Simulating Dispersion in Porous Media and the Influence of Segmentation on Stagnancy in Carbonates

F. Gray¹, J. Cen¹, S. M. Shah¹, J.P. Crawshaw^{1*} and E.S. Boek^{1,2},

¹ *Qatar Carbonates and Carbon Storage Research Centre (QCCSRC),
Department of Chemical Engineering, South Kensington Campus, Imperial
College London, London SW7 2AZ, United Kingdom.*

² *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge
CB2 1EW, UK*

*j.crawshaw@imperial.ac.uk

Abstract

Understanding the transport of chemical components in porous media is fundamentally important to many reservoir processes such as contaminant transport and reactive flows involved in CO₂ sequestration. Carbonate rocks in particular present difficulties for pore-scale simulations because they contain large amounts of sub-micron porosity. In this work, we introduce a new hybrid simulation model to calculate the hydrodynamic dispersion in pore-scale images of real porous media and use this to elucidate the origins and behaviour of stagnant zones arising in single phase flow simulations using micro-CT images of carbonates. For this purpose a stochastic particle model for simulating the transport of a solute is coupled to a Lattice-Boltzmann algorithm to calculate the flow field. The particle method incorporates second order spatial and temporal resolution to resolve finer features of the domain. We demonstrate how dispersion coefficients can be accurately obtained in capillaries, where corresponding analytical solutions are available, even when these are resolved to just a few lattice units. Then we compute molecular displacement distributions for pore-spaces of varying complexity: a pack of beads; a Bentheimer sandstone; and a Portland carbonate. Our calculated propagator distributions are compared directly with recent experimental PFG-NMR propagator distributions (Scheven *et al.* (2005) and Mitchell *et al.*, (2008)), the latter excluding spin relaxation mechanisms. We observe that the calculated transport propagators can be quantitatively compared with the experimental

distribution, provided that spin relaxations in the experiment are excluded, and good agreement is found for both the sandstone and the carbonate. However, due to the absence of explicit micro-porosity from the carbonate pore space image used for flow field simulations we note that there are fundamental differences in the physical origins of the stagnant zones for micro-porous rocks between simulation and experiment. We show that for a given micro-CT image of a carbonate, small variations in the parameters chosen for the segmentation process lead to different amounts of stagnancy which diffuse away at different rates. Finally, we use a filtering method to show that this is due to the presence of spurious isolated pores which arise from the segmentation process and suggest an approach to overcome this limitation.

Introduction

The hydrodynamic dispersion of solute particles in porous media is of great importance in many scientific and engineering applications (Adler 1992), including ground water pollution, CO₂ sequestration and hydrocarbon recovery. The upscaling of dispersion phenomena from the pore to core scale is complex and a rigorous theoretical description remains an outstanding scientific challenge (Bijeljic and Blunt 2006). Various numerical methods have been proposed to investigate dispersion at the pore scale. Historically, network modelling has been widely used (Bruderer and Bernabé 2001, Bijeljic, Muggeridge *et al.* 2004, Bijeljic and Blunt 2006, Acharya, Van der Zee *et al.* 2007). However, for heterogeneous porous media, such as carbonate rocks, it is very difficult to extract reliable and unique pore networks (Knackstedt, Arns *et al.* 2006). For this reason, direct calculation on three-dimensional pore space images obtained from e.g. micro-CT scanning or Confocal Laser Scanning Microscopy (CLSM) (Shah, Crawshaw *et al.* 2013) has been proposed to avoid the problems associated with network extraction (Ramstad, Idowu *et al.* 2012). Coelho *et al.* (Coelho, Thovert *et al.* 1997) used a finite difference method to solve for the flow and dispersion in unconsolidated bead packs and sandstones. (Maier, Kroll *et al.* 1998) used a hybrid method, consisting of lattice-Boltzmann (LB) simulations to calculate the flow field combined with a random-walk particle-tracking method to simulate dispersion in a sphere pack. They found good agreement with nuclear magnetic resonance (NMR) experiments for both transient and asymptotic dispersion. Kandhai extended this model to include effective diffusion inside porous beads (Kandhai, Hlushkou *et al.* 2002) and found this to lead to

stagnant zones which diffuse out over long time-scales. Recently, Scheven *et al.* (Scheven, Verganelakis *et al.* 2005, Scheven, Harris *et al.* 2007) reported molecular displacement (or propagator) distributions for different rock samples obtained from Pulsed Field Gradient—Nuclear Magnetic Resonance (PFG-NMR) experiments. They observed that the character of the propagator distributions strongly depends on the heterogeneity of the porous medium. Bijeljic *et al.* (Bijeljic, Raeini *et al.* 2013), used a Stokes solver for the flow field and a streamline-based algorithm for solute dispersion which included interpolation of the velocity field at the fluid-solid boundary (Mostaghimi, Bijeljic *et al.* 2012, Nunes, Bijeljic *et al.* 2015), and observed agreement with the experimental NMR propagator results (Scheven, Verganelakis *et al.* 2005). Mitchel (Mitchel *et al.* 2008) improved the analysis of PFG-NMR experiments by correcting for the loss of signal due to spin relaxation and these results have also been compared to propagators calculated from micro-CT images (Bijeljic *et al.* 2011). The extent of agreement between the calculated and measured propagator distributions is surprising for the carbonate rocks, given that a significant fraction of the porosity in such samples is below the resolution of the CT scan (Crawshaw and Boek 2013) and therefore excluded from the simulations. Yang *et al.* (Yang and Boek 2013) developed a new LB algorithm to calculate both the flow field and solute dispersion in pore space images of different heterogeneity. They quantified the degree of heterogeneity and calculated the fraction of solute particles trapped by integrating over the stagnant peak (Yang and Boek 2013). However, it appeared to be difficult to study the diffusive coupling for long time scales in a quantitative fashion. For this reason, we propose here a new hybrid algorithm, using LB simulations to solve the flow field coupled with a streamline-based algorithm for solute dispersion. In addition, we propose a second order velocity-field interpolation scheme for particle advection, which is more accurately able to compute the dispersion of solute in finer features of the pore-space. We observe good agreement with the experimental propagator distributions (Scheven, Verganelakis *et al.* 2005, Mitchell, Graf von der Schulenburg *et al.* 2008).

Although several of the aforementioned studies have reported quantitative matches with NMR data in the case of the Portland carbonate, the origins of the stagnant fraction of solute in the simulations of flow in this micro-porous rock deserve further consideration. We investigate here the origins of the stagnant peak in transport simulations based on micro-CT

data, since the limited resolution of these images cannot have accurately represented micro-porous regions, while the fluid in these regions is included in the NMR data after the correction for spin relaxation effects noted above. Necessarily for such investigations, a segmentation procedure must convert grey-scale microporous regions of the micro-CT image into discrete pore or grain regions. This suggests that unphysical isolated pores could have arisen from this procedure and may cause an artificial stagnancy. To determine whether this hypothesis is sound, we obtained several segmented images of a Portland carbonate sample from the same scan by varying the segmentation parameters, and we demonstrate that this changes the magnitude and transient behaviour of the stagnant peak. Finally, we apply a filtering algorithm to remove isolated pores from the segmented images which enables us to differentiate between a) small isolated pores containing permanently trapped solute and b) regions of poorly connected structure whose solute would be expected to diffuse into flowing paths over long time-scales.

Method

The simulation is performed on a 3-dimensional Cartesian lattice with nodes marked as either fluid or solid describing the geometry. Fluid nodes are associated with a flow vector which is the solution to the incompressible Stokes flow at the centre of the grid element. This flow-field is computed using the single-phase multiple-relaxation-time (MRT) lattice Boltzmann model (Gray and Boek 2016).

The stochastic tracer method consists of transporting particles through the domain in two steps. First, a forward integration along the flow vectors describes the advection part, followed by a random-walk step to simulate diffusion by Brownian motion. To derive the second order advection scheme, we interpolate a second order velocity field around each node's flow vector $\mathbf{V}_0$ using the 6 neighbouring vectors $\mathbf{V}_{\pm x, y, z}$ (figure 1). Generally, these polynomials are written as

$$v^i(x, y, z) = V_0^i(a_x^i x^2 + b_x^i x + c_x^i)(a_y^i y^2 + b_y^i y + c_y^i)(a_z^i z^2 + b_z^i z + c_z^i) \quad (1)$$

where $i = x, y, z$ is the component of the flow vector. The position x, y, z is relative to the centre of the node and the grid spacing is such that the distance between the centres of

120 each neighbour is unity. The coefficients a, b and c are to be determined in terms of the
 121 neighbouring vectors.

122 We may then impose boundary conditions to calculate the 27 advection coefficients for
 123 each node. Two of these conditions are

$$v^i(0,0,0) = V_0^i \quad (2)$$

$$v^i(\pm 1, y, z) = V_{\pm x}^i \quad (3)$$

124 These conditions imply that all the c coefficients are equal to 1, and thus we only need store
 125 18 coefficients for each fluid node.

126 Expressions for the a and b coefficients for a case without adjoining solid nodes can then be
 127 obtained for each component i in terms of the neighbouring vectors. For the x coefficients

$$a_x^i = \frac{V_x^i + V_{-x}^i}{2V_0} - 1 \quad (4)$$

$$b_x^i = \frac{V_x^i - V_{-x}^i}{2V_0} \quad (5)$$

128 When a neighbouring node is solid, we impose a 0 velocity vector at the boundary, in line
 129 with the half-way bounce-back lattice Boltzmann scheme. For a solid at the $+x$ node, the
 130 condition is

$$v^i\left(\frac{1}{2}, y, z\right) = 0 \quad (6)$$

131 Then we obtain expressions for the coefficients with different combinations of adjoining
 132 solids. For the x coefficients, with a single solid node at $\pm x$

$$a_x^i = \frac{2}{3} \frac{V_{\pm x}^i}{V_0} - 2 \quad (7)$$

$$b_x^i = \pm \frac{1}{3} \frac{V_{\pm x}^i}{V_0} \pm 1 \quad (8)$$

133 For solids at both $+x$ and $-x$

$$a_x^i = 4 ; \quad b_x^i = 0 \quad (9)$$

134 These expressions are directly extended to the y and z coefficients.

135 In poorly resolved features of a geometry represented with just a few fluid nodes,
 136 calculating the average velocity by naively averaging the flow vectors can introduce
 137 systematic error. It should be clarified that the flow vectors from the lattice-Boltzmann
 138 algorithm represent the solution to the Navier-Stokes equation at the centre of the fluid
 139 node rather than the average flow velocity through the node. Therefore, we can extract a
 140 better estimate of the average flow velocity by integrating the 2nd order velocity field over
 141 the node volume.

$$v_{av}^i = \iiint v^i(x, y, z) d\mathbf{r} = V_0^i \left(1 + \frac{1}{12} a_x^i\right) \left(1 + \frac{1}{12} a_y^i\right) \left(1 + \frac{1}{12} a_z^i\right) \quad (10)$$

142 To transport a particle along the flow-field, we carry out a standard second order accurate
 143 predictor-corrector time-step in a similar way to other stochastic approaches (Szymczak and
 144 Ladd 2003)

$$\mathbf{x}_p(t + dt) = \mathbf{x}(t) + \mathbf{v}(\mathbf{x}(t))dt \quad (11)$$

$$\mathbf{x}(t + dt) = \mathbf{x}(t) + \frac{1}{2} [\mathbf{v}(\mathbf{x}(t)) + \mathbf{v}(\mathbf{x}_p)]dt \quad (12)$$

145 where $\mathbf{x}$ is the position of the particle at time t , $\mathbf{x}_p$ is the ‘predicted’ position of the particle
 146 at time $t + dt$ with time-step dt and $\mathbf{v}$ is the flow vector calculated from the polynomial
 147 function of position in equation (1).

148 Diffusion is simulated by translating the particle over a random-walk vector. The expected
 149 distance a diffusing particle will have travelled in 3D random walk given a diffusion
 150 coefficient D_m and time-step dt is $L = \sqrt{6D_m dt}$. We generate a spherically isotropic unit
 151 vector by taking 2 uniform random variates r_1 and r_2 on $[0,1]$ and apply the following
 152 transformation to obtain polar coordinates

$$\varphi = 2\pi r_1 \quad (13)$$

$$\theta = \cos^{-1}(1 - 2r_2) \quad (14)$$

These transformations are derived in appendix 1. Finally, we apply the standard transformation to Cartesian coordinates to obtain a random-walk diffusion vector (Mostaghimi, Bijeljic et al. 2012)

$$\begin{bmatrix} dx \\ dy \\ dz \end{bmatrix} = L \begin{bmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{bmatrix} \quad (15)$$

Validation

We compute the longitudinal dispersion coefficient of a solute undergoing advection and diffusion in lowly resolved capillaries of three different cross-sections: parallel plates with infinite width, a square channel and a circular capillary. Each has different merits as a test case. The parallel-plates geometry is represented exactly by the Cartesian grid and the Poiseuille flow field is precisely represented to second order. For the square channel, the geometry is again exactly represented although the analytical flow distribution is no longer a finite-order polynomial but given by a convergent series. Finally, the circular capillary is not smoothly represented on the Cartesian lattice (figure 2).

The longitudinal dispersion coefficient D , often called dispersivity, is defined as half the time-rate of change in the variance, σ^2 , of a solute distribution: $D = \frac{1}{2} \frac{d}{dt} \sigma^2$. It can be shown that for any channel geometry the asymptotic (long time) dispersivity is given by (Chatwin and Sullivan 1982, Dutta and Leighton 2001):

$$\frac{D_m(D - D_m)}{v_{av}^2} = ka^2 \quad (16)$$

where v_{av} is the average flow velocity, D_m the molecular diffusivity and a is the radius or half the height of the capillary. The constant k is a dimensionless parameter, which is solely dependent on the cross-sectional geometry of the capillary. For a circular capillary $k = \frac{1}{48}$ (Aris 1956, Deen 1998), for parallel-plates with infinite width $k = \frac{2}{105}$ (Deen 1998, Dutta and Leighton 2001), and for a square capillary $k \approx \frac{173}{5250}$ (Doshi et al. 1978, Chatwin and Sullivan

1982, Dutta and Leighton 2001). The exact value of k for the square capillary can be computed using the equations in the paper by Doshi et al. 1978 or Chatwin & Sullivan 1982.

We generate geometries of heights/diameters varying from 1 to 25 lattice units (l.u.) for the three cases of parallel plates ($2a$ is the plate separation), square cross-section capillary ($2a$ is the height and width), and circular cross-section capillary ($2a$ is the diameter). We compute the flow-field inside each geometry with lattice Boltzmann simulation and using a uniform body-force. The dispersion coefficient is computed by initialising 10^6 point particles at the flow distance coordinate $x = 0$ uniformly over the cross-section and running the simulation until the dispersion coefficient reaches an asymptotic value. The time-step is chosen such that a particle's maximum displacement is 10% the characteristic length of the medium, i.e. $2a$ in our simulations which corresponds to 0.5 lattice units.

Figures 3 and 4 show the simulation results plotted against the analytical expressions and the error from the analytical values respectively for each cross-section and resolution. The error values themselves will have a contribution from the statistical fluctuations of the particle distribution during sampling the asymptotic dispersion coefficient of the order 1%. For the case of parallel plates, we find no systematic deviation from the analytical result, as expected. For the square capillary resolved to a 1 and 2 l.u. dimension, the error stems from fitting a single second order curve to the true infinite order flow-field function. This error decays quickly as the resolution increases and is negligible for resolutions above 5 l.u. For the circular case, the diameter is not well defined in the small blocky geometries and so we have extracted an effective value from the true cross-sectional area A such that $2a = \sqrt{4A/\pi}$. The deviation from the analytical result is most pronounced in this case, yet generally below 10% above a 5 l.u. diameter and gradually decreasing over the larger dimensions.

Propagator Distributions

We now use the model to compute molecular displacement distributions inside images of real pore-spaces. Three cases are examined, of varying complexity: a pack of beads exhibiting high regularity and connectivity; a Bentheimer sandstone with a non-homogeneous but well-connected structure; and a Portland carbonate with a

heterogeneous pore-space. Samples were obtained from micro-CT imaging, followed by segmentation on a Cartesian lattice of solid and pore voxels (Shah, Gray et al. 2015). In highly micro-porous carbonate rocks, this segmentation procedure can be subjective and its effects are considered in this work.

The three porous media chosen allow us to compare the results of simulation with the experimental NMR data of Scheven *et al.* (Scheven, Verganelakis *et al.* 2005) for the three samples, and the spin loss-corrected data of Mitchell *et al.* (Mitchell, Graf von der Schulenburg *et al.* 2008) for the Bentheimer and Portland samples. Representative samples are chosen and given in table 1 (Shah, Gray et al. 2015)

Sample	Dimension (mm)	Image Size (Voxels)	Voxel Size (μm)	Porosity
Beadpack	0.625	250^3	2.50	37.9%
Bentheimer	1.810	400^3	4.52	20.9%
Portland	1.810	400^3	4.52	13.7%

Table 1 – Samples used in the simulation

The beadpack consists of spheres of $86 \pm 10\mu\text{m}$, which we have found to give the best quantitative fit to the NMR data, in which beads of $100 \pm 20\mu\text{m}$ are reportedly used. We have applied the mirroring concept to these samples to guarantee flow and transport continuity over the boundaries (Yang and Boek 2013). In this approach, the samples are reflected about the $x = 0$ axis, where x is the flow direction. Thus the computational domain size is now doubled, for example, $500 \times 250 \times 250$ lattice units for the beadpack.

The calculations are performed by initialising a set of tracer particles uniformly throughout each medium and computing the displacement of each particle from its initial position. A displacement density function can then be obtained at different sample times, or equivalently, mean Darcy displacements $\bar{d} = v\Delta t$ where v is the mean Darcy velocity in the pore-space and Δt is the sample time. The two experimental papers obtain data in different ways: Scheven *et al.* employ a constant flow rate, sampling the displacement distribution at different times whereas Mitchell *et al.* sample the distribution at a fixed time of $\Delta t = 1\text{s}$ for a set of different flow rates. The diffusion coefficient of water at ambient temperature is used: $D_m = 2.0 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, and the timescale is derived by matching the experimental mean Darcy flow velocities or flow rates.

The distributions are shown for each medium at 3 different sample distances in figures 5, 6, and 7 respectively, overlaid with the corresponding NMR data from Scheven *et al.* (Scheven, Verganelakis *et al.* 2005) for the beadpack and Mitchell *et al.* (Mitchell, Graf von der Schulenburg *et al.* 2008) for the sandstone and carbonate. Scheven *et al.* also computed propagators for Bentheimer and Portland samples which include the influence of spin-relaxation. This is demonstrated by comparing the time-dependent mean particle displacements in the experiment to calculations performed by imposing the same mean Darcy flow velocity in the samples. Figure 8 shows the mean displacement of the solute particles, $\langle x \rangle$ relative to the mean Darcy displacement for each medium, and may be compared with Scheven's experimental data. Our calculations imply that the mean particle displacement is very close to the Darcy displacement: $\frac{\langle x \rangle}{d} \approx 1$ for all cases whereas the experimental ratios converge to 1.03 (beadpack), 1.2 (Bentheimer) and 1.3 (Portland). In later publications, the authors of the experimental NMR work considered this to be due to loss of spins, particularly close to solid grain boundaries and is thus most pronounced in the micro-porous carbonate (Scheven, Seland *et al.* 2004, Mitchell, Graf von der Schulenburg *et al.* 2008, Hussain, Mitchell *et al.* 2013). To solve this problem, Mitchell *et al.* (2008) have obtained flow propagators excluding the influence of NMR relaxation times T_1 and T_2 . These spin relaxation mechanisms usually give a loss of signal that depends on the displacement of the flowing spins, however the exclusion of T_1 and T_2 effects allowed acquisition of quantitative propagator data (Mitchell *et al.* (2008)). For this reason, we directly compare in figure 6 our calculated propagators for the Bentheimer sandstone and micro-porous Portland carbonate, with the recent experimental propagator data obtained by Mitchell *et al.* (2008). We note that to obtain different displacements in this set of NMR experiments the flow rate was changed and the time interval for acquisition kept constant. This resulted in a range of Peclet numbers, in contrast to the simulations of the beadpack in which the flow rate and therefore the Peclet number was kept constant.

With the adjusted mean, the beadpack distributions agree well with the experimental data which converges to a Gaussian distribution. Two statistical measures are useful for quantifying the convergence behaviour: the Skewness and Kurtosis Excess, defined as

$$\gamma = \frac{\mu_3}{\mu_2^{3/2}} \quad \text{and} \quad \kappa = \frac{\mu_4}{\mu_2^2} - 3 \quad (17)$$

where μ_i is the i th central moment of the distribution, such that μ_2 is recognised as the variance. The skewness measures the symmetry of a distribution about the mean and the kurtosis excess is a measure of peakedness: 0 for a Gaussian distribution; <0 for a more sharply peaked distribution; and >0 for a flatter distribution. These are shown in figure 9 for the beadpack which are seen to be converging towards 0, implying that the beadpack distribution tends towards a Gaussian in the long-time limit.

The time-dependent skewness of the Bentheimer and Portland distributions are also given in figure 10 using the experimental parameters of Scheven *et al.* Since we can identify two peaks in the propagator distributions (figures 6 and 7) of these samples: a stagnant component about zero displacement and a moving peak around the mean displacement, the kurtosis excess is not meaningful in these cases. The Bentheimer skewness tends towards 0 on a longer timescale than the beadpack and in accordance with the observation that the stagnant peak in the propagator distribution decreases with time as solute in less-well-connected areas of the pore structure diffuse into flowing regions. The carbonate distributions however are not seen to become symmetric over the time-scale examined.

This observation is further quantified by measuring the fraction of solute which is contained in the stagnant peak of the propagator distributions over time. We adopted the following measure of this fraction, $S(t)$

$$S(t) = 2 \int_{-\infty}^0 P(x', t) dx' \quad (18)$$

where x' is the scaled unit x/d and we are assuming that the stagnant peak is symmetric about zero displacement. The stagnant fractions against time for the three samples are given in figure 11 using the experimental parameters of Scheven *et al.* The beadpack stagnant fraction disappears the most quickly, but is not immediately 0. This can be seen in the early propagator distribution figure 5a as the slightly pronounced bump at the zero displacement and might reasonably be explained as the small amount of solute in the immediate vicinity behind beads having to diffuse a short way into a flowing streamline. The stagnant component in the sandstone appears to decay to almost zero on the simulation time-scale, but takes considerably longer than the beadpack, reflecting the increased complexity of the sandstone structure. Nonetheless, this implies that the pore structure is

completely connected. The same conclusion cannot be drawn for the carbonate, whose stagnant fraction asymptotically persists as around 20% of the normalised distribution. This suggests that a similar fraction of the pore-space has no connection to a flowing path through the domain. Such an effect may be an artefact of the image segmentation process, rather than a physical one. We also note that the stagnant fractions for the beadpack and sandstone samples match the NMR data of Scheven *et al.* very closely, suggesting that spurious spin relaxation mechanisms are at least uniform over the displacement distributions. The stagnant peak is greatly over-predicted in the carbonate sample which is consistent with experimental spin losses being most pronounced in the low-flow micro-porous regions.

Figure 12 gives the stagnant fractions computed for the Bentheimer and Portland samples for the Peclet numbers (flow rates) alongside the loss-corrected NMR data of Mitchell *et al.* (2008). The trapped fraction in the Bentheimer is again seen to reach near-zero as the flow rate (flow distance at $t = 1s$) increases with Peclet number. The carbonate once again apparently reaches an asymptotic trapped fraction of 20% – 25%. Agreement with the experimental NMR data is relatively good but differences in the Bentheimer propagator distributions (figure 6a,b and c) suggests some uncertainty in matching the flow rates or diffusion coefficients with experiment. Nonetheless, the stagnant peak of the carbonate is much more closely matched as would be expected from excluding spin-loss effects concentrated in the micro-porous zones.

Despite the quantitative agreement, there are important differences between the simulations and experiment for the Portland carbonate which need to be pointed out. Chiefly, we note that simulation is performed on a segmented version of the pore-space. As such, any transport through micro-porous zones in the experiment is not incorporated into the calculation, but binarized into either fully permeable porous zones, or impermeable solid phase. This process is inherently subjective and we now demonstrate this systematically, returning to the time-dependant calculation of stagnant peaks which helps to elucidate the connectivity of the pore-space.

The segmentation process takes a continuum-valued (grey-scale) image from a micro-CT scan and converts this to a discrete set of phases. In general the principle for all

segmentation methods is based on separating the phases by detecting similarities and discontinuities in intensity grey value and partitioning the phases accordingly with the help of different edge detection algorithms and labelling similar regions of each phase. In this study, a non-local means filter followed by a seeded watershed algorithm was used to segment the images into 2 phases: pore and grain (Jones, Arns et al. 2009, Andrew, Bijeljic et al. 2013, Shah, Crawshaw et al. 2013). A seeded watershed algorithm relies not only on the intensity of an image but also on the gradient magnitude of an image with the seed generated by the use of 2D histograms. The 2D Histogram Segmentation module within the Avizo Fire 8.0 program has two main processes: (1) initialization of voxels into two or more phases using the concept of the region growing method based on 3D voxel intensity and gradient magnitude and (2) expansion of initially assigned voxels in step 1 so that all the voxels are labelled using the watershed transform. For highly micro-porous samples, the histogram data in step 1 is not sharply defined, so that the researcher's choice may play a role in the result.

To highlight the subjectivity of this process further, we took the same initial grey-scale image of Portland carbonate and performed four new segmentations leading to a range of porosities 9.0%, 12.9%, 15.0% and 17.9%. Figure 13 shows a slice of the original image along with the equivalent segmented result. Also highlighted is an example of a clearly micro-porous grey-scale zone segmented into pore in the 12.9% porosity sample, but as a solid zone in the 9.0% sample.

The flow rate used was that of Scheven *et al.* (2005). The stagnant fraction was computed again by equation 18 and the result shown against time in figure 14. The discrepancy between the different samples is immediately obvious, a factor of more than 2 difference between the lowest and highest porosities. The lowest porosity sample had the highest fraction of stagnant solute over the simulation, with a gradually decreasing trapped fraction with increasing porosity. The physical interpretation is less clear. We might expect that in the lowest porosity sample, only fully porous areas of the original image have been segmented into pore-space and a few of the most porous micro-pore zones. As the porosity of the segmented images increases, more of the micro-porous (grey-scale) areas are included. These pores of micro-porous origin would be expected to have the highest likelihood of being isolated from flowing zones, and thus comprise permanently trapped

solute. This then suggests that stagnant zone of the 9.0% porous sample should decay most fully in the long-time limit and the higher porosity images should reach asymptotic values increasing with porosity.

Whether such behaviour is observed in reality is beyond the time-scale of our simulations. However it is possible to illuminate this issue further. As a final analysis, we applied a filtering algorithm to each image which removed isolated pores i.e. any pore not percolating to a flowing face through at least one of its 6 Cartesian neighbours. A comparison of stagnant fractions between filtered and unfiltered images is given in figure 15. The order of the curves is maintained: the 9.0% sample most stagnant and the 17.9% sample the least so. However, where the curves for the 3 highest porosity samples are consistently lower in the filtered image (consistent with discounting the permanently trapped solute), the 9.0% porous sample maintains roughly the same profile in both filtered and unfiltered simulations. This confirms that most or all of the stagnant solute in this image is not permanently trapped, but should diffuse out of slow regions after a longer time. On the other hand, the higher porosity segmentations do contain isolated stagnant zones so that the curves in the unfiltered cases should eventually reach an asymptotic, non-zero value. Finally, the slower decay of the 9.0% porous sample indicates that the flowing pore-space is more constricted, becoming less so with increasing porosity.

Conclusion

We detailed a stochastic transport simulation method able to resolve the velocity field smoothly in fine areas of a simulation domain. This was compared with the analytical dispersion results in capillaries and shown to be accurate even with very lowly resolved channels.

Using this method, it was possible to match transport propagators to corresponding NMR experimental data quantitatively for a beadpack and sandstone. For the micro-porous Portland carbonate sample, we compared our calculated propagator distributions directly with recent experimental propagator distributions (Mitchell *et al.*, (2008)). These measurements excluded spin relaxation mechanisms associated with NMR relaxation times T_1 and T_2 , thus allowing acquisition of quantitative propagator data (Mitchell *et al.* (2008)). Indeed, this comparison shows that the calculated transport propagators can be semi-

quantitatively compared with the experimental distribution, provided that spin relaxations in the experiment are excluded, but note that the experiment and simulations are not entirely physically consistent because stagnant zones arising from micro-pores are not included in the simulation, but instead stem from badly-connected or isolated macro-pores which can depend on the segmentation procedure.

For such geometries whose transport behaviour is strongly influenced by micro-porous zones, models which incorporate continuum porosity and permeability grid cells are more appropriate. If effective dispersion coefficients can be assigned to micro-porous areas, combined with a probabilistic entry/exit scheme for particles crossing from porous to micro-porous zones (see for example the model used by Kandhai (Kandhai 2002)), the transport behaviours can be more consistently predicted, avoiding subjective segmentation procedures.

Acknowledgments. We gratefully acknowledge funding from the Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), provided jointly by Qatar Petroleum, Shell, and Qatar Science and Technology Park. Also we gratefully acknowledge useful discussions with U. Scheven and M. Blunt.

Figures

Fig 1. Centre node velocity vector $\mathbf{V}_0$ and its 6 nearest neighbours

Fig 2. Capillaries of differing cross-section: parallel plates, square channel and circular cross-section of height (diameter) 20 lattice units. Velocity profiles range from fastest zones in red to slowest in blue.

Fig 3. The value of ka^2 computed for capillaries of the given cross-sections compared to the analytical solution.

Fig 4. The percentage error in the calculation relative to the exact expression. These values themselves are subject to an error of $\pm 1\%$ because of the statistical fluctuation of the particle distribution

Fig 5a, b, c. Propagator distribution in Beadpack at different sample times compared to the NMR results of *Scheven et al.* (2005) (dashed lines).

Fig 6a, b, c. Propagator distribution in Bentheimer sandstone at the same sample time ($t = 1s$) with increasing flow rates and Peclet numbers: a) $Pe = 5$; b) $Pe = 64$; c) $Pe = 81$. Calculated distributions are indicated with a blue line, in comparison with the propagator data obtained by Mitchell *et al.* (2008), indicated by a black dashed line.

Fig 7a, b, c. Propagator distribution in Portland carbonate at the same sample time ($t = 1\text{s}$) with increasing flow rates and Peclet numbers: a) $Pe = 7.2$; b) $Pe = 36$; c) $Pe = 116$. Calculated distributions are indicated with a blue line, in comparison with the propagator data obtained by Mitchell *et al.* (2008), indicated by a black dashed line. Isolated pores are present in the calculations, which add to the stagnant peak. The segmented image porosity is 13.5%.

Fig 8. Computed mean particle displacement relative to mean Darcy displacement. Parameters match the experimental values used by Scheven *et al.*: constant mean Darcy flow rates of $910\mu\text{ms}^{-1}$ (beadpack), $1030\mu\text{ms}^{-1}$ (Bentheimer) and $1260\mu\text{ms}^{-1}$ (Portland) sampled over time.

Fig 9. Kurtosis Excess and Skewness of propagators computed for the beadpack propagator distribution over time with a flow rate of $910\mu\text{ms}^{-1}$.

Fig 10. Skewness computed for propagators of Bentheimer sandstone and Portland carbonate with parameters used by Scheven *et al.*: mean Darcy velocities of $1030\mu\text{ms}^{-1}$ (Bentheimer) and $1260\mu\text{ms}^{-1}$ (Portland) sampled over time.

Fig 11. Fraction of solute stagnant over time computed for the three samples using the experimental parameters and against the NMR data of Scheven *et al.*

Fig 12. Fraction of solute stagnant over time computed for the Bentheimer and Portland samples against Peclet number using the parameters and against the NMR data of Mitchell *et al.*

Figure 13. Two-dimensional cross-section of three dimensional micro-CT image of Portland carbonate. (a) Original image. (b) Segmented porosity – 9 %. (c) Segmented porosity – 12 %. (d) Segmented porosity – 15 %. (e) Segmented porosity – 18 %. Circled in a), b), and c) – a microporous region segmented into macro-pore as the segmented porosity is increased from 9% to 12%.

Fig 14. Fraction of solute stagnant over time for different segmentations of Portland carbonate, labelled by their porosity.

Fig 15. Fraction of solute stagnant for Portland carbonate overlaid with data from filtered images (isolated pores removed) and labelled by the unfiltered image porosity.

References

- Acharya, R., et al. (2007). "Approaches for modeling longitudinal dispersion in pore-networks." Advances in Water Resources **30**(2): 261-272.
- Adler, P. M. (1992). Porous media: geometry and transports, Butterworth-Heinemann.
- Andrew, M., et al. (2013). "Pore - scale imaging of geological carbon dioxide storage under in situ conditions." Geophysical Research Letters **40**(15): 3915-3918.
- Bijeljic, B. and M. J. Blunt (2006). "Pore-scale modeling and continuous time random walk analysis of dispersion in porous media." Water Resources Research **42**(1): n/a-n/a.
- Bijeljic, B., et al. (2004). "Pore - scale modeling of longitudinal dispersion." Water Resources Research **40**(11).
- Bijeljic, B., et al. (2013). "Predictions of non-Fickian solute transport in different classes of porous media using direct simulation on pore-scale images." Physical Review E **87**(1): 013011.
- Bruderer, C. and Y. Bernabé (2001). "Network modeling of dispersion: Transition from Taylor dispersion in homogeneous networks to mechanical dispersion in very heterogeneous ones." Water Resources Research **37**(4): 897-908.
- Coelho, D., et al. (1997). "Geometrical and transport properties of random packings of spheres and aspherical particles." Physical Review E **55**(2): 1959.

485
486 Gray, F. and E. Boek (2016). "Enhancing Computational Precision for Lattice Boltzmann Schemes in
487 Porous Media Flows." Computation **4**(1): 11.

488
489 Hussain, R., et al. (2013). "Monitoring water transport in sandstone using flow propagators: A
490 quantitative comparison of nuclear magnetic resonance measurement with lattice Boltzmann and
491 pore network simulations." Advances in Water Resources **60**: 64-74.

492
493 Jones, A. C., et al. (2009). "The correlation of pore morphology, interconnectivity and physical
494 properties of 3D ceramic scaffolds with bone ingrowth." Biomaterials **30**(7): 1440-1451.

495
496 Kandhai, D. (2002). "Numerical simulation and measurement of liquid hold-up in biporous media
497 containing discrete stagnant zones." Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences **360**(1792): 521-534.

498
499
500 Kandhai, D., et al. (2002). "Influence of Stagnant Zones on Transient and Asymptotic Dispersion in
501 Macroscopically Homogeneous Porous Media." Physical review letters **88**(23).

502
503 Knackstedt, M., et al. (2006). "3D imaging and flow characterization of the pore space of carbonate
504 core samples."

505
506 Maier, R. S., et al. (1998). "Simulation of flow through bead packs using the lattice Boltzmann
507 method." Physics of Fluids (1994-present) **10**(1): 60-74.

508
509 Mitchell, J., et al. (2008). "Determining NMR flow propagator moments in porous rocks without the
510 influence of relaxation." Journal of Magnetic Resonance **193**(2): 218-225.

511
512 Mostaghimi, P., et al. (2012). "Simulation of flow and dispersion on pore-space images." SPE Journal
513 **17**(4): 1131-1141.

514
515 Nunes, J. P., et al. (2015). "Time-of-flight distributions and breakthrough curves in heterogeneous
516 porous media using a pore-scale streamline tracing algorithm." Transport in Porous Media **109**(2):
517 317-336.

518
519 Ramstad, T., et al. (2012). "Relative permeability calculations from two-phase flow simulations
520 directly on digital images of porous rocks." Transport in Porous Media **94**(2): 487-504.

521
522 Scheven, U., et al. (2007). "Intrinsic dispersivity of randomly packed monodisperse spheres." Physical review letters **99**(5): 054502.

523
524
525 Scheven, U., et al. (2004). "NMR propagator measurements on flow through a random pack of
526 porous glass beads and how they are affected by dispersion, relaxation, and internal field
527 inhomogeneities." Physical Review E **69**(2): 021201.

Scheven, U., et al. (2005). "Quantitative nuclear magnetic resonance measurements of preasymptotic dispersion in flow through porous media." Physics of Fluids **17**(11): 7107.

Shah, S., et al. (2015). "Micro-computed tomography pore-scale study of flow in porous media: Effect of voxel resolution." Advances in Water Resources.

Shah, S. M. K., et al. (2013). Predicting Porosity and Permeability of Carbonate Rocks From Core-Scale to Pore-Scale Using Medical CT Confocal Laser Scanning Microscopy and Micro CT. SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers.

Szymczak, P. and A. Ladd (2003). "Boundary conditions for stochastic solutions of the convection-diffusion equation." Physical Review E **68**(3): 036704.

Yang, J. and E. S. Boek (2013). Quantitative determination of molecular propagator distributions for solute transport in homogeneous and heterogeneous porous media using lattice Boltzmann simulations. Unpublished.

Appendix 1

We have the area of a small surface element, dS on a sphere in terms of the radial distance r , azimuthal angle θ on the range $[0, \pi]$ and the polar angle φ on the range $[0, 2\pi]$

$$dS = r^2 \sin\theta d\theta d\varphi \quad A1.1$$

A random isotropic point on the spherical surface has the following probability of being in the infinitesimal ranges $[\theta, \theta + d\theta]$ and $[\varphi, \varphi + d\varphi]$

$$P(\theta, \varphi) d\theta d\varphi = \frac{dS}{4\pi r^2} = \frac{1}{4\pi} \sin\theta d\theta d\varphi \quad A1.2$$

We require the probability to be the same everywhere and therefore we will equate the cumulative probability for the respective variables with those of uniform variates. The cumulative probability distribution is thus

$$P_c(\theta, \varphi) = \int_0^\theta d\theta \int_0^\varphi d\varphi \quad P(\theta, \varphi) = \frac{1}{4\pi} (1 - \cos\theta) \varphi \quad A1.3$$

The complete cumulative probability distributions for the variables φ and θ are therefore respectively

$$P_c(\pi, \varphi) = \frac{1}{2\pi} \varphi \quad A1.4$$

$$P_c(\theta, 2\pi) = \frac{1}{2} (1 - \cos\theta) \quad A1.5$$

556 For a random variate r_i , uniformly distributed over the interval $[0, 1]$, we have the probability of
557 being in the range $[r_i, r_i + dr_i]$ and the cumulative probability respectively

$$P(r_i)dr_i = dr_i \quad \text{A1.6}$$

$$P_c(r_i) = r_i \quad \text{A1.7}$$

558 Finally, taking two uniform random variates r_1 and r_2 , we equate these with the cumulative
559 probability distributions for φ and θ respectively to obtain expressions for random spherical
560 coordinates in terms of uniform distributions

$$\varphi = 2\pi r_1 \quad \text{A1.8}$$

$$\theta = \cos^{-1}(1 - 2r_2) \quad \text{A1.9}$$

561