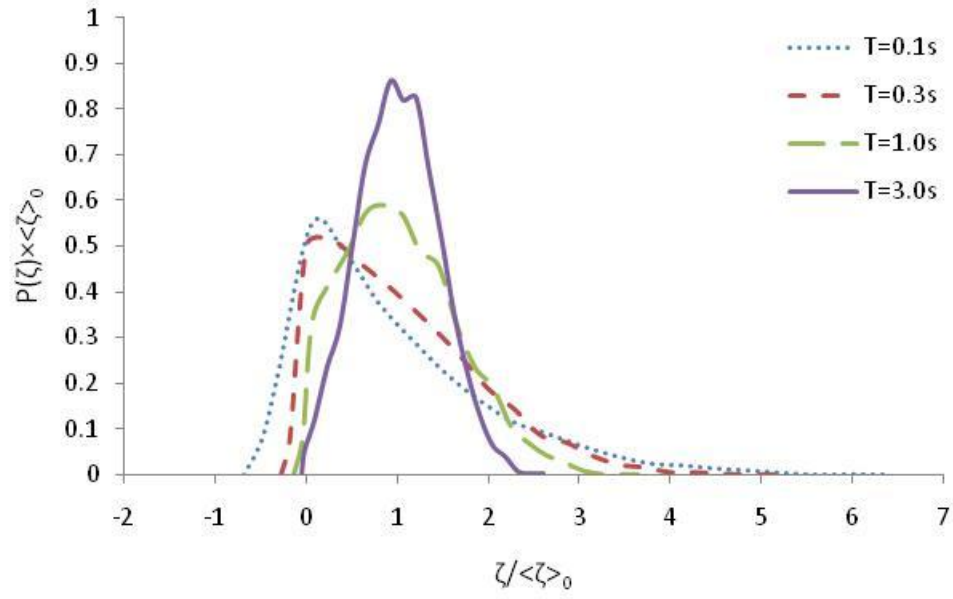


Figure 5.6: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=100$ in F42.

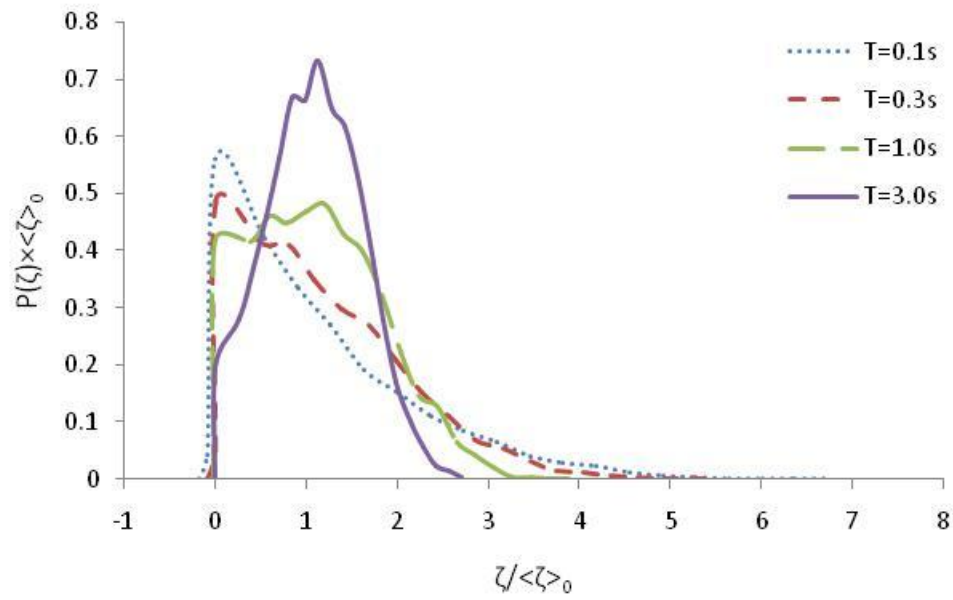


Figure 5.7: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=800$ in F42.

Figures 5.8, 5.9, and 5.10 show propagator simulation results for Berea sandstone in different time for three Peclet regimes. The impact of Pe is similar to that in sandpacks – sampling of the velocity field due to the difference in contribution by diffusion. For low Peclet regime, the Gaussian distribution is established and can be seen approximately after 1 s.

For the higher Peclet number regime, however, an immobile peak is observed which represents retarded particles. It takes more time for velocity field to be sampled by all particles, as effects of diffusion are smaller for higher Pe . These retarded particles eventually meet the faster particles with time and dispersion becomes Fickian.

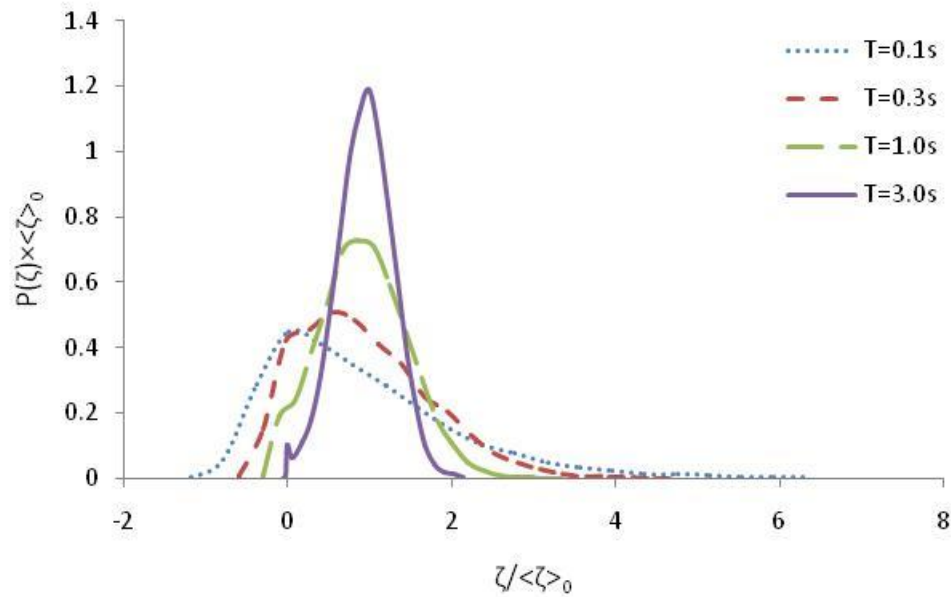


Figure 5.8: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=5$ in Berea.

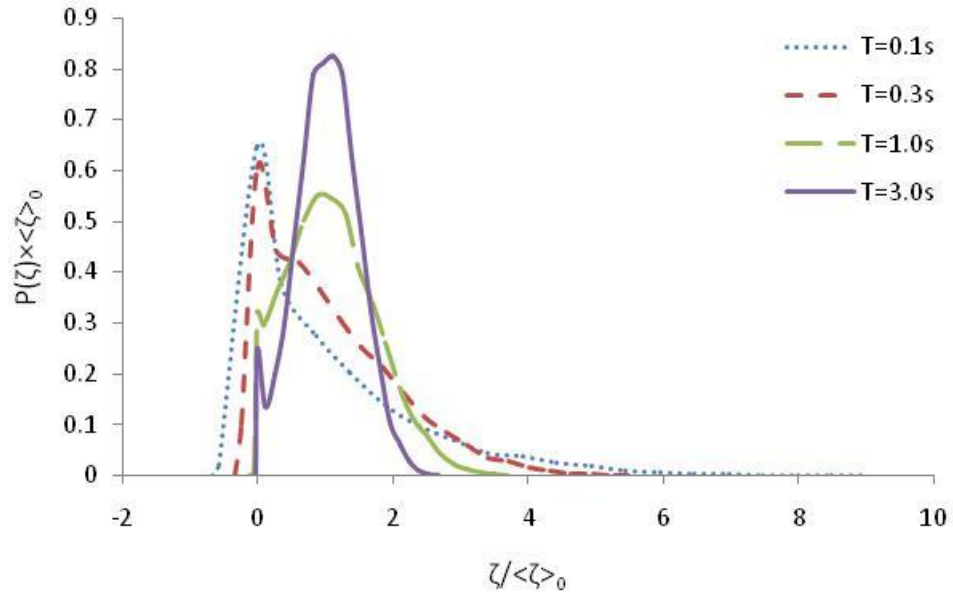


Figure 5.9: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=100$ in Berea.

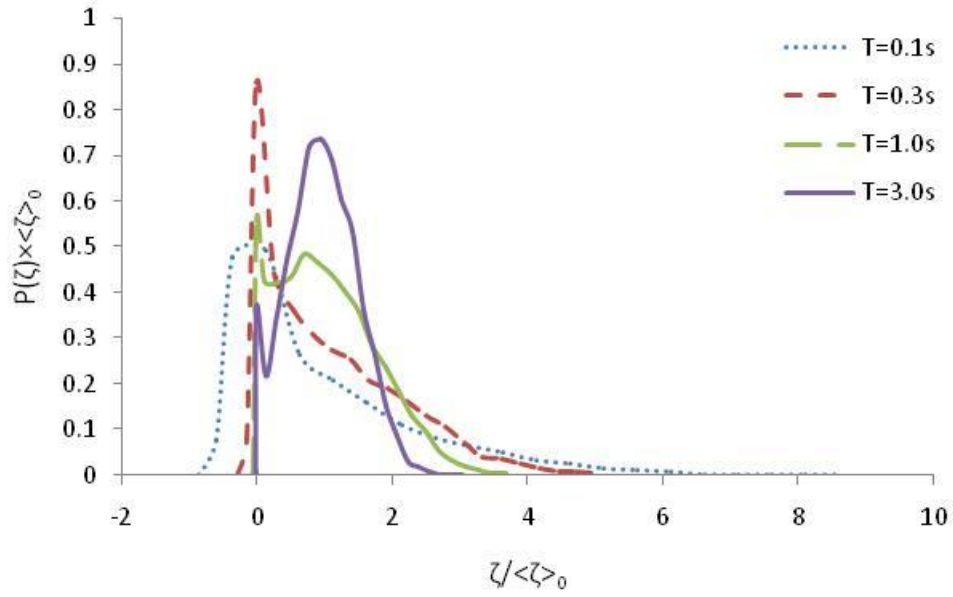


Figure 5.10: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=800$ in Berea.

Figures 5.11, 5.12, and 5.13 show the propagator simulations in a reservoir sandstone - S1. Similar to Berea sandstone, S1 has a higher degree of heterogeneity in comparison with sandpacks and it can be seen from the propagator results as well. The heterogeneity causes existence of dead-end and slow-flow zones which contribute in dispersion more significantly. The effects of these regions are intensified in the high Peclet regime. Figure 5.11 show the propagator distribution for $Pe = 5$. As it can be seen at the early time - $t=0.1s$ and $0.3s$ - there are particles displaced five times the nominal average displacement. For this porous medium, in contrast to sandpacks, the effects of high velocity regions are appeared from low Peclet regime. In the high Peclet number regimes, we see that a considerable number of particles are trapped in stagnant zones which causes a persistent high immobile peak from early time. This peak does not vanish as early as homogeneous porous media while a second peak is formed - Figures 5.12 and 5.13. The first peak represents the stagnant zones while the second peak represents the well-connected pores associated with spreading of solute particles.

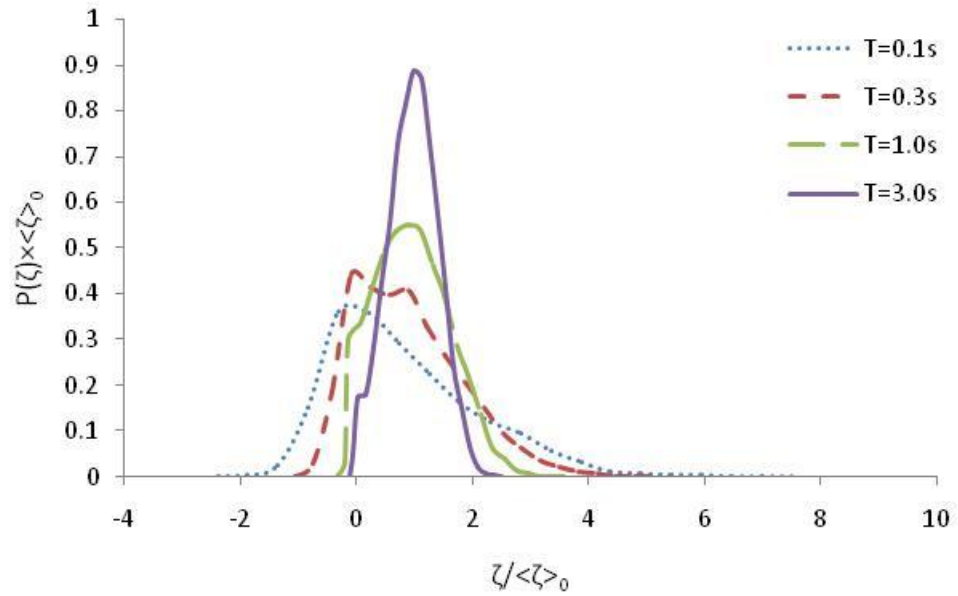


Figure 5.11: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=5$ in S1.

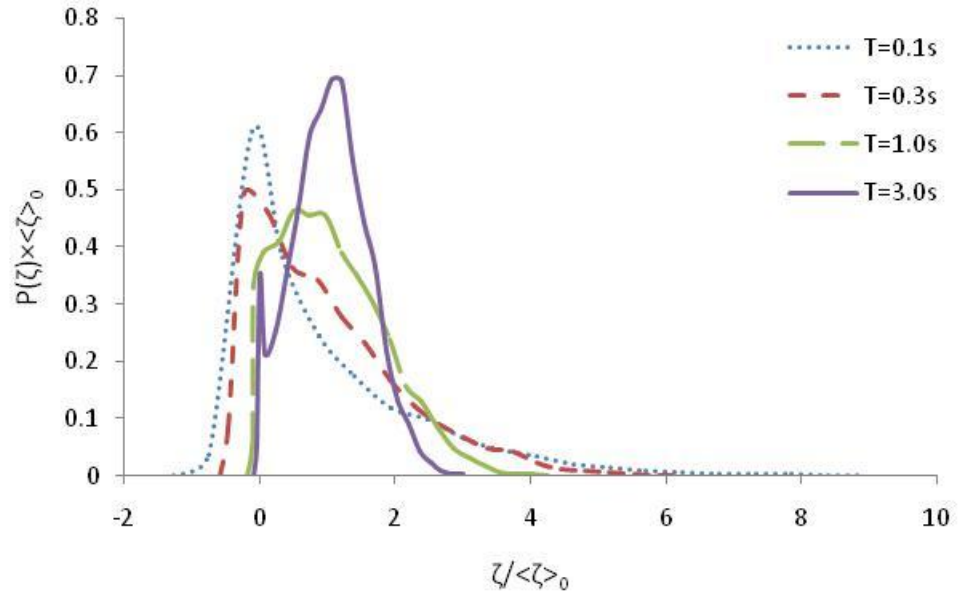


Figure 5.12: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=100$ in S1.

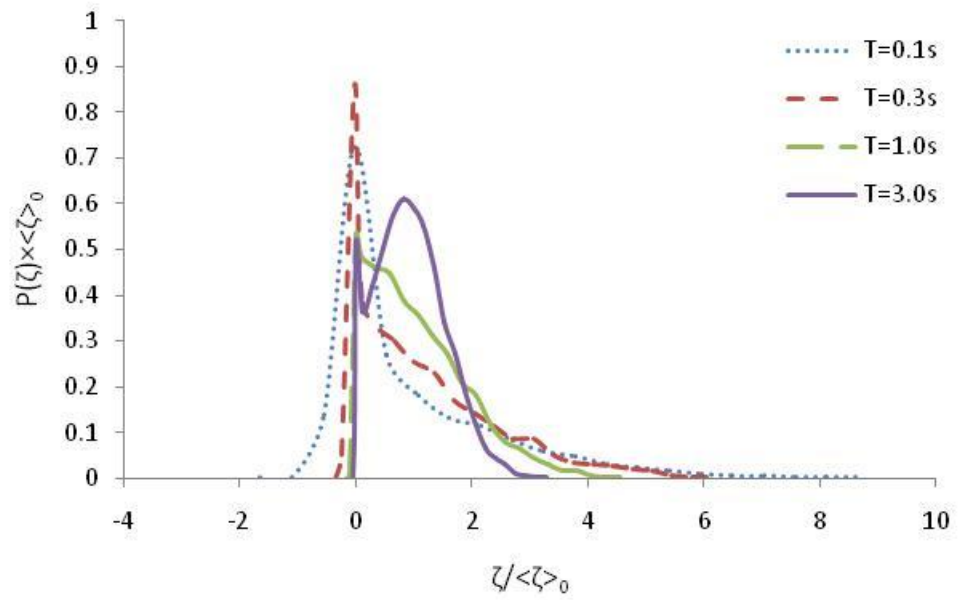


Figure 5.13: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=800$ in S1.

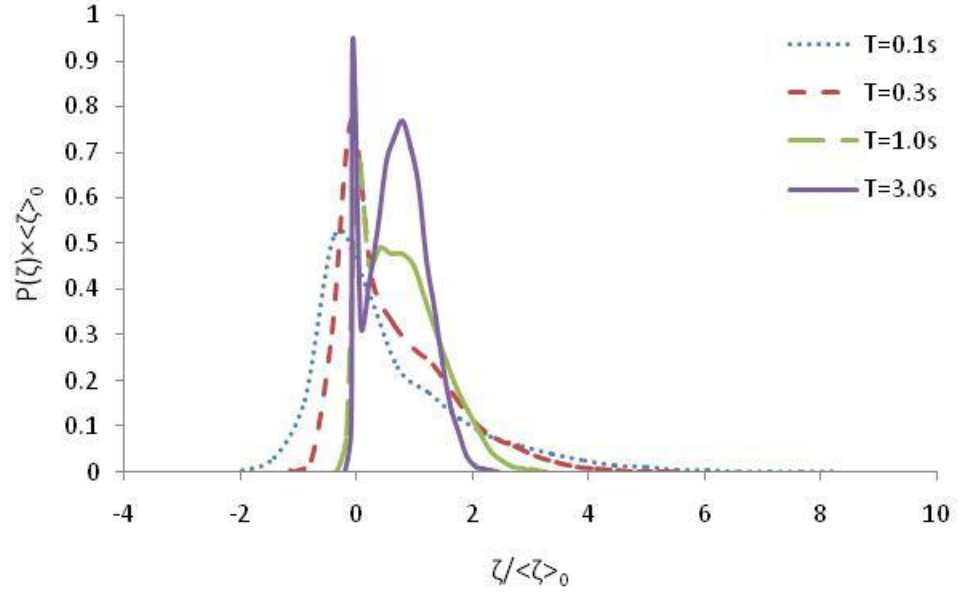


Figure 5.14: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=5$ in Portland.

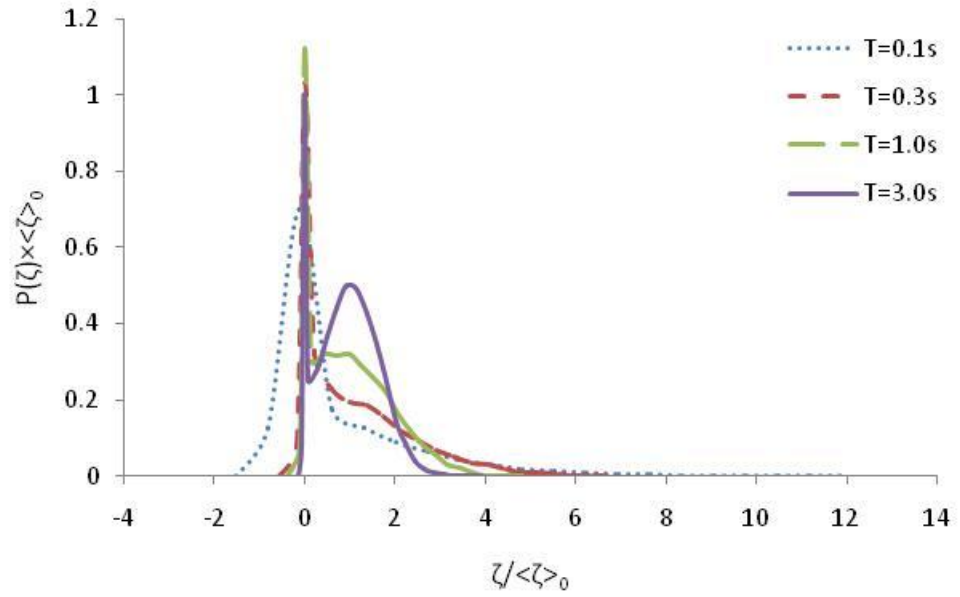


Figure 5.15: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=100$ in Portland.

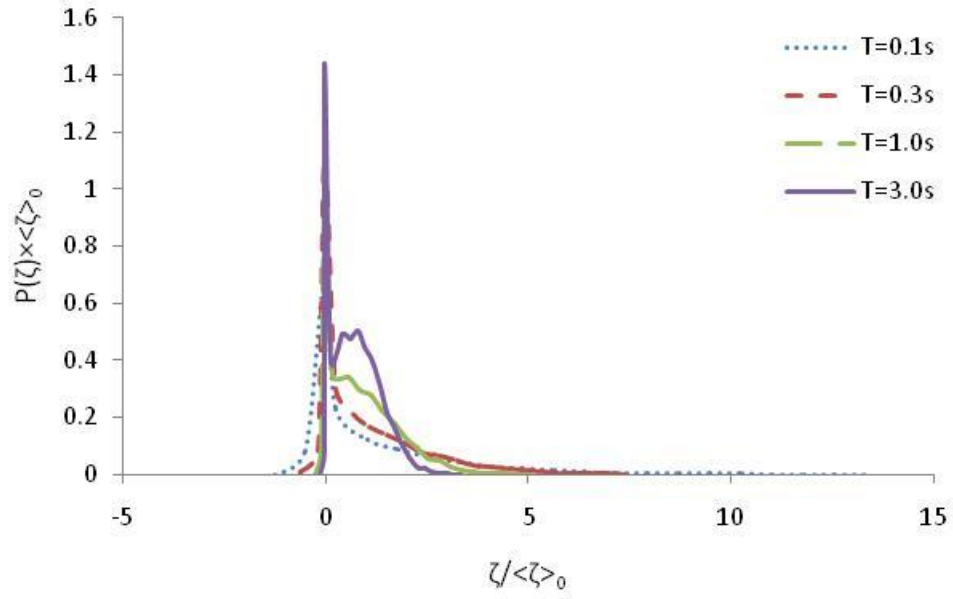


Figure 5.16: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=800$ in Portland.

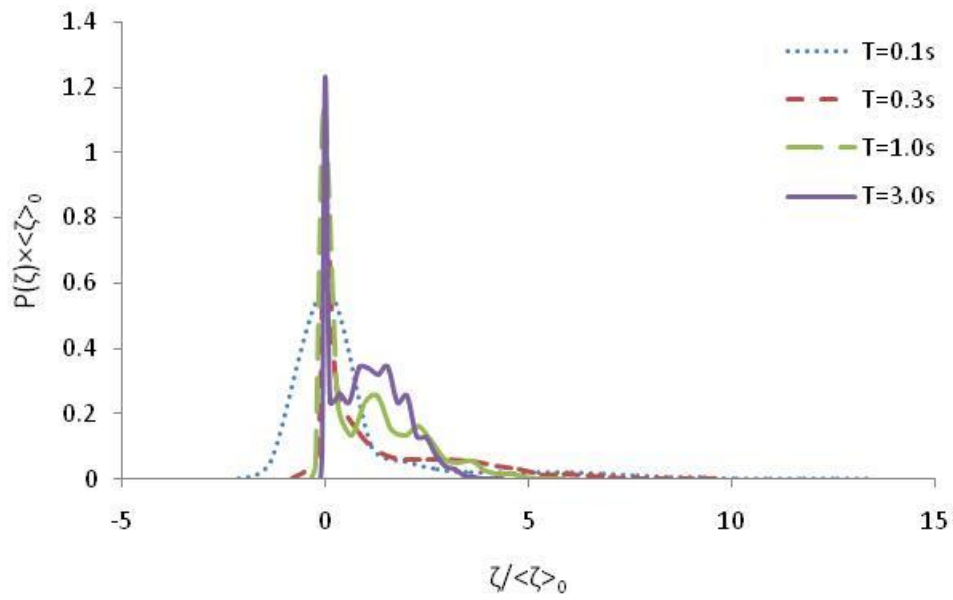


Figure 5.17: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=5$ in C2.

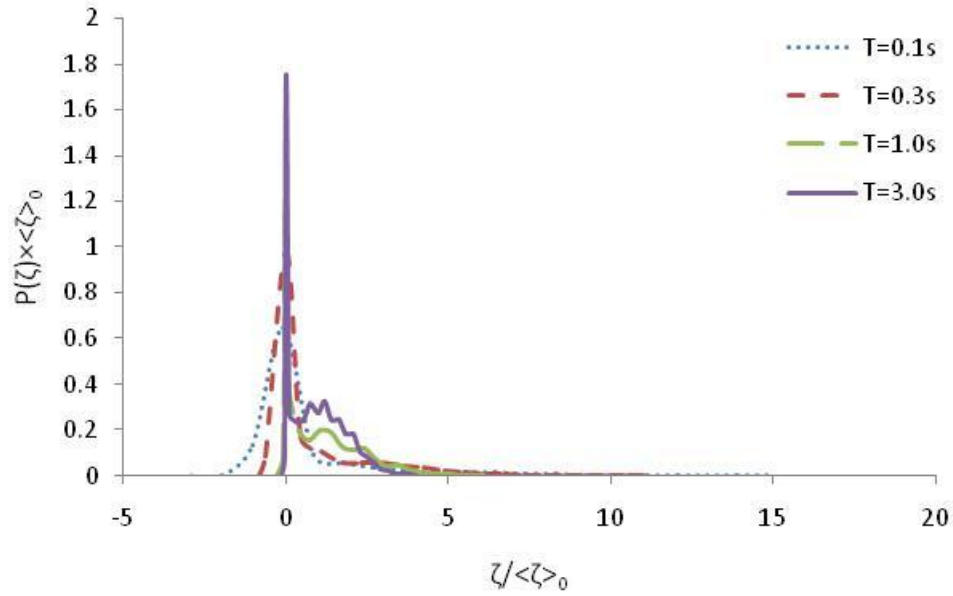


Figure 5.18: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=100$ in C2.

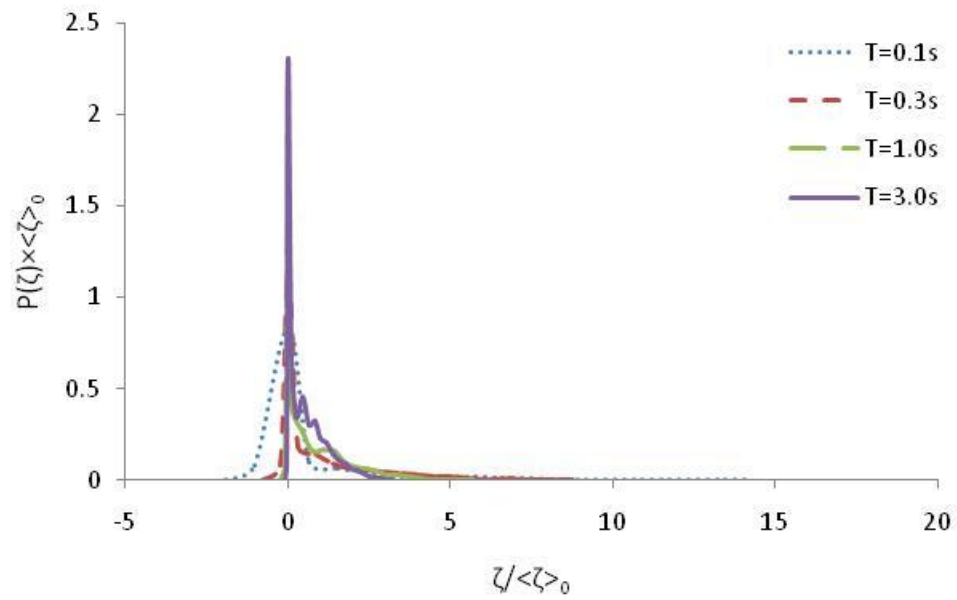


Figure 5.19: Evolution of normalized probability distribution function of fluid displacement with time, $Pe=800$ in C2.

Figures 5.14 - 5.19 are devoted to study the dependence of pre-asymptotic dispersion behaviour to heterogeneity and Peclet number regime in the complex geometry of carbonate rocks. The behaviour for the carbonate is quite different, with most of the plume effectively stagnant and a very dispersed profile. This cannot be captured – even qualitatively – by traditional advection-diffusion models. The results of the two carbonates follow the same pattern with a persistent high peak due to a large fraction of particles being in the slow velocity regions. A second lower peak is formed by the contribution of particles on faster streamlines, and it becomes more pronounced with time. As it can be seen from Figures 5.16 and 5.19, the first peak's impact on dispersion becomes more important in the higher Peclet number regimes. In contrast, the second peak establishes earlier for $Pe=5$. It can be explained by the diffusion process. In low Peclet regimes, the role of diffusion is more pronounced in comparison with advection. Therefore, due to larger diffusion, there is a higher transfer of solute particles between slow regions and faster ones.

Figure 5.20 illustrates the immobile first peak observed in carbonates and the importance of diffusion. We see an even distribution of particles - red particles show trapped particles in slow- or no-flow regions and green ones are particles on a fast streamline. Green particles spread within the porous medium while red ones are retarded. The high fractions of slow velocity regions cause a high peak of immobile particles in early time. The only mechanism that can cause red particles to move forward is diffusion.

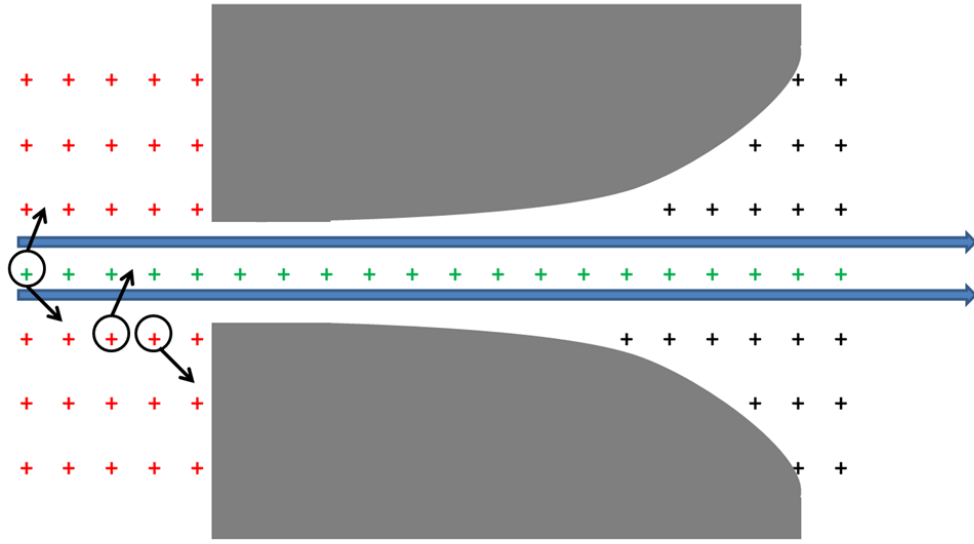


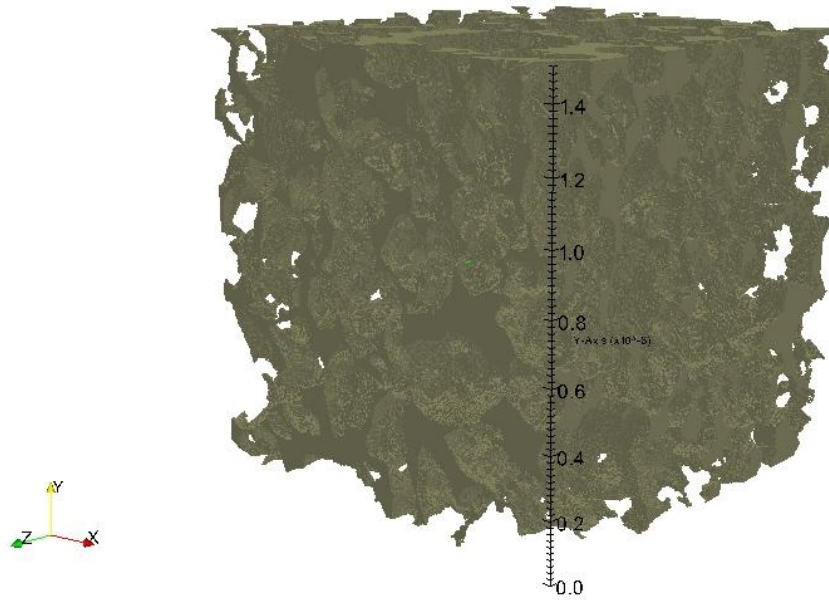
Figure 5.20: The high peak at near zero displacement for transport in carbonates is illustrated. Red dots show trapped particles and green ones are particles on a fast streamline. The only mechanism which can cause red particles join the flowing zone is diffusion.

5.1.2. Numerical predictions in comparison with NMR measurements

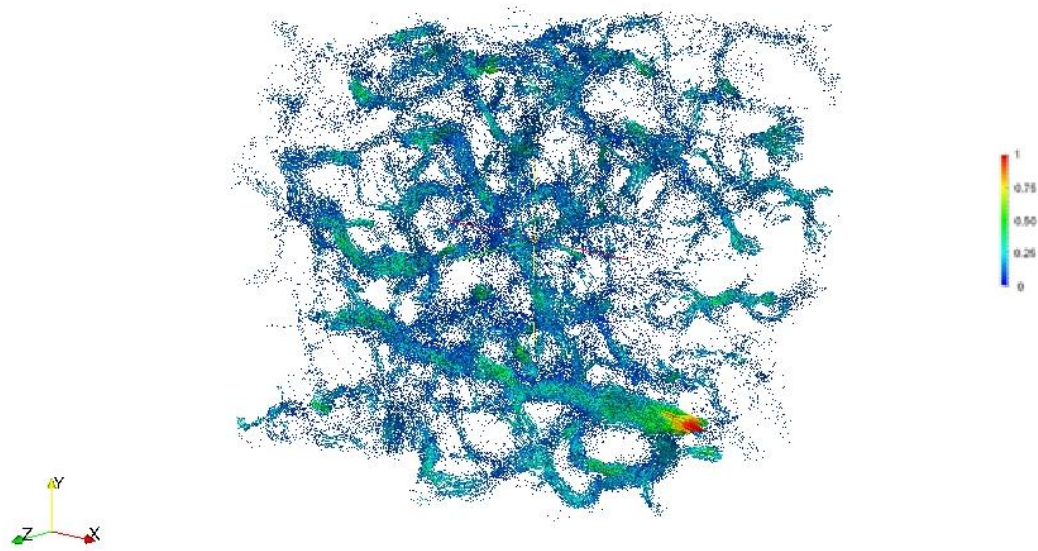
We also compare our numerical results with NMR measurements on a sandstone and a carbonate. We compare our propagator results for Bentheimer sandstone with NMR measurement performed by Scheven et al. (2005) on the same sandstone. The micro-CT image of Bentheimer sandstone with resolution of 3 μm and the flow field simulated on it are shown in Figure 5.21. The image size is 500×500×500. The average velocity of flow in experiment and our simulation is 1.03 mm/s. The standard value for free molecular self-diffusion coefficient of water is used: $D_m = 2.2 \times 10^{-9} \text{ m}^2/\text{s}$.

We compare numerical simulation with NMR measurement for time elapses of $t=0.1\text{s}$, 0.2s, 0.45s, and 1s. The agreement is very good as it can be seen in Figure 5.22. At early time there is a high immobile peak since the solute particles have not had enough time to displace through the porous medium – see Figures 5.22 (a) and (b). With progress of time the immobile peak exists but a second peak forms which represents moving particles in

connected pores that have sampled different flow regions in the porous medium. After $t = 1s$ - Figure 5.22 (d) - the second peak is more pronounced as the immobile particles trapped in slow-flow regions or dead-end pores join the plume by diffusion.



(a)



(b)

Figure 5.21: Pore structure (a), and normalized flow distribution in Bentheimer sandstone (b). The image size is $500 \times 500 \times 500$ and the image resolution is $3\mu\text{m}$.

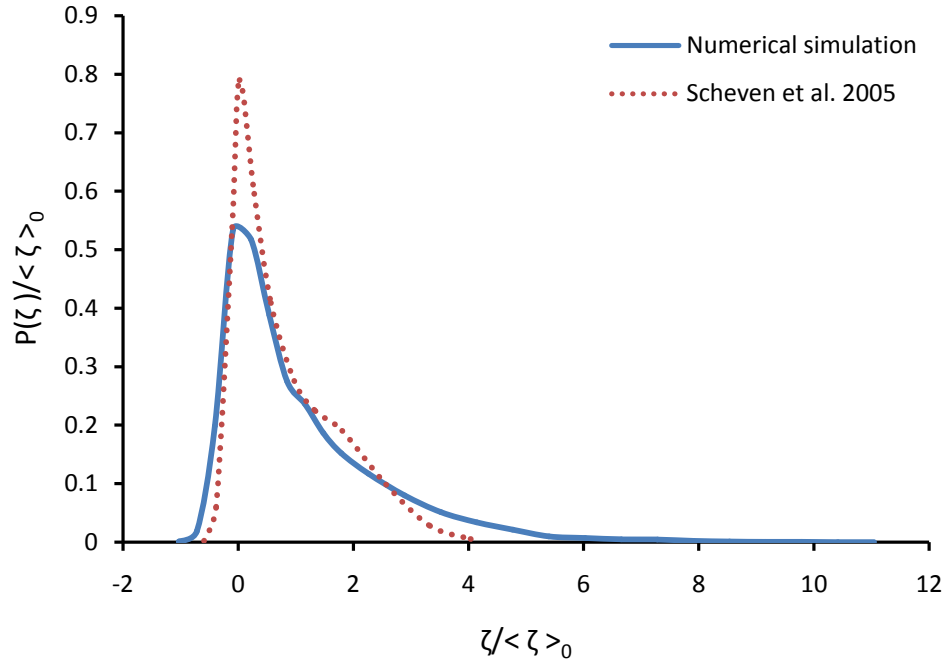


Figure 5.22(a): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Bentheimer sandstone as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Bentheimer sandstone by Scheven et al. (2005) for the same set of evolution time of $t = 0.1$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.03$ mm/s.

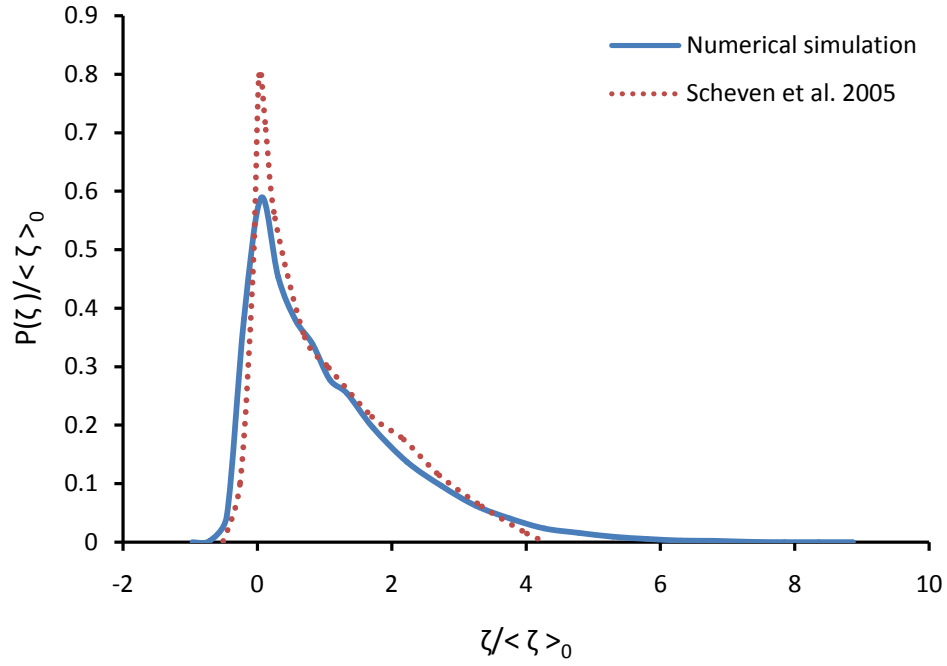


Figure 5.22(b): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Bentheimer sandstone as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Bentheimer sandstone by Scheven et al. (2005) for the same set of evolution time of $t = 0.2$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.03$ mm/s.

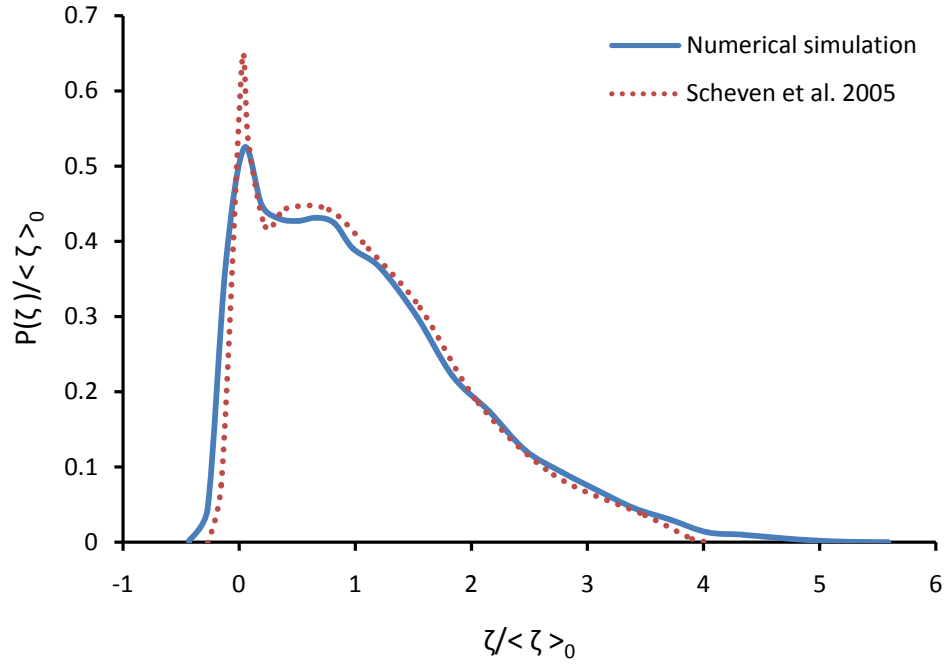


Figure 5.22(c): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Bentheimer sandstone as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Bentheimer sandstone by Scheven et al. (2005) for the same set of evolution time of $t = 0.45$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.03$ mm/s.

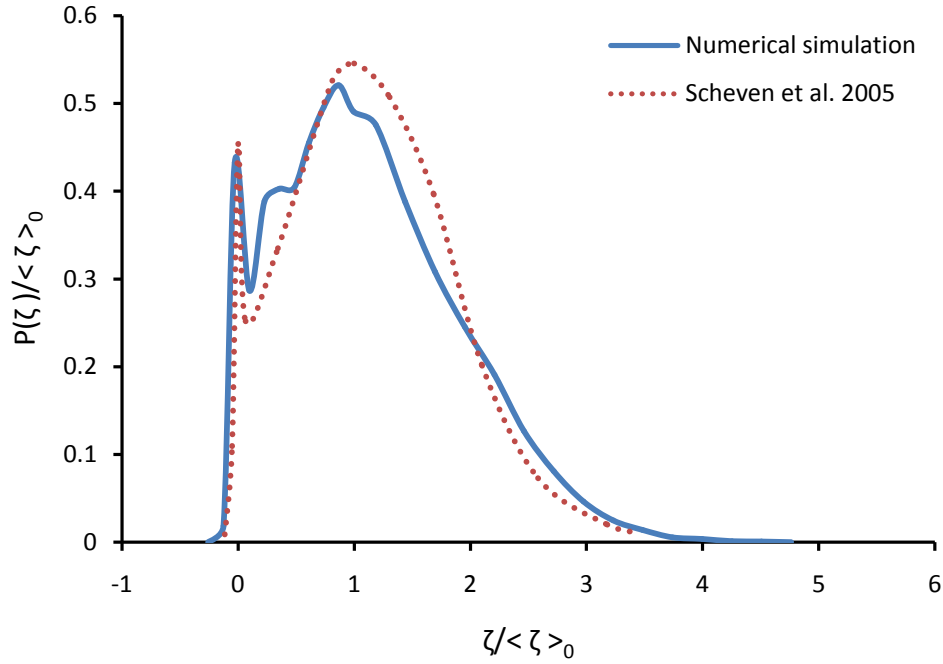
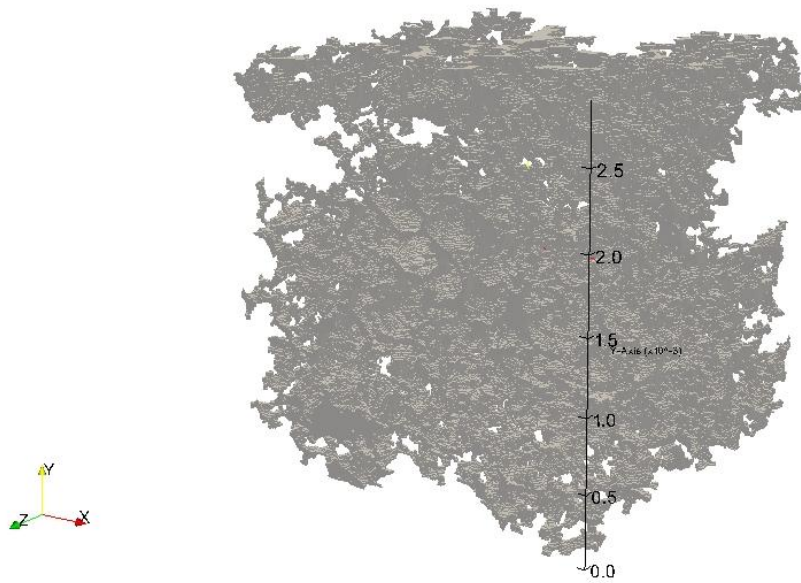


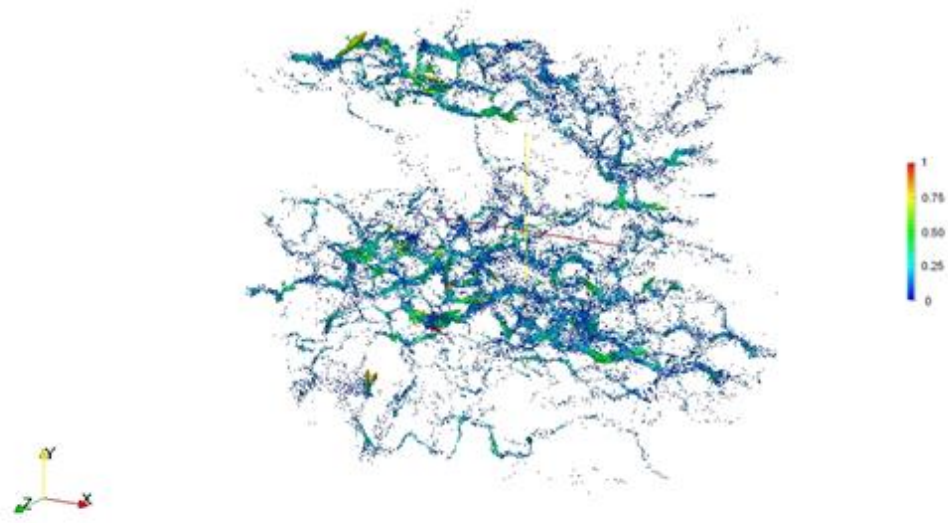
Figure 5.22(d): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Bentheimer sandstone as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Bentheimer sandstone by Scheven et al. (2005) for the same set of evolution time of $t = 1.0$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.03$ mm/s.

In addition, we compare our numerical simulation on Portland carbonate with NMR measurements on the same rock (Scheven et al., 2005). The pore structure obtained from micro-CT imaging and flow field are shown in Figures 5.23. The image size is $300 \times 300 \times 300$ with the resolution of $9 \mu\text{m}$. The average velocity used in our simulation is 1.3 mm/s - the same as the one in experiment and $D_m = 2.2 \times 10^{-9} \text{ m}^2/\text{s}$. Figure 5.24 shows numerical results along with NMR measurement after $t = 0.1, 0.3, 0.45$, and 1 s. For $t = 1$ s, another independent NMR measurement is also available from Mitchell et al. (2008) on the same carbonate as shown in Figure 5.24 (d). The propagator profile for the carbonate is very different from any prediction by the ADE. It is evident that in carbonate samples the peak concentration is virtually immobile with a highly dispersed fast-moving tail: particles reside for a long time in slow or no-flow regions which are a high fraction of pore space in carbonate, close to pore walls, dead-end pores or in narrow pore spaces,

eventually diffusing out and moving rapidly through the better connected, wider regions. Our numerical simulation is in a very good agreement with experimental observations and we capture the secondary peak of fast-moving solute that represents transport in spatially continuous, large channels – this is a feature that will be difficult to observe with the traditional CTRW formulation (Cortis and Berkowitz, 2005) that ignores spatial correlations and the particles are injected to the porous medium. This is in contrast to NMR measurement where particles are initially resident in the porous medium.



(a)



(b)

**Figure 5.23: Pore structure (a), and normalized flow distribution in Portland carbonate (b).
The total system size is a cube 2.7 mm on each side.**

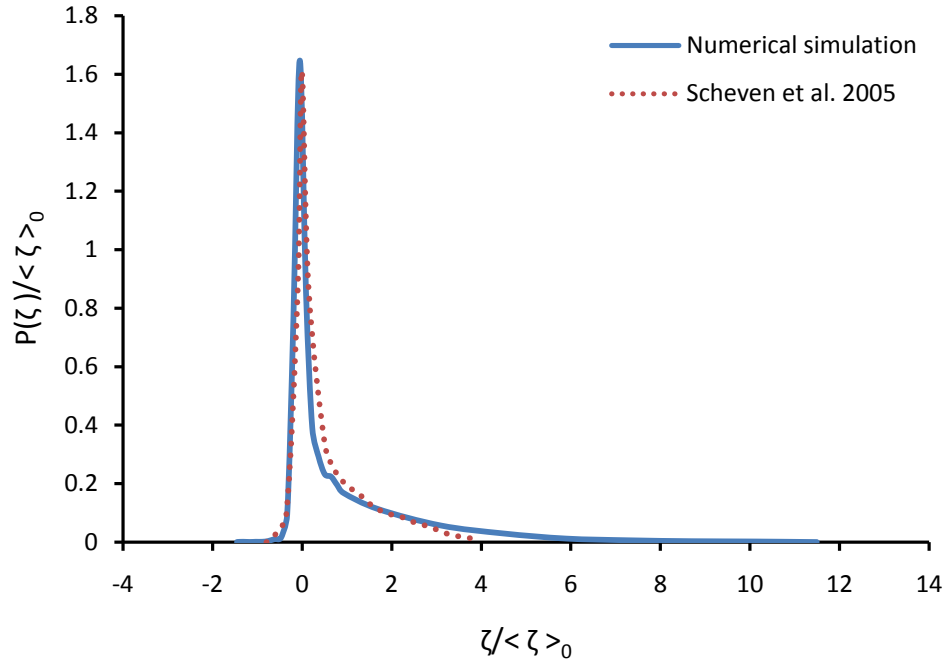


Figure 5.24(a): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Portland carbonate as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Portland carbonate by Scheven et al. (2005) for the same set of evolution times of $t = 0.1$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.3$ mm/s.

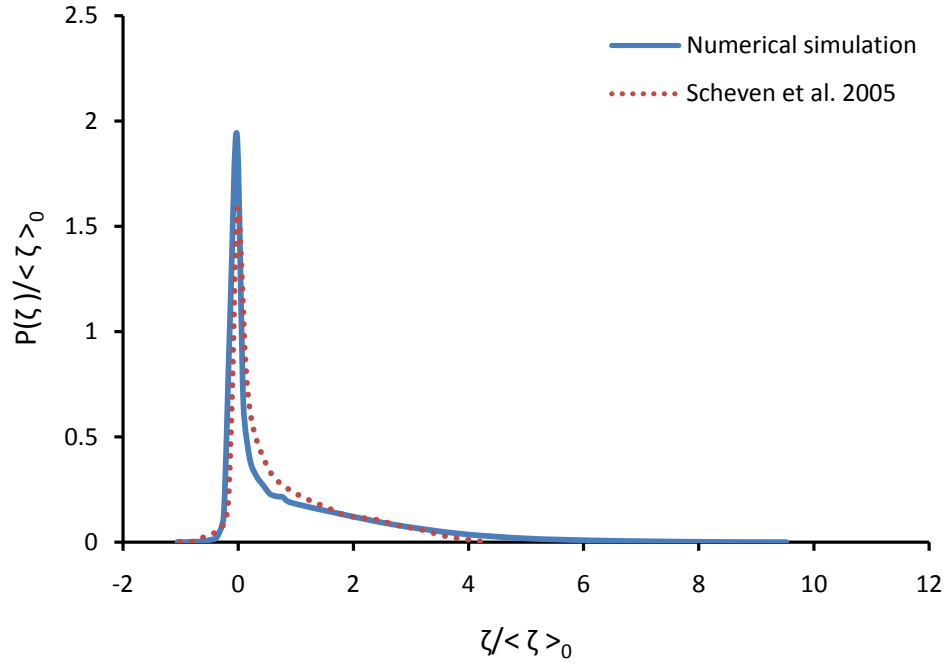


Figure 5.24(b): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Portland carbonate as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Portland carbonate by Scheven et al. (2005) for the same set of evolution times of $t = 0.2$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.3$ mm/s.

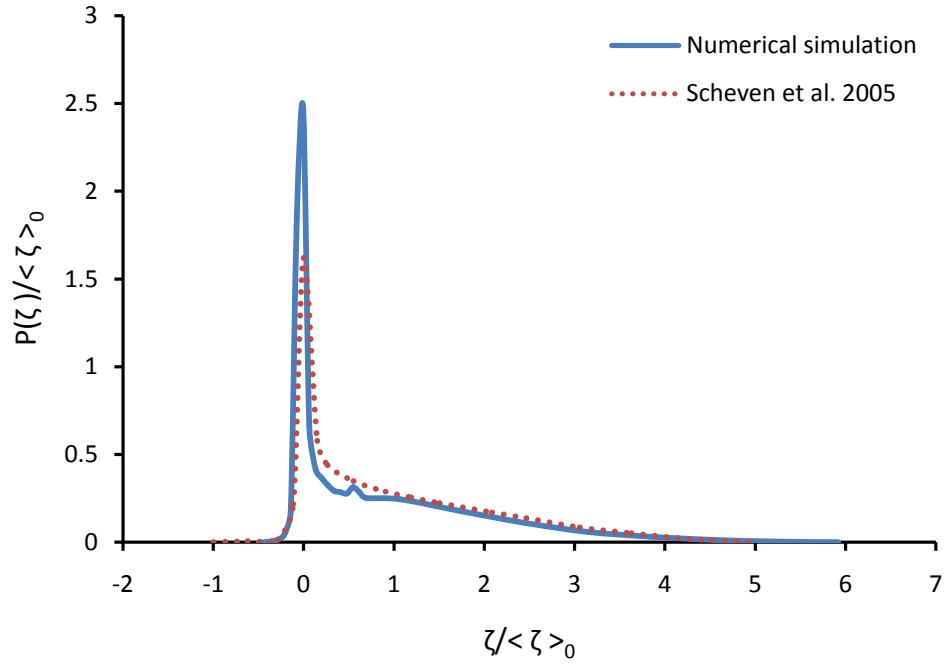


Figure 5.24(c): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Portland carbonate as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Portland carbonate by Scheven et al. (2005) for the same set of evolution times of $t = 0.45$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.3$ mm/s.

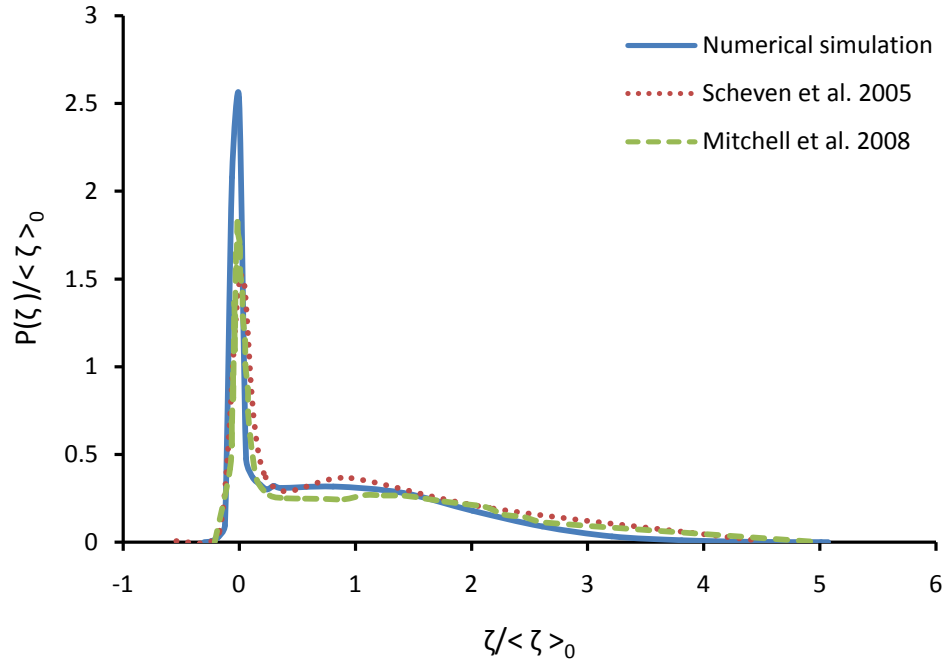
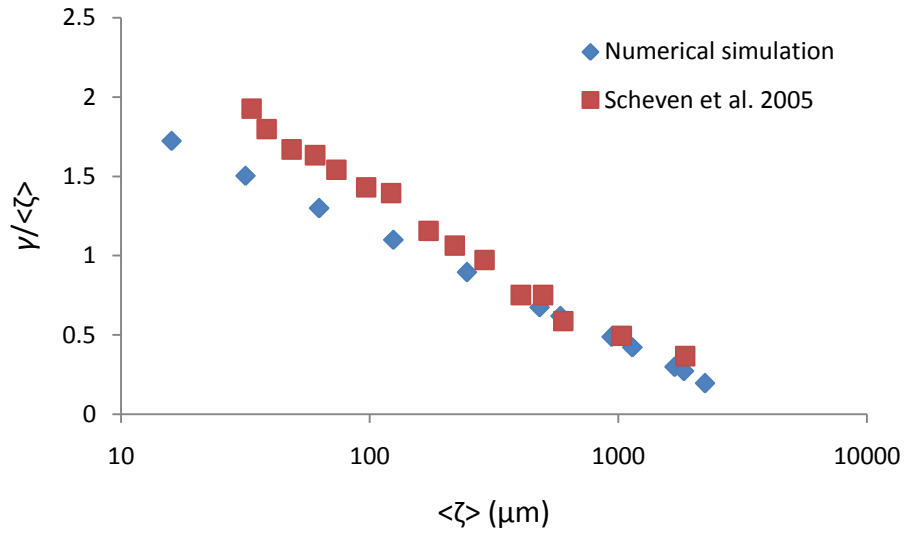
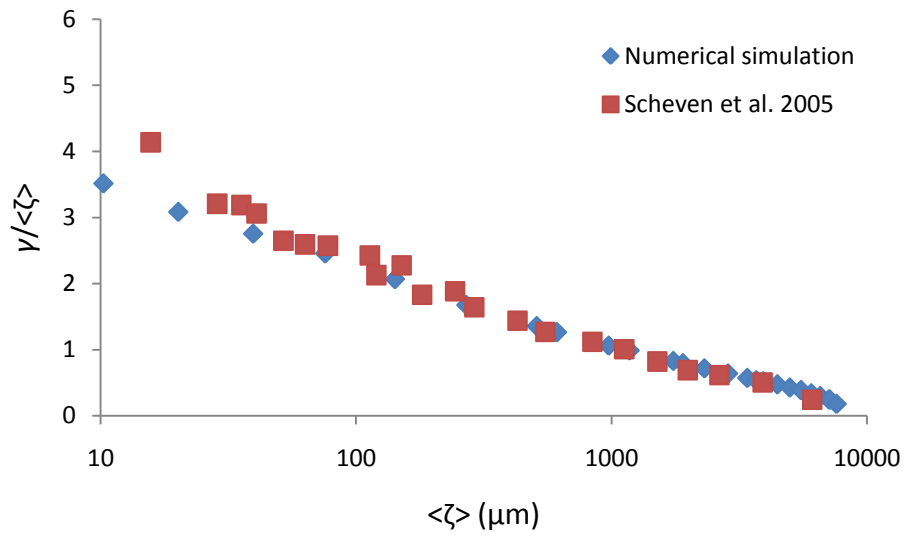


Figure 5.24(d): Probability of molecular displacement $P(\zeta)$ on micro-CT image of Portland carbonate as a function of displacement ζ , compared with the propagators obtained by NMR experiments on Portland carbonate by Scheven et al. (2005) and by Mitchell et al. (2008) for the same set of evolution times of $t = 1$ second. The co-ordinates are rescaled by the nominal mean displacement $\zeta_0 = u_{av}t$. $u_{av} = 1.3$ mm/s.

We also compare the skewness $\gamma^3 = \langle (\zeta - \langle \zeta \rangle)^3 \rangle$ of displacement probability as a function of mean displacement for Portland carbonate and Bentheimer sandstone with NMR measurement by Scheven et al. (2005) – Figure 5.25. The skewness is normalized by the mean displacement. The skewness as a measure of asymmetry of the displacement probability decreases in time since retarded particles join faster streamlines by diffusion. Our numerical simulation is in a reasonably good agreement with NMR measurements by Scheven et al. (2005) for the carbonate and sandstone samples. At early time, there is a 20% difference between numerical prediction and NMR measurement on Bentheimer sandstone indicating, perhaps, the different size of samples for numerical simulations and NMR experiments.



(a)



(b)

Figure 5.25: Numerical simulation of normalized skewness $\gamma/\langle \zeta \rangle$ as a function of mean displacement for the Bentheimer sandstone (a) and Portland carbonate (b) compared with NMR measurements by Scheven et al. (2005).

5.1.3. Time-dependent dispersion coefficient

In this section we study the time-dependent dispersion coefficient in different types of porous media. At very early times a narrow distribution of velocity is sampled so dispersion is low; however as the time progresses a wider distribution of velocities is sampled and dispersion coefficient increases with time. After the solute particles fully sample the velocity field, the dispersion becomes Fickian and dispersion coefficient does not vary with time.

Continuous Time Random Walk (CTRW) as an analytical approach is also used to interpret the scaling of the dispersion coefficient with time in the pre-asymptotic regime of dispersion.

Figures 5.26 and 5.27 show the time-dependent dispersion coefficients for LV60 and F42 sandpacks for three Peclet regimes as a function of dimensionless time $\tau = t/t_1$, where $t_1 = \frac{L}{u_{av}}$ is the mean advective transit time based on the characteristic length of the porous media as presented in Table 4.1. Solid lines show a power-law scaling with the slope of 0.2. Considering $D_L/D_m \sim Pe \tau^{2-\beta}$ based on CTRW prediction, we obtain $\beta = 1.8 \pm 0.05$. This is in agreement with the power-law transit time probability as discussed in chapter 4. In addition, Figures 5.26 and 5.27 shows that the non-Fickian regime in $Pe=5$, the Fickian dispersion starts from $\tau = 5$. However for $Pe=100, 800$ we can see non-Fickian regime up to $\tau = 20$. This shows that diffusion accelerates the procedure of gradual sampling of the velocity field by solute particles and the Fickian dispersion occurs in an earlier time for lower Pe .

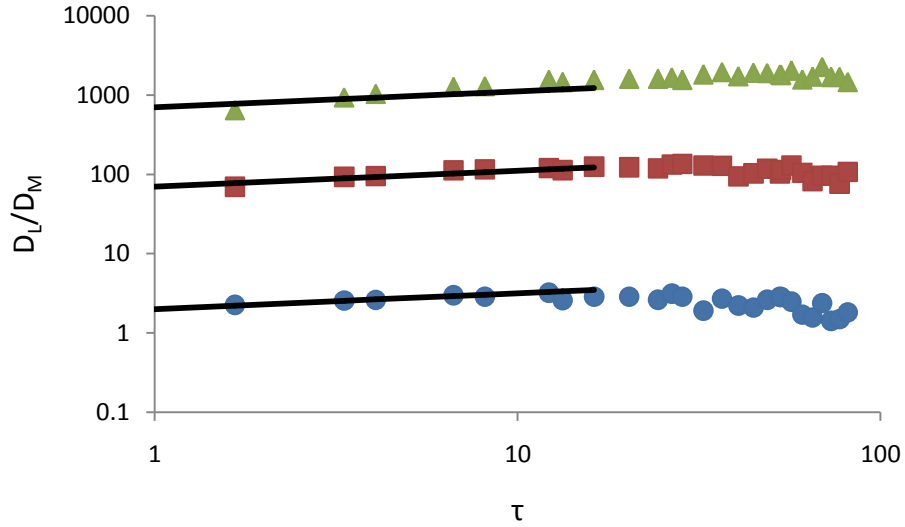


Figure 5.26: The pre-asymptotic behaviour of D_L for LV 60 sandpack computed from the pore-scale model is plotted for Peclet numbers 5 (circles), 100 (squares), and 800 (triangles). The solid lines with the slope of 0.2 indicate the predicted scaling from CTRW framework: $D_L/D_m \sim Pe \tau^{2-\beta}$, where the slope is $2-\beta = 0.2$ and so $\beta=1.8$.

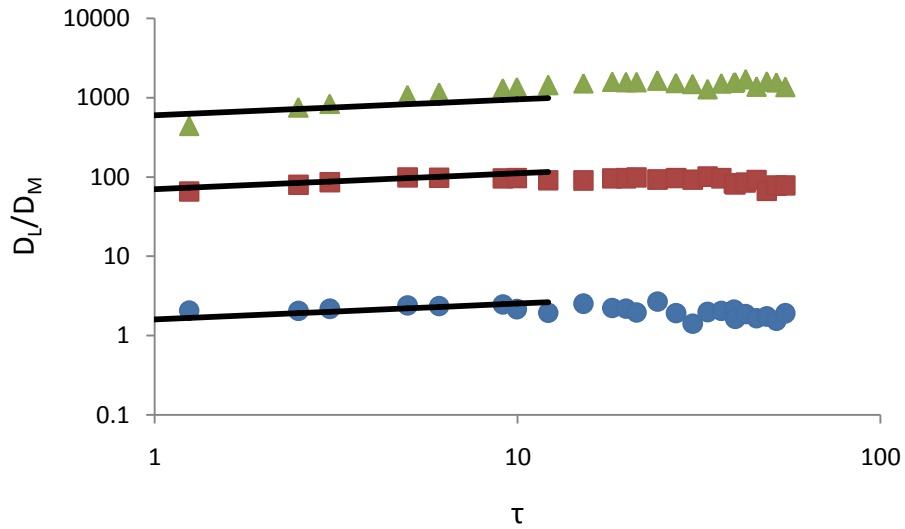


Figure 5.27: The pre-asymptotic behaviour of D_L for F 42 sandpack computed from the pore-scale model is plotted for Peclet numbers 5 (circles), 100 (squares), and 800 (triangles). The solid lines with the slope of 0.2 indicate the predicted scaling from CTRW framework: $D_L/D_m \sim Pe \tau^{2-\beta}$, where the slope is $2-\beta = 0.2$ and so $\beta=1.8$.

Figures 5.28 and 5.29 show dispersion coefficients for Berea and S1 sandstones respectively. Again, solid lines show a power-law scaling with slopes 0.2 indicating $\beta = 1.8 \pm 0.05$ – as observed from transit time probability. In the low Peclet regime, we see the dispersion coefficient becomes constant in time from $\tau = 10$. However, the Fickian dispersion is observed from $\tau = 30$ in higher Peclet regime. In sandstones it takes a longer time in comparison with sandpacks for solute particles to experience all flow regimes indicating higher degree of heterogeneity associated with sandstones in comparison with unconsolidated homogeneous porous media.

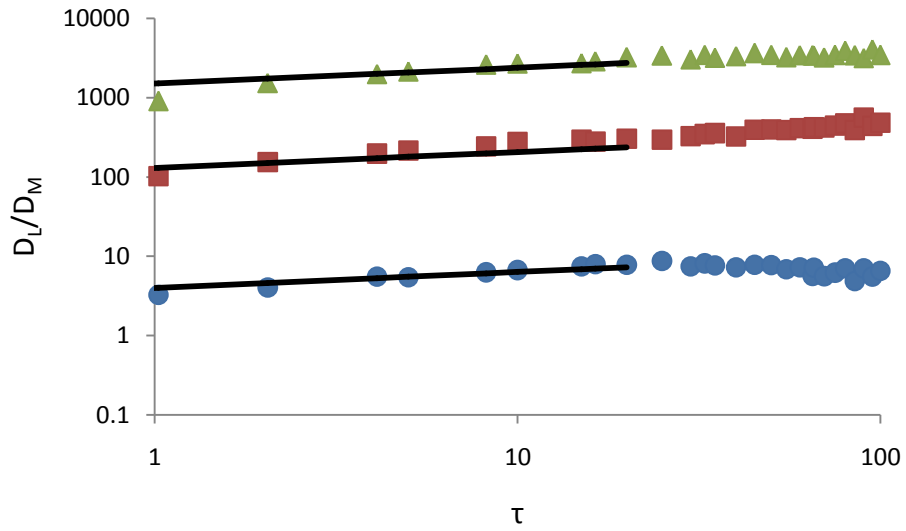


Figure 5.28: The pre-asymptotic behaviour of D_L for Berea sandstone computed from the pore-scale model is plotted for Peclet numbers 5 (circles), 100 (squares), and 800 (triangles). The solid lines with the slope of 0.2 indicate the predicted scaling from CTRW framework: $D_L/D_m \sim Pe \tau^{2-\beta}$, where the slope is $2-\beta = 0.2$ and so $\beta=1.8$.

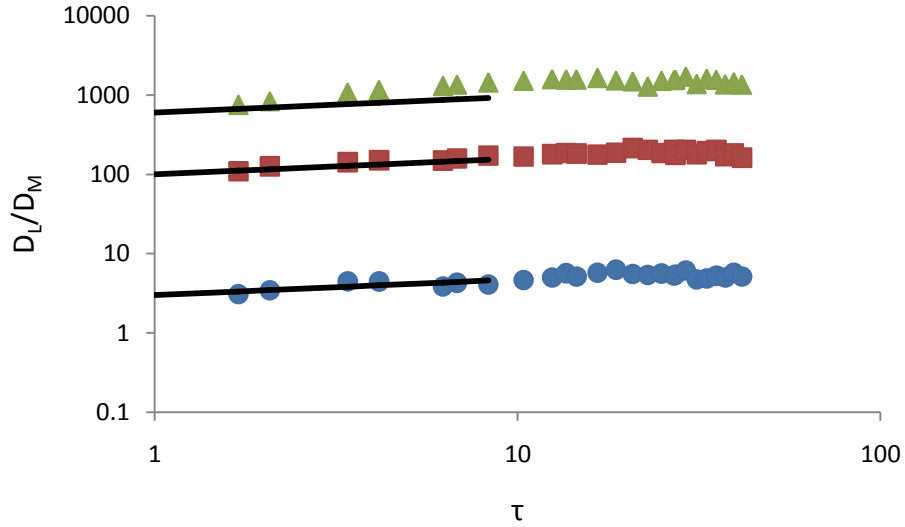


Figure 5.29: The pre-asymptotic behaviour of D_L for S1 sandstone computed from the pore-scale model is plotted for Peclet numbers 5 (circles), 100 (squares), and 800 (triangles). The solid lines with the slope of 0.2 indicate the predicted scaling from CTRW framework: $D_L/D_m \sim Pe \tau^{2-\beta}$, where the slope is $2-\beta = 0.2$ and so $\beta = 1.8$.

The time-dependent dispersion coefficients for carbonates are shown in Figures 5.30 and 5.31. In the case of carbonate samples, $\beta < 1$. Therefore, based on the CTRW prediction, the second moment of displacement is proportional to $t^{2\beta}$. Drawn solid lines on the graph have slopes of 0.4 and 0.5. For transport through carbonates, CTRW predicts $D_L/D_m \sim Pe \tau^{2\beta-1}$ indicating $\beta = 0.7 \pm 0.05$ and 0.75 ± 0.05 for Portland and C2 carbonates respectively. Due to heterogeneity of carbonates, it takes a longer time for particles to spread and sample the porous medium in comparison with sandstones and sandpacks. In Portland carbonate, for $Pe = 5$, $\tau = 20$ is start of Fickian regime. $\tau = 30$ and $\tau = 40$ are starts of Fickian regimes for $Pe = 100$ and 800 respectively.

In C2 carbonate, for $Pe = 5$ dispersion coefficient becomes constant after $\tau = 30$ and for $Pe = 100$ and 800, the Fickian dispersion is reached at $\tau = 40$. For $Pe = 800$, we have extended our simulation for up to 50 seconds (approximately corresponding to $\tau = 400$) and we observed that the dispersion coefficient is constant and the dispersion can be considered Fickian.

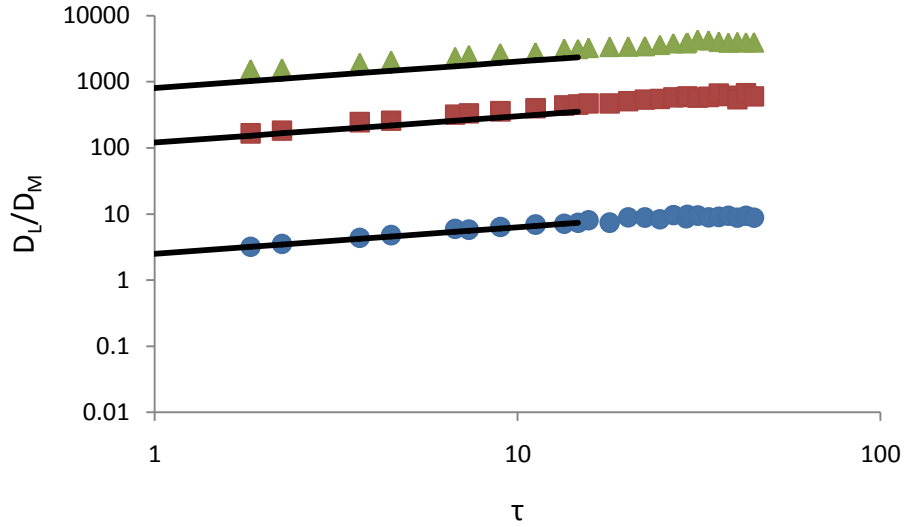


Figure 5.30: The pre-asymptotic behaviour of D_L for Portland carbonate computed from the pore-scale model is plotted for Peclet numbers 5 (circles), 100 (squares), and 800 (triangles). The solid lines with the slope of 0.4 indicate the predicted scaling from CTRW framework: $D_L/D_m \sim Pe \tau^{2\beta-1}$, where the slope is $2\beta-1 = 0.4$ and so $\beta=0.7$.

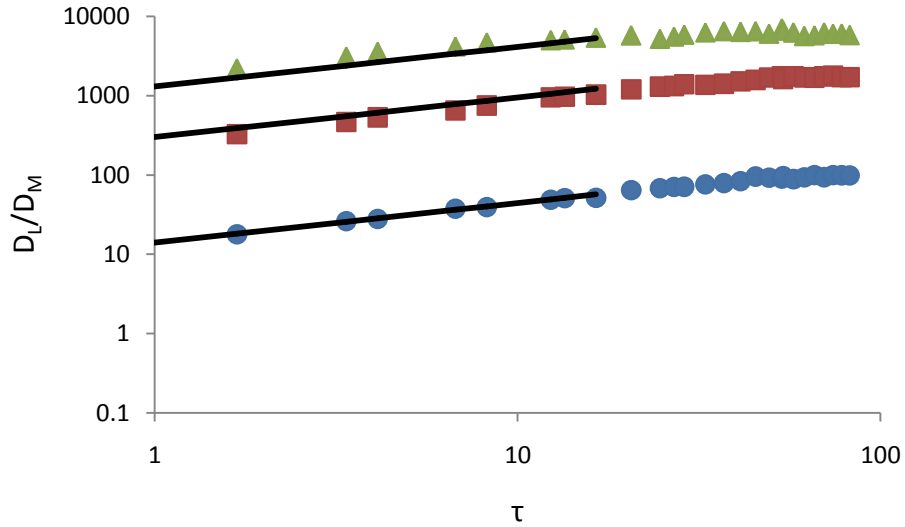


Figure 5.31: The pre-asymptotic behaviour of D_L for C2 carbonate computed from the pore-scale model is plotted for Peclet numbers 5 (circles), 100 (squares), and 800 (triangles). The solid lines with the slope of 0.5 indicate the predicted scaling from CTRW framework: $D_L/D_m \sim Pe \tau^{2\beta-1}$, where the slope is $2\beta-1 = 0.5$ and so $\beta=0.75$.

To summarize, the pre-asymptotic dispersion coefficient at early time has a power-law scaling with time as predicted by CTRW and in contrast to the ADE assumption which does not allow for variation of the dispersion coefficient with time. The scaling observed in the evolution of the time-dependent dispersion coefficient interpreted by CTRW confirms that $\beta = 1.8 \pm 0.05$ for sandpacks and sandstones. This study is also in agreement with $\beta < 1$ for carbonates. Moreover, we can observe that after the solute particles experience different velocity regions in the porous medium, the dispersion coefficient becomes constant in time. This indicates that the transport after a certain time depending on the heterogeneity of the porous media becomes Fickian. The transit time to Fickian transport increases with increment in heterogeneity of the porous medium.

6. Conclusions and future work

6.1. Conclusions

This thesis has described methods and results of numerical simulation of flow and dispersion on pore-space images obtained from micro-CT scanning of porous rock samples. We have presented an accurate algorithm to solve for Stokes flow at pore scale directly on binarized pore-space images. The method uses an efficient algebraic multigrid solver to solve the resultant systems of linear equations and imposes no-flow exactly at grain boundaries. We use it to model flow and estimate permeability on sandpacks, sandstone and carbonate rocks. The permeability comparison was in a good agreement with the previous study using the lattice Boltzmann technique by Dong and Blunt (2009).

We show that the Carman-Kozeny equation tends to over-predict permeability – it is in error by a large factor for the consolidated sandstone and carbonate samples studied. We obtain different permeability variations for different-sized image slices in sandpacks, sandstones and carbonates - this can be explained by the degree of tortuosity and connectedness of the pore space. We compute properties on images of different size to estimate the representative elementary volume (REV) which increases with sample heterogeneity – for the carbonates the REV appears to be larger than the sample size.

Flow-based measures of the REV are larger than geometry-based ones, since we also have to account for the tortuosity and connectedness of the pore space.

Furthermore, we have developed a new streamline-tracing technique to model advection. For voxels with no solid boundary, the method is identical to the Pollock (1988) algorithm that is now standard in field-scale streamline-based reservoir simulators. Where a solid boundary is present, zero tangential and normal velocity is strictly imposed, resulting in a bilinear variation of tangential velocity away from the boundary. A semi-analytic description of the velocity field within a grid block is obtained for all combinations of solid boundaries. An ensemble of particles is moved along streamlines, while a random walk method is used to capture molecular diffusion. We predict asymptotic longitudinal diffusion coefficient as a function of Peclet number for different types of porous media. We introduce a new characteristic length based on the ratio of volume to pore/grain surface area, applicable to images where a typical grain size cannot be easily obtained. Our results compare well with measurements in the literature and show the different regimes, including restricted dispersion, a power-law dependence of dispersion coefficient on Peclet number and the mechanical dispersion regime at high Peclet number. We have also applied CTRW analysis to explain the power-law regime of dispersion in highly heterogeneous porous media such as carbonates as well as sandstones and sandpacks.

We have also simulated the propagator as a function of time and compared the results with NMR experiments on similar materials and showed a very good agreement. We have also modelled pre-asymptotic dispersion coefficient as a function of Peclet number and time. While we have only studied small samples of each rock type, our results indicate that the behaviour of transport in carbonates is generically different from sandstones, with a very slow-moving peak concentration, a highly dispersed tail, an extremely gradual approach to an asymptotic regime and a non-linear scaling of dispersion coefficient with Peclet number, consistent with a CTRW analysis of the grid-block travel times.

This work implies that in carbonates, the peak plume position will be retarded relative to the mean flow field with a very wide spread. This may tend to suppress convective mixing of solute and lead to long residence times for tracers and pollutants. As another example, during carbon dioxide, CO_2 , storage, some of the CO_2 dissolves in brine and this denser CO_2 -laden brine sinks. This motion allows the development of a gravitational instability, further mixing and eventual secure storage. However, recent analytical and numerical analyses of the problem (Riaz et al., 2006, Hidalgo and Carrera, 2009) presume Fickian dispersion, which we suggest is inappropriate for most deep, heterogeneous porous formations, and is almost certainly qualitatively incorrect for carbonates and which may significantly over-estimate the degree of dissolution.

6.2. Future Work

6.2.1. Simulation employing parallel machines

The flow simulator applied in this work employs a series processing algorithm. Two approaches can be used to improve the run time for flow simulation. Firstly, a parallel processing solver can be used to solve the associated algebraic systems of equations. In addition, the applied algorithm for flow simulation (SIMPLE) has the potential to be modified for parallel processing machines. Considering that three components of velocity are independent in each time step, after correcting the pressure field, solving for u , v , and w can be performed in a parallel manner. Employing high-performance parallel processing machine, it will be possible to simulate fluid flow on binarized images with up to 2000^3 grid blocks considering the advances in micro-CT imaging and availability of high-resolution images on larger samples.

6.2.2. Simulation on more carbonate rock samples

This work serves as a basis for further analysis of dispersion on a variety of different porous media especially carbonate cores. In this work we limited our analysis on a few carbonate samples in a comparative study. In order to establish a fundamental

understanding of transport in carbonates, more simulation on carbonate samples is necessary.

6.2.3. Treatment for reactive transport

Our methodology is also a useful first step in the development of a rigorous pore-scale treatment of reactive transport. In this study the two main mechanism of dispersion have been modelled in the absence of reaction. However, modelling reaction is of importance in ground water modelling and especially carbon capture and storage applications. Therefore, as a further subject of studies, effects of reaction on dispersion can be studied applying the platform used in this study.

To model reaction between fluids, at $t = 0$, the injected particles to the porous media can be labelled as A and B representing two types of reactant solute particles. Solute particles A and B are reactants and particle C is generated by their reaction



In each time step, particles A and B move within the porous medium by advection and diffusion. To model the advection the same approach described in chapter 3 can be applied. Diffusion also is modelled using the same method – random walk. Particle A and B diffuse with molecular diffusion coefficients of D_{mA} and D_{mB} respectively. Therefore the mean free path of motion of particle A and B can be written as:

$$\lambda_A = \sqrt{6D_{mA}\Delta t} \quad 6.2$$

$$\lambda_B = \sqrt{6D_{mB}\Delta t} \quad 6.3$$

Before passing to the next time step, a further mechanism must be modelled – reaction between solute particles A and B. If the distance between a particle A and a particle B moved by advection and diffusion is less than $\lambda_A + \lambda_B$, then those particles react and a particle C is generated.

Now, particles C also exist in the porous medium. Particles C also move with advection and diffusion in each time step. The molecular diffusion coefficient of solute particles C and its mean free path are D_{mC} and λ_C respectively where

$$\lambda_c = \sqrt{6D_{mC}\Delta t}$$

6.4

In brief, in the presence of reaction, modelling dispersion contains three mechanisms – advection, diffusion and reaction. In each time step particles A, B, and C move by advection and diffusion. Then distance between particles A and B is controlled, if they are in reaction distance from each other, a particle C is generated. This approach can be applied on the platform used in this work to enable it to capture reactions as well as diffusion and advection.

A fluid-solid interaction can also be captured by adding or removing solid phases-precipitation and dissolution- when a solute particle hits a solid surface. The volumetric change in the solid phase balances the volumetric change in the fluid phase. To model this interaction, flow field must be updated after each time step of particle movement. The reduction/increase in porosity and changes in pore geometry due to reaction may lead to significant change in flow pattern within the porous domain. Therefore, there will be an updating of position of particles, pore-space geometry and flow field at the end of each time step. For this aim, applying a parallel flow simulation seems essential due to time consuming simulation of reactive transport. In addition in the presence of reaction, not only the Peclet number and heterogeneity of pore space but the rate of reaction affects the dispersion of solute particles. Damköhler number is a dimensionless number equal to the ratio of time needed for a particle to move a characteristic length by advection to the time it takes the chemical reaction to be completed. In this work, we studied the effect of Peclet regime along with heterogeneity on transport of solute particles in porous media. Reactive transport is an interplay between advection, diffusion and reaction. Therefore, by adding reactive effects on the developed numerical code, the rigorous coupling between transport and reaction can be captured as a function of Peclet number, Damköhler number, and of course pore-space heterogeneity.

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Appendix

As mentioned in chapter 4, for voxels with no solid boundaries, we apply Pollock's algorithm (Pollock, 1988) where velocity normal to a face varies linearly across the block. For the voxels adjacent to a solid surface, we have modified the formulation to be able to capture no-slip boundary condition on the surface. We categorize different cases where one or more nearest neighbour voxel is solid. In all cases the velocity field everywhere is divergence free and obeys a zero velocity at all solid boundaries. The case where one of the neighbouring voxel is solid is shown in chapter 4.

Two of the neighbouring voxels are solid

This condition can happen for fifteen cases that can be categorized in two groups: (1) when the two solid voxels block opposing faces (this can happen in three cases, for the x-, y- or z-directions); and (2) when the solid voxels are located on adjoining faces that can happen in twelve cases.

There are two opposing solid faces

We show the equations where both solid blocks normal to the x-direction (Figure A.1); formulations for the two other cases can be obtained in the same way. Since both x-faces are blocked, the velocity component in the x-direction is zero. The velocity distribution is:

$$u = 0 \quad \text{A.1}$$

$$v = \frac{6v_1}{\Delta x^2} (x_2 - x)(x - x_1) + \frac{6(v_2 - v_1)}{\Delta x^2 \Delta y} (x_2 - x)(x - x_1)(y - y_1) \quad \text{A.2}$$

$$w = \frac{6w_1}{\Delta x^2} (x_2 - x)(x - x_1) + \frac{6(w_2 - w_1)}{\Delta x^2 \Delta z} (x_2 - x)(x - x_1)(z - z_1) \quad \text{A.3}$$

The time of flight increment across the block is:

$$\Delta \tau_y = \frac{\Delta x^2 \Delta y}{6(v_2 - v_1)(x_2 - x_p)(x_p - x_1)} \ln\left(\frac{v_2 \Delta y}{v_1 \Delta y + (v_2 - v_1)(y_p - y_1)}\right) \quad \text{A.4}$$

$$\Delta \tau_z = \frac{\Delta x^2 \Delta z}{6(w_2 - w_1)(x_2 - x_p)(x_p - x_1)} \ln\left(\frac{w_2 \Delta z}{w_1 \Delta z + (w_2 - w_1)(z_p - z_1)}\right) \quad \text{A.5}$$

$$\Delta \tau = \min(\Delta \tau_y, \Delta \tau_z) \quad \text{A.6}$$

Having the time of flight, the exit location is:

$$x_e = x_p \quad \text{A.7}$$

$$y_e = y_1 - \frac{v_1 \Delta y}{v_2 - v_1} + \frac{v_1 \Delta y + (v_2 - v_1)(y_p - y_1)}{(v_2 - v_1) \Delta y} e^{\frac{6(v_2 - v_1)(x_p - x_1)(x_2 - x_p)}{\Delta x^2 \Delta y} \Delta \tau} \quad \text{A.8}$$

$$z_e = z_1 - \frac{w_1 \Delta z}{w_2 - w_1} + \frac{w_1 \Delta z + (w_2 - w_1)(z_p - z_1)}{(w_2 - w_1) \Delta z} e^{\frac{6(w_2 - w_1)(x_p - x_1)(x_2 - x_p)}{\Delta x^2 \Delta z} \Delta \tau} \quad \text{A.9}$$

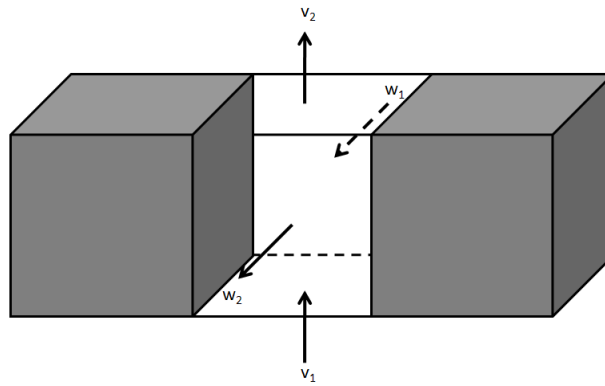


Figure A.1: Two opposing voxels are solid.

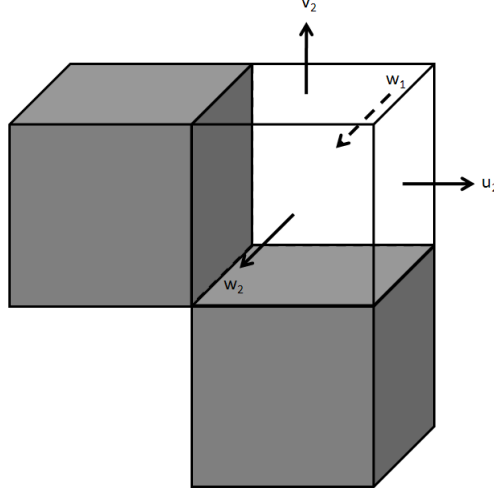


Figure A.2: Two adjacent voxels are solid.

Two adjacent voxels are solid

We show the equations for the case where one of solid voxels blocks the x_2 -face and the other blocks the z_1 -face (Figure A.2); for the other eleven cases, the formulation can be obtained similarly. The velocity distribution is:

$$u = \frac{2u_2}{\Delta x^2 \Delta y} (x - x_1)^2 (y - y_1) \quad \text{A.10}$$

$$v = \frac{2v_2}{\Delta y^2 \Delta z} (x - x_1)(y - y_1)^2 \quad \text{A.11}$$

$$w = \frac{4w_1}{\Delta x \Delta y} (x - x_1)(y - y_1) + \frac{4(w_2 - w_1)}{\Delta x \Delta y \Delta z} (x - x_1)(y - y_1)(z - z_1) \quad \text{A.12}$$

The time of flight increment across the block is:

$$\Delta \tau_x = \frac{\left(\frac{w_1 \Delta x \Delta y}{u_2 \Delta y + v_2 \Delta x} + z_1 - z_p \right)^{0.5} \Delta x^2 \Delta y^2}{2(x_p - x_1)(y_p - y_1)[w_1 \Delta x \Delta y (u_2 \Delta y + v_2 \Delta x) + (z_1 - z_p)(u_2 \Delta y + v_2 \Delta x)^2]^{0.5}} \times \left(1 - \left(\frac{\Delta x}{x_p - x_1} \right)^{\frac{u_2 \Delta y + v_2 \Delta x}{u_2 \Delta y}} \right) \quad \text{A.13}$$

$$\Delta\tau_y = \frac{\left(\frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} + z_1 - z_p\right)^{0.5} \Delta x^2 \Delta y^2}{2(x_p - x_1)(y_p - y_1)[w_1\Delta x\Delta y(u_2\Delta y + v_2\Delta x) + (z_1 - z_p)(u_2\Delta y + v_2\Delta x)^2]^{0.5}} \times$$

$$\left(1 - \left(\frac{\Delta y}{y_p - y_1}\right)^{\frac{u_2\Delta y + v_2\Delta x}{v_2\Delta x}}\right)$$
A.14

$$\Delta\tau_z = \frac{\Delta x^2 \Delta y^2}{2(x_p - x_1)(y_p - y_1)[w_1\Delta x\Delta y(u_2\Delta y + v_2\Delta x) + (z_1 - z_p)(u_2\Delta y + v_2\Delta x)^2]^{0.5}} \times$$

$$\left(\left(\frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} + z_1 - z_p\right)^{0.5} - \left(\frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} - \Delta z\right)^{0.5}\right)$$
A.15

$$\Delta\tau = \min(\Delta\tau_x, \Delta\tau_y, \Delta\tau_z)$$
A.16

And the exit location coordinates are:

$$x_e = x_1 + (x_p - x_0) \times$$

$$\left(1 - \frac{2(x_p - x_1)(y_p - y_1)[w_1\Delta x\Delta y(u_2\Delta y + v_2\Delta x) + (z_1 - z_p)(u_2\Delta y + v_2\Delta x)^2]^{0.5}}{\left(\frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} + z_1 - z_p\right)^{0.5} \Delta x^2 \Delta y^2} \Delta\tau\right)^{-\frac{u_2\Delta y}{u_2\Delta y + v_2\Delta x}}$$
A.17

$$y_e = y_1 + (y_p - y_0) \times$$

$$\left(1 - \frac{2(x_p - x_1)(y_p - y_1)[w_1\Delta x\Delta y(u_2\Delta y + v_2\Delta x) + (z_1 - z_p)(u_2\Delta y + v_2\Delta x)^2]^{0.5}}{\left(\frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} + z_1 - z_p\right)^{0.5} \Delta x^2 \Delta y^2} \Delta\tau\right)^{-\frac{v_2\Delta x}{u_2\Delta y + v_2\Delta x}}$$
A.18

$$z_e = z_1 + \frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} - \left(\left(\frac{w_1\Delta x\Delta y}{u_2\Delta y + v_2\Delta x} + z_1 - z_p\right)^{0.5} -$$

$$\frac{2(x_p - x_1)(y_p - y_1)[w_1\Delta x\Delta y(u_2\Delta y + v_2\Delta x) + (z_1 - z_p)(u_2\Delta y + v_2\Delta x)^2]^{0.5}}{\Delta x^2 \Delta y^2} \Delta\tau\right)^2$$
A.19

Three of the neighbouring voxels are solid

This condition can happen in twenty ways depending on the locations of solid voxels and can be categorized in two groups. The three surrounding solid voxels block all three coordinate directions; one solid voxel is on x-, the other one on y- and the last one on the z-direction face. This condition can happen in eight different ways. The second group is when two of the three solid voxels block the same direction (for example both are in the x-direction) and the third one is in another direction.

Three of the neighbouring voxels are solid that block in different directions

We have one solid voxel in each coordinate direction and in each direction we have two potential positions, so there are eight cases. We show the equations for one of them (Figure A.3) and the others can be calculated in the same way.

$$u = \frac{4u_1}{\Delta x^2 \Delta y \Delta z} (x_2 - x)^2 (y_2 - y)(z - z_1) \quad \text{A.20}$$

$$v = \frac{4v_1}{\Delta x \Delta y^2 \Delta z} (x_2 - x)(y_2 - y)^2 (z - z_1) \quad \text{A.21}$$

$$w = \frac{4w_2}{\Delta x \Delta y \Delta z^2} (x_2 - x)(y_2 - y)(z - z_1)^2 \quad \text{A.22}$$

The time of flight increment across the block can be calculated:

$$\Delta \tau_x = \frac{\Delta x^2 \Delta y \Delta z}{4(x_2 - x_p)(y_2 - y_p)(z_p - z_1)u_1} \ln\left(\frac{x_2 - x_p}{\Delta x}\right) \quad \text{A.23}$$

$$\Delta \tau_y = \frac{\Delta x \Delta y^2 \Delta z}{4(x_2 - x_p)(y_2 - y_p)(z_p - z_1)v_1} \ln\left(\frac{y_2 - y_p}{\Delta y}\right) \quad \text{A.24}$$

$$\Delta \tau_z = \frac{\Delta x \Delta y \Delta z^2}{4(x_2 - x_p)(y_2 - y_p)(z_p - z_1)w_2} \ln\left(\frac{\Delta z}{z_p - z_1}\right) \quad \text{A.25}$$

$$\Delta \tau = \min(\Delta \tau_x, \Delta \tau_y, \Delta \tau_z) \quad \text{A.26}$$

And the exit location is:

$$x_e = x_2 - (x_2 - x_p)e^{\frac{-4u_1(x_2 - x_p)(y_2 - y_p)(z_p - z_1)}{\Delta x^2 \Delta y \Delta z} \Delta \tau} \quad \text{A.27}$$

$$y_e = y_2 - (y_2 - y_p)e^{\frac{-4v_1(x_2 - x_p)(y_2 - y_p)(z_p - z_1)}{\Delta x \Delta y^2 \Delta z} \Delta \tau} \quad \text{A.28}$$

$$z_e = z_1 + (z_p - z_1)e^{\frac{4w_1(x_2 - x_p)(y_2 - y_p)(z_p - z_1)}{\Delta x \Delta y \Delta z^2} \Delta \tau} \quad \text{A.29}$$

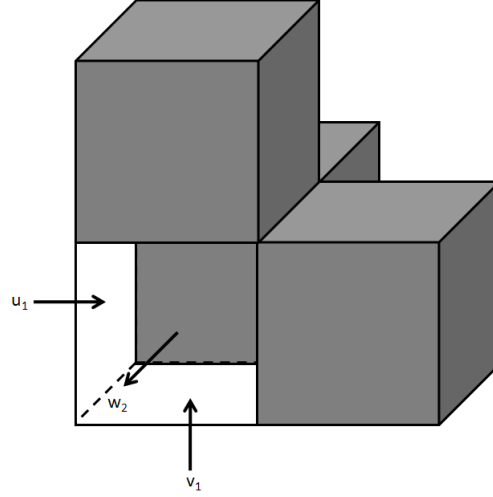


Figure A.3: Three nearest-neighbour solid voxels blocking the three coordinate directions.

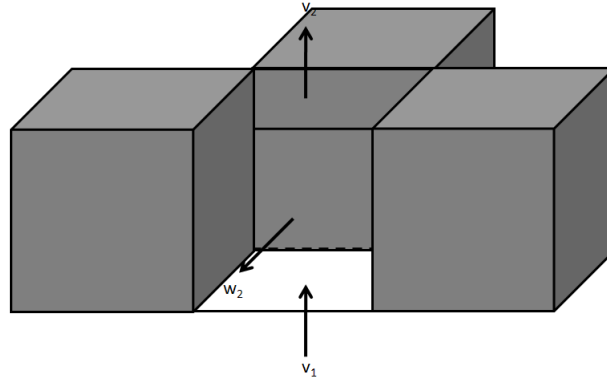


Figure A.4: Three nearest-neighbour solid voxels in where two of them block the same coordinate direction.

Three of the neighbouring voxels are solid and two of them are in the same direction

This condition can happen for twelve cases; we show the equations for the case where two solid voxels have blocked the x -direction (Figure A.4). Therefore, the velocity component in the x -direction will be zero. The velocity distribution is:

$$u = 0 \quad \text{A.30}$$

$$v = \frac{12v_1}{\Delta x^2 \Delta z} (x_2 - x)(x - x_1)(z - z_1) + \frac{12(v_2 - v_1)}{\Delta x^2 \Delta y \Delta z} (x_2 - x)(x - x_1)(z - z_1)(y - y_1) \quad \text{A.31}$$

$$w = \frac{6w_2}{\Delta x^2 \Delta z^2} (x_2 - x)(x - x_1)(z - z_1)^2 \quad \text{A.32}$$

Time of flight increment across the block is:

$$\Delta \tau_y = \frac{\Delta x^2 \Delta z^2}{6w_2(x_2 - x_p)(x_p - x_1)(z_p - z_1)} \left(1 - \left(\frac{v_1 \Delta y + (v_2 - v_1) \Delta y}{v_1 \Delta y + (v_2 - v_1)(y_p - y_1)}\right)^{\frac{-w_2 \Delta y}{2(v_2 - v_1) \Delta z}}\right) \quad \text{A.33}$$

$$\Delta \tau_z = \frac{\Delta x^2 \Delta z^2}{6(x_2 - x_p)(x_p - x_1)w_2} \left(\frac{1}{z_p - z_1} - \frac{1}{\Delta z}\right) \quad \text{A.34}$$

$$\Delta \tau = \min(\Delta \tau_y, \Delta \tau_z) \quad \text{A.35}$$

And the exit coordinations are:

$$x_e = x_p \quad \text{A.36}$$

$$y_e = y_1 - \frac{v_1 \Delta y}{v_2 - v_1} + \left(1 - \frac{6w_2(x_2 - x_p)(x_p - x_1)(z_p - z_1)}{\Delta x^2 \Delta z^2} \Delta \tau\right)^{\frac{-2(v_2 - v_1) \Delta z}{w_2 \Delta y}} \times \left(\frac{v_1 \Delta y}{v_2 - v_1} + (y_p - y_1)\right) \quad \text{A.37}$$

$$z_e = z_1 + \frac{\Delta x^2 \Delta z^2 (z_p - z_1)}{\Delta x^2 \Delta z^2 - 6w_2(x_2 - x_p)(x_p - x_1)(z_p - z_1) \Delta \tau} \quad \text{A.38}$$

Four of the neighbouring voxels are solid

This condition can happen in fifteen cases that can be categorized in two groups: (1) when in two directions we have just one solid voxel and in the third direction there are two solid voxels; and (2) when there is no solid voxel in one of the three coordinate directions.

Four of the neighbouring voxels are solid and three of them are in three different directions

We consider the case where there are two solid voxels in the x-direction and the other two are in the y- and z- directions (Figure A.5). Since the x-direction is blocked from both sides, the velocity component in the x-direction is zero. The equations for the other cases can be obtained similarly.

$$u = 0 \quad \text{A.39}$$

$$v = \frac{12v_1}{\Delta x^2 \Delta y^2 \Delta z} (x_2 - x)(x - x_1)(y_2 - y)^2 (z - z_1) \quad \text{A.40}$$

$$w = \frac{12w_2}{\Delta x^2 \Delta y \Delta z^2} (x_2 - x)(x - x_1)(y_2 - y)(z - z_1)^2 \quad \text{A.41}$$

The time of flight increment is:

$$\Delta \tau_y = \frac{\Delta x^2 \Delta y^2 \Delta z}{12v_1 (y_2 - y_p)(z_p - z_1)(x_2 - x_p)(x_p - x_1)} \ln\left(\frac{y_2 - y_p}{\Delta y}\right) \quad \text{A.42}$$

$$\Delta \tau_z = \frac{\Delta x^2 \Delta z^2 \Delta y}{12w_1 (y_2 - y_p)(z_p - z_1)(x_2 - x_p)(x_p - x_1)} \ln\left(\frac{\Delta z}{z_p - z_1}\right) \quad \text{A.43}$$

$$\Delta \tau = \min(\Delta \tau_y, \Delta \tau_z) \quad \text{A.44}$$

And the exit location is:

$$x_e = x_p \quad \text{A.45}$$

$$y_e = y_2 - (y_2 - y_p)e^{\frac{-12v_1 (x_p - x_1)(x_2 - x_p)(y_2 - y_p)(z_p - z_1)}{\Delta x^2 \Delta y^2 \Delta z} \Delta \tau} \quad \text{A.46}$$

$$z_e = z_1 + (z_p - z_1)e^{\frac{12w_1 (x_p - x_1)(x_2 - x_p)(y_2 - y_p)(z_p - z_1)}{\Delta x^2 \Delta z^2 \Delta y} \Delta \tau} \quad \text{A.47}$$

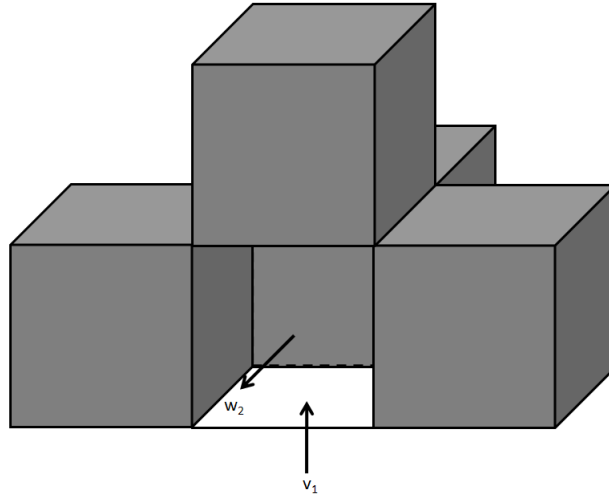


Figure A.5: Four nearest-neighbour solid voxels and there is at least one solid voxel at each coordinate direction.

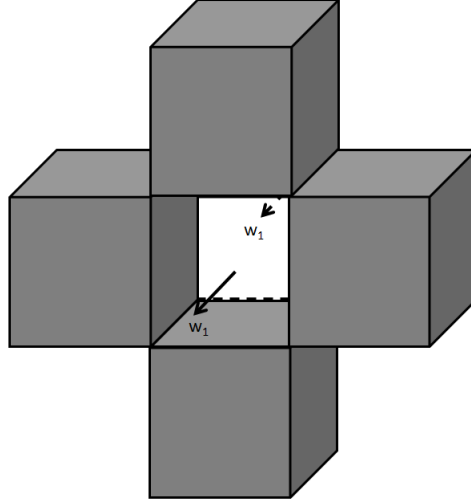


Figure A.6: Four nearest-neighbour solid voxels where there is no solid voxel blocking one of the coordinate directions.

Four of the neighbouring voxels are solid and they block two directions

We present the equations for the case where there is no solid voxel in the z-direction and the velocity components in x- and y-directions are zero (Figure A.6). The formulation for the other cases can be obtained similarly.

$$u = 0 \quad \text{A.48}$$

$$v = 0 \quad \text{A.49}$$

$$w = \frac{36w_1}{\Delta x^2 \Delta y^2} (x_2 - x)(x - x_1)(y_2 - y)(y - y_1) \quad \text{A.50}$$

The time of flight increment across the block is:

$$\Delta \tau = \frac{\Delta x^2 \Delta y^2}{36w_1(x_2 - x_p)(x_p - x_1)(y_2 - y_p)(y_p - y_1)} \quad \text{A.51}$$

The exit location is:

$$x_e = x_p \quad \text{A.52}$$

$$y_e = y_p \quad \text{A.53}$$

$$z_e = z_p + \frac{36w_1}{\Delta x^2 \Delta y^2} (x_2 - x)(x - x_1)(y_2 - y)(y - y_1) \Delta \tau \quad \text{A.54}$$

If five or six faces are solid, the velocity everywhere is zero.