Tortuosity of unsaturated porous fractal materials

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Abstract

The tortuosity of a capillary-condensed film of inviscid fluid adsorbed onto fractal substrates as a function of the filling fraction of the fluid has been calculated numerically. This acts as a way of probing the multi-scale structure of the objects. It is found that the variation of tortuosity $\alpha$ with filling fraction $\phi$ is found to follow a power law of the form $\alpha \sim \phi^{-\epsilon}$ for both deterministic and stochastic fractals. These numerically calculated exponents are compared to exponents obtained from a phenomenological scaling and good agreement is found, particularly for the stochastic fractals.

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1. INTRODUCTION

There has been considerable interest recently in the unusual transport properties of porous fractal materials. Understanding the correlation between these properties and the material’s microstructure is crucial for their use to become widespread. Examples of man-made porous fractal materials include aerogel [1] and metal foams [2], whilst naturally occurring examples include fracture surfaces [3] and the lungs [4]. In all these cases the multi-scale structure has a significant impact on important properties. For example, the permeability of a fracture, which is used to determine macroscopic flow rates through porous materials, is substantially increased if the fracture interface has fractal characteristics [5]. Moreover, multiscale materials can possess remarkable transport properties (thermal conductivity and permeability for example) when compared to more conventional materials. Aerogel for instance, is 39 times more insulating than the best fibreglass, yet a thousand times less dense [6]. The characterisation of porous materials and their transport properties has historically been limited to the measurement of macroscopic parameters, which tells one little about the mesoscopic structure of these materials. There has been much progress [7, 8] in using micro-tomography images to generate 3-D networks from which flow properties can be predicted. However it is not always easy to draw a relationship between observable transport properties and simple geometrical quantities. Furthermore, despite the advances mentioned, predictions of these properties is still largely based on empirical relationships based on observable characteristics of the geometry, such as porosity [9].

Aerogel is of particular interest in this work. An experimental technique has recently been described [10], which measures the tortuosity of various samples of aerogel as a function of the volume filling fraction $\phi$ of an adsorbed superfluid $^4$He film on the surface of the aerogel. The main idea of this technique was to use tortuosity as a way of characterising the inner structure of fractal materials at different length scales. Tortuosity quantifies the tortuous or twisted nature that a fluid would have to take to pass through the porous material and is defined here as a dimensionless quantity which quantifies the added mass effect caused by fluid flowing around an obstruction [11], $\alpha = \frac{\rho_*}{\rho_f}$, where $\rho_*$ is the effective density and $\rho_f$ is the bulk fluid density. As will be seen later, tortuosity has a simple physical interpretation of the ratio of the kinetic energies of an unobstructed flow to the actual tortuous flow through the porous medium.
When the fractal is saturated with fluid, the majority of the fluid only ‘sees’ the large scale features of the flow. If thinner helium films are deposited on the fractal surface, then gradually small scale features of the fractal become important. At these low filling fractions, the fluid is forced to flow around all the small scale features of the fractal, which results in the fluid having a low kinetic energy relative to an unobstructed flow and hence, a high tortuosity. In this way, the film thickness acts as a way of probing different length scales of the fractal. This ‘defractalisation’ idea is shown schematically in Fig. 1. It was found in [10] that the tortuosity scaled with the amount of condensed helium as a power law, with an exponent close to -1. This can be treated as the scaling of a dynamical property, i.e., a transport property, in a fractal environment. A phenomenological argument has been given by the authors [12, 13] for how the tortuosity varies with the filling fraction $\phi$ of fluid in the porous medium, with the exponent being a function of the box-counting dimension $D_f$ and random walk dimension $D_w$ (see [14] for definitions of these dimensions) of the adsorbed fluid. The explicit form of this relationship is

$$\alpha \sim \phi^{\frac{D_w - 2}{d_E}},$$

(1)

where $d_E$ is the Euclidean dimension.

This paper aims to investigate the validity of this relationship between the scaling of tortuosity and the fractal characteristics of the adsorbant material. This is done by using both the phenomenological scaling argument given in eq. 1 and numerical simulations. The numerical techniques are discussed in the next section.
2. NUMERICAL TECHNIQUES

2.1. Lattice gas model

In order to simulate the experiments of [10] numerically, it is necessary to have a model of the fractal/adsorbant system. The morphology of an adsorbed liquid film is governed by the capillary forces, van der Waals forces and chemical potential of the liquid, if gravity, is neglected. On this point, gravity has been shown in [15] to have no effect on the qualitative adsorption process in aerogel. Obviously, the capillary, and to a lesser extent the van der Waals forces, are largely a function of the geometry of the adsorbant surface. Classically, for geometries such as wedges and flat surfaces, the problem has been solved by writing the total free energy of the adsorbed film and then minimising this quantity to find the equilibrium configuration, as in [16] for example. Even for simple geometries, such as wedges, this free energy is not simple to write down [17] and is naturally different for every different geometry. It becomes clear that this technique would be difficult to apply to adsorption onto fractal objects.

It is therefore necessary to have a framework which is general and flexible enough to cope with the complicated geometries required, whilst still retaining the salient features of the adsorption process. Particularly important is that the geometrical complexity of the problem is retained as this is naturally crucial to determining the tortuosity and inner structure of a given fractal. This eliminates the possibility of using network models, where the porous material is modelled as a collection of independent pores of simple geometry but varying sizes, given by the pore size distribution, as in [18]. Although this picture may be valid for regular, templated materials (MCM-41 for example), where there are no connections between the pores and all pores have free access to the gas reservoir, it seems doubtful that this is the case for more complex materials, such as aerogel.

The method we use is virtually identical to that developed in [19], which allows the complicated gel structure to be taken into account from the outset. As the range of length scales in the problem can be of the order of hundreds of nanometres, simulations at a molecular scale become prohibitive. Hence, a coarse-grained description is used, which incorporates the essential physical ingredients, in particular the energetic and geometric disorder of the solid. In the model, which will be detailed below, metastability and hysteresis
occur not as a result of single pore level effects or from a network model but arise from the structure of the solid, which induces for the fluid a complex free-energy landscape with many local minima, corresponding to metastable states in which the system can settle. A brief description of the method is given below.

The fluid is described by the lattice gas model, with only nearest neighbour (nn) attractions being considered [20]. A lattice of coordination number $c$ is considered. Each of the $N$ sites of this lattice may be occupied by a fluid or by a solid particle. Multiple occupancy of a site is forbidden. The fluid particles can equilibrate with a reservoir that fixes their chemical potential $\mu$ and their temperature $T$, whereas the solid particles are quenched into position. This leads to the following Hamiltonian for the problem,

$$H = -w_{ff} \sum_{i<j}^{nn} \tau_i \tau_j \eta_i \eta_j - w_{sf} \sum_{i<j}^{nn} \left[ \tau_i \eta_i (1 - \eta_j) + \tau_j \eta_j (1 - \eta_i) \right],$$

(2)

where the sums run over nn sites and the terms will be explained presently. $\tau_i$, $i = 1, \ldots, N$ is a fluid occupation variable, which indicates whether site $i$ is occupied by fluid ($\tau_i = 1$) or not ($\tau_i = 0$). $\eta_i$ is a quenched random variable that characterises the presence of gel particles at lattice site $i$. In this framework it is relatively easy to incorporate complicated geometries via the quenched variable sets $\eta_i$. The porosity of the materials is given by $(1/N) \sum_i \eta_i$.

The thermodynamic behaviour of the fluid confined in such a model porous material is given by the solution of the fluid model eq. 2 in the grand canonical ensemble, which is treated using local mean field theory (LMFT) [21]. This procedure leads to a set of $N$ coupled nonlinear equations for the densities $\rho_i$,

$$\rho_i = \frac{1}{1 + e^{-X_i}},$$

(3)

where $X_i = \beta \left( \sum_j^{nn} [w_{ff} \rho_j + w_{sf} (1 - \eta_j)] + \mu \right)$. This system of equations can be solved iteratively to find local minima of the grand-potential surface [22], which correspond to metastable states. For a given configuration of porous material, described by the set $\eta_i$, the sorption isotherms

$$\rho_f(\mu, T) = \frac{1}{N} \sum_i \rho_i$$

(4)

are obtained by increasing or decreasing the chemical potential in steps $\delta \mu$ and using an iteration procedure to solve the equations. The initial condition is all non-gel sites empty.
for adsorption ($\rho_i = 0$) and all non-gel sites full for desorption ($\rho_i = 1$). At each subsequent $\mu$, the converged solution at $\mu - \delta\mu$ for adsorption or $\mu + \delta\mu$ for desorption is used to start the iterations. To accelerate the convergence of the numerical procedure, two techniques used in [22] are also used here, i.e., the local densities $\rho_i$ are updated during each iteration step, and lattice sites are sorted into active and passive sites. The slope of the isotherms can change rapidly, so rather than use equally sized steps in $\mu$ as in [22], $\delta\mu$ is chosen to attempt to yield a constant density increase for each iteration of the value of $\mu$, by using the updating procedure

$$\delta\mu = \delta\rho^0 \frac{\mu^n - \mu^{n-1}}{\rho^n_j - \rho^{n-1}_f},$$

where $\delta\rho^0$ is the target increase in density. This generally produces quite smooth isotherms, although at sharp steps or constant $\rho_f$ sections in the isotherm, the method fails and $\delta\mu$ defaults to a very small constant.

It has been shown in [23, 24] that the usual periodic boundary conditions, employed in [25], for example, are not acceptable for the simulation of desorption isotherms, as they suppress nucleation of the low density phase and therefore display greatly exaggerated hysteresis. In order to prevent this, one surface of the simulated system is connected to a reservoir of bulk vapour for desorption calulations [24]. This condition is implemented in the $z$ direction, whilst in the $x$ and $y$ directions periodic boundary conditions are used. In order to introduce the reservoir whilst still retaining a structure comparable with a periodic boundary condition model, the original system is first duplicated in the $z$-direction, to have dimensions $L_x \times L_y \times 2L_z$. The gas phase reservoir is simulated by adding an extra cavity of dimensions $L_x \times L_y \times 50$. The central $x - y$ plane of ten lattice points of this reservoir is forced to remain in the gas phase by imposing $\rho_i < 0.5$ during the iteration procedure described above. The resulting $L_x \times L_y \times 2L_z + 50$ system is simulated using normal periodic boundary conditions, but all data obtained from the simulation, such as adsorption isotherms, is taken from an interior box $L_x \times L_y \times [L_z/2 : 3L_z/2]$; this volume has the same statistical properties as the original periodic boundary condition system and is ‘far’ from the gas reservoir. For ease of implementation of the finite element method described in the next section, a square lattice has been used for the 2-D case, i.e. $c = 4$, and a simple cubic for the 3-D case, i.e., $c = 6$. 

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2.2. Calculating the tortuosity

Firstly, we introduce the velocity potential $\psi$, defined so that $\nabla \psi = \mathbf{v}$, where $\mathbf{v}$ is the velocity field of an incompressible, inviscid fluid through the porous medium due to an applied pressure gradient. The porous medium occupies the space $0 < x < L$, where $L$ is large compared to the size of the pores, and has a total lateral area $A$. A potential difference $\psi_L$ is applied across the porous medium and zero-flux boundary conditions are enforced on all other boundaries. The conditions of incompressibility and irrotationality associated with the superfluid $^4$He lead to a classic potential problem for the velocity potential $\psi$

\[
\nabla^2 \psi(\mathbf{r}) = 0 \quad \forall \mathbf{r} \quad \text{where } \gamma(\mathbf{r}) = 1 \tag{6}
\]

\[
\psi(\mathbf{r}) = 0 \text{ at } x = 0 \tag{7}
\]

\[
\psi(\mathbf{r}) = \psi_L \text{ at } x = L \tag{8}
\]

\[
\nabla \psi \cdot \mathbf{n} = 0 \text{ at all other boundaries}, \tag{9}
\]

where $\gamma(\mathbf{r}) = 0, 1$ is a function which denotes the presence of fluid at position $\mathbf{r}$. Clearly, $\phi = \frac{1}{A} \int \gamma(\mathbf{r}) d^3 \mathbf{r}$. The function $\gamma(\mathbf{r}) = \text{1}$ can be seen to be closely related to the fluid occupancy variable $\tau_i$ of the previous section. In fact, $\tau_i$ is simply a discretised version of $\gamma(\mathbf{r})$ on the lattice. Finite elements have been chosen as the numerical method to solve equations 6-9, due to their widespread use and ease of implementation. Finite element schemes for the solution of these equations can be found in standard textbooks, such as [26].

The tortuosity is a measure of how obstructed a flow path in a porous medium is and can be considered as the ratio of the kinetic energy of an equivalent unobstructed flow to the kinetic energy of a flow that has to follow the tortuous path. Using this, a relationship has been obtained for the tortuosity of a fluid in a fully saturated pore space [11]. Here, their arguments are extended to take account of a partially saturated pore space.

Solving the potential problem for the tortuous flow, the kinetic energy of the tortuous flow is given by $E(\psi) = \frac{1}{2} \rho_f \int \gamma(\mathbf{r})(\nabla \psi)^2 d^3 \mathbf{r}$. Now consider a porous material whose pores were all straight and perfectly aligned with the direction of the incoming flow. This would provide zero resistance to the flow. The velocity would only be non-zero in the $x$-direction and would be given by $\frac{\partial \psi}{\partial x} = \frac{\psi}{L}$. Then the kinetic energy of this unobstructed flow is
\[ E_{\text{modes}}(\psi) = \frac{1}{2\pi} \rho f \phi A(\psi_L)^2. \] Taking the ratio of these two quantities gives

\[ \alpha = \frac{\phi A(\psi_L)^2}{L \int \gamma(r)(\nabla \psi)^2 d^3r}. \tag{10} \]

This reduces to the expression given in [11] when the pores are saturated with fluid, i.e. \( \phi = \mathcal{P} \), where \( \mathcal{P} \) is the porosity of the material.

3. RESULTS

Results are now presented from the numerical simulations of adsorption in stochastic and deterministic fractal environments in both 2-D and 3-D. Deterministic fractals are those generated from a set of deterministic rules and always have the same appearance, whereas stochastic fractals are generated from stochastic processes and each realisation takes a different form. The generators for the deterministic fractals are shown in fig. 2, along with the numerically calculated value of the exponent, \( \epsilon_{\text{num}} \), in the power law \( \alpha \sim \phi^{-\epsilon} \). Also shown is the predicted value of the exponent from eq. 1, \( \epsilon_{\text{pre}} \). This figure is placed here primarily for reference as in the text the fractals are referred to according to their position in the table. Fractal 1 is associated with the top left generator in the table. The generators are then counted by progressing along the rows i.e. position (row 2, col 1) in the table is fractal 4.

The black squares in the 2-D generators are the solid material, and the generator is applied iteratively to the solid squares to give a fractal distribution of solid material. In the 3-D case three cross-sections of the generator are shown. The black squares again represent solid material and the generator is applied iteratively to these squares. An example for the 2-D case is given in fig. 3, which shows the generator and the resultant fractal at iteration number \( n = 4 \). Stochastic fractals have also been considered and 10 2-D and 5 3-D stochastic fractals have been generated using the original algorithm of [27].

3.1. Morphology of the adsorbed films

The lattice gas model only contains two free parameters, the fluid-solid interaction parameter, \( y \), and the temperature \( T \). Since it is meaningless in the mean field approximation to calculate \( y \) from actual particle van der Waals attractions [22], it is necessary to choose these values. Unless otherwise stated, the values of \( y \) and \( T \) are set at 2.0 and 0.8 respectively,
FIG. 2: The generators of the fractals used for unsaturated simulations, along with the numerically obtained tortuosity/filling fraction power law exponent, $\epsilon_{num}$ and the predicted exponent, $\epsilon_{pre}$

<table>
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FIG. 3: Illustration of the generation of deterministic fractals from the generator for the unsaturated simulations.

with $w_{ff} = 1$ being the energy unit and $w_{ff}/k_B$ the temperature unit. This temperature corresponds to $T/T_c = 0.8$ in the 2-D case and $T/T_c \approx 0.53$ in the 3-D case, where $T_c$ is the critical temperature for hysteresis and is equal to $T_c = 1$ in the 2-D case and $T_c = 1.5$ in 3-D, in the mean field approximation.

It was suggested in [28] that by increasing the filling fraction of adsorbed fluid in a fractal
FIG. 4: Morphology of the adsorbed fluid on a 2-D DLA of linear size $L = 100$ for $y = 1.5$ and $k_B T = 0.8$. As the filling fraction increases small scale features are smoothed out. Colour online.

material, one could probe different length scales of the fractal geometry by defractalising the object, but they provided no evidence that this was the case. As the model implemented for the adsorption process is capable of providing the morphologies of the adsorbed fluid, it is useful to observe how the film evolves with increased filling fraction. Fig. 4 shows the configuration of adsorbed fluid films at different filling fractions for a 2-D DLA cluster of linear size $L = 100$, whereby linear size is meant the diameter of a circle in which the DLA cluster fits. The 2-D case in particular is a very good example of how defractalisation happens in practice, as opposed to the previous schematic diagrams. In general, as the filling fraction increases, the thickness of the film naturally increases smearing out the small scale features. Fig. 4(c) shows the importance of the geometrical disorder. Whilst there are large regions of the fractal where only a thin uniform film has developed on the fractal, there are ‘bottleneck’ regions where fairly major condensation events have occurred and the ‘pore’ has been completely filled with fluid. These avalanches of fluid are caused by the geometrical disorder of the system and the complex energy landscape this provides for the adsorbed fluid [19]. Similar events occur in 3-D, although these are harder to visualise. Fig. 5 shows a 2-D cross-section, taken from an adsorption process in a 3-D DLA cluster of linear dimension $L = 50$. The first stage of the adsorption process is the formation of a liquid layer that
coats the DLA cluster strands. As the filling fraction increases, the gaps between proximate groups of gel strands are bridged. The process is completed by a major final condensation event which fills the large void. This process is similar to that discussed for highly porous DLCA clusters in [22, 24].

When compared to the adsorption patterns in deterministic fractals, it is clear that the disorder of the stochastic fractals has a large effect on the morphology of the adsorbed film. Fig. 6 shows the adsorption pattern on a deterministic fractal, where the adsorption pattern is much more regular, in the sense that there is a strict symmetry imposed by the geometrical disorder. The film thickness is also more uniform, by which is meant that, again due to the symmetry, features of comparable size are coated with films of similar thicknesses.

These effects can also be observed in the adsorption isotherms of the systems. Fig. 7 shows the adsorption isotherms for a 3-D DLA cluster and deterministic fractal 7. The fluid morphology patterns described previously are clearly visible in the adsorption isotherms. The DLA clusters’ isotherms show a slow adsorption at low chemical potentials (low filling fractions), which corresponds to the initial coating of the strands, and then gradually steep-
ens as larger and larger crevices are filled in with fluid, until a final avalanche sweeps the whole system, as shown by the large final jump in the adsorption isotherms. Note however that overall, the isotherm possesses a largely smooth characteristic, albeit a steepening one, until the final jump corresponding to the avalanche. The deterministic fractal isotherms on the other hand have a much more stepped appearance, with the height of the steps gradually growing larger. This difference can be explained by the slightly different range of length scales present in the different type of fractals. The deterministic fractal, due to its method of construction, contains obstacles of a small number of length scales, whose number are equal to its iteration number. The steps in the adsorption isotherm can be viewed as points where there is a coherent filling of crevices of these length scales. This also explains the increasing size of the step height as larger and larger features of the deterministic fractal are filled. DLA clusters, on the other hand, have a much larger number of length scales and hence produce a smoother isotherm.

### 3.2. Fractal dimensions of the adsorbed fluid

A more quantitative analysis of this defractalisation can be performed by box counting [29] the fluid morphology at different filling fractions and observing the variation of the fractal dimension and the range of length scales, \( a \) to \( \delta_{\text{max}} \), over which fractal behaviour can be observed. Fig. 8 shows results from the box counting algorithm for different filling fractions for a 3-D DLA cluster and a 3-D deterministic fractal (fractal number 7). Both cases illustrate how the increasing film thickness affects the fractal dimension of the adsorbed fluid. At low filling fractions a clear power law with non-integer exponent is visible for over
a decade of length scales. In the 3-D case shown in Fig. 8(a), at $\phi = 0.169$ the exponent $D_f = 2.17$ between $a \approx 2$ and $\delta_{\text{max}} \approx 10$. As the filling fraction is increased the upper limit of fractal behaviour $\delta_{\text{max}}$ remains unchanged, whilst the lower limit $a$ progressively becomes greater. For example at $\phi = 0.277$, $a \approx 7$. Eventually a point is reached where it becomes meaningless to talk of a fractal regime, as the extent over which the non-integer exponent can be observed becomes too small. The box counting results with $\phi = 0.419$ show an example of such a regime, where the adsorbed fluid is Euclidean with dimension 2. The same comments are applicable to the 3-D case shown in Fig. 8(b). Although all three filling fractions share a common range of fractal behaviour at length scales $l \approx 7$ to $l \approx 20$, for the lower filling fractions $\phi = 0.116$ and 0.062 this range extends back to $l \approx 5$ and 2 respectively.

The algorithm described in [29] also returns the minimum length scale $a$, from which fractal behaviour can be observed. Fig. 9 shows this minimum length as a function of $\phi$ for a 2-D DLA cluster and deterministic fractal 1. Both of the fractals exhibit the already established pattern of a general increase in $a$ with increasing filling fraction, but the process by which this increase takes place is noticeably different in the two cases. In the case of the DLA cluster the increase of $a$ is fairly smooth with filling fraction, whereas in the case of the deterministic fractal, three clear jumps in $a$ can be observed with $a$ remaining relatively constant in between these jumps. The magnitude of these jumps increases with increasing filling fraction. This behaviour is not surprising given the different nature of the stochastic
FIG. 8: Results from the box counting algorithm showing the number of boxes $N(l)$ of size $l$ required to cover the fluid for (a) a 2-D DLA cluster of linear size $L = 100$ and (b) a 3-D deterministic fractal (fractal number 7) of linear size $L = 81$. In both cases it is clear how the minimum length scale at which fractal behaviour is observed increases with filling fraction. Colour online.

and deterministic fractals and is another manifestation of the effect of the limited number of discrete scales of the deterministic fractal (in this case 3 scales). The stepped nature of the minimum length scale is the same effect as the stepped nature of the adsorption isotherm for the deterministic case, in that the discrete scales of the deterministic fractals seem to be removed by an avalanche of fluid which causes a sudden jump in $a$. On the other hand the smooth adsorption isotherm of the stochastic fractals is reflected in the smooth nature of the increase of $a$.

In order to compare the predicted exponent of the scaling of tortuosity with filling fraction
from eq. 1, it is necessary to perform random walks on the adsorbed fluid morphologies. This is achieved using the exact enumeration algorithm described in [30]. In both 2-D and 3-D cases, random walks of length $N = 5000$ are performed. Typical results are shown in Fig. 10 for both 2-D and 3-D stochastic fractals at a range of filling fractions for the reduced variables $\langle R^2 \rangle / a^2$, where $\langle R^2 \rangle$ is the mean square distance of the random walker, and $t/t_{min}$, where $t_{min}$ is the average time taken at a given filling fraction for the random walker to diffuse a distance $a$. Qualitatively identical results are obtained for deterministic fractals. The use of the scaled variables collapses all the data from all filling fractions onto a single curve, with the expected departures at large times, where the random walker begins to reach the edge of the finite size adsorbed fluid. At this point boundary effects become important and the random walker is restricted. The value of $D_w$ is extracted by finding the slope of the ensemble average scaled squared distance with the scaled time for all filling fractions up to which fractal behaviour can be observed, in the regime $1 < \langle R^2 \rangle / a^2 < \delta_{max}^2 / a^2$. The mean value of these $D_w$ values at different filling fractions is then taken as the value of $D_w$ for the adsorbed fluid.
FIG. 10: Results from the exact enumeration rescaled with the minimum length scale associated with fractal characteristics and the timescale associated with this length scale (a) a 2-D DLA cluster of linear size $L = 100$ for a range of filling fractions $\phi = 0.274$ to $\phi = 0.432$ and (b) a 3-D DLA cluster of linear size $L = 50$ for a range of filling fractions $\phi = 0.332$ to $\phi = 0.466$. Colour online.

3.3. The numerically obtained variation of the tortuosity with filling fraction for adsorption

Having obtained the morphology of the adsorbed fluid film, the calculation of the tortuosity consists of the solution of equations 6 - 9, with the geometry defined by the presence
of fluid sites on the lattice-gas model of adsorption. Fig. 11 shows the variation for both 2-D and 3-D deterministic fractals (fractals 1 and 7 respectively) and DLA fractals and it is clear that all of the data is fitted by a power law of the form $\alpha \sim \phi^{-\epsilon}$. As expected the value of the exponents $\epsilon$ are significantly lower in the 3-D cases when compared to the 2-D cases. This is simply a manifestation of the fact that it is significantly easier to generate an obstacle to a 2-D flow than to a 3-D flow. The exponent for the 3-D DLA cluster, $\epsilon = 1.06$, is very close to the experimentally measured exponent of $\epsilon = 1.16$ reported for aerogel in [10]. One surprising observation is again that the power law seems to extend in most cases (with the possible exception of the 2-D DLA cluster) to filling fractions $\phi = \phi$. This is surprising, as one would expect any fractal characteristics of the fluid flow to be lost at much lower filling fractions, when the fractal nature of the adsorbed fluid is lost. It is, however, difficult to be conclusive about how far the power law extends to high filling fractions from the numerical data obtained. There is some evidence, particularly in the 2-D plots, that the power law at higher filling fractions may be different but the lack of data points means it is impossible to be conclusive with regards to this.
3.4. The effect of the fluid interaction parameter and the temperature

The two free parameters of the LMFT theory model of adsorption are the fluid interaction parameter, \( y \), and the temperature, \( T \). Simulations were performed at a range of \( y \)-values and at different temperatures on both stochastic and deterministic fractals in 2-D. Fig. 12 shows the isotherms for a 2-D DLA fractal of linear size \( L = 100 \) for \( y = 1.5 \) (\( - \)), and \( y = 3 \) (\( - \)). Changing the value of the fluid-solid interaction has the effect of altering the nature of the sorption isotherm. The greatest hysteresis is observed at \( y = 3 \), but there is significant hysteresis at the other values of \( y \). The calculated tortuosities for both adsorption and desorption morphologies are shown in Fig. 13. It is clear that all of the adsorption morphologies follow a power law \( \alpha \sim \phi^{-1.43} \) for all values of \( y \), for all filling fractions up to \( \phi = 0.5 \). However, there is a clear departure in the power law behaviour for the desorption morphologies at filling fractions \( \phi > 0.6 \), although at lower filling fractions, the desorption morphologies also follow the power law \( \alpha \sim \phi^{-1.43} \).

Similar patterns for the sorption isotherms for temperatures \( T/T_c = 0.4, 0.6, 0.7, 0.8 \) and \( 0.9 \) for the same 2-D DLA cluster can be seen in Fig. 14. As expected, the hysteresis decreases with increasing temperature, to the point where it has almost disappeared at \( T/T_c = 0.9 \) (recall \( T_c = 1 \) in the simple square 2-D lattice). These isotherms show a similar trend of decreasing hysteresis with increasing temperature to those shown in [19] and this acts as a validation of the implementation of the LMFT model. Fig. 15 shows the tortuosities.
FIG. 13: The variation of tortuosity corresponding for both adsorption and desorption, for $y = 1.5, 3$ and $5$ and $T = 0.8$ in all cases. Tortuosities for the adsorption branches all follow $\alpha \sim \phi^{-1.43}$, whilst those from the desorption branches follow this law only for $\phi < 0.6$. Colour online.

FIG. 14: The sorption isotherms for a 2-D DLA cluster of linear size $L = 100$ for $T = 0.6$ (-) and $T = 0.9$ (-). $y = 1.5$ in both cases. Colour online.

obtained from these sorption isotherms for both adsorption and desorption. As in the case of varying $y$, all the tortuosities follow a power law $\alpha \sim \phi^{-1.43}$ for $\phi < 0.6$, whereas for filling fractions larger than this only the adsorption morphologies follow this power law and the desorption morphologies show a markedly different behaviour.

The filling fractions at which the desorption morphologies have tortuosities that differ from the power law $\alpha \sim \phi^{-1.43}$ can be seen to be those that correspond to fluid densities that are in the hysteresis regime, whether this hysteresis is caused by decreased temperature
FIG. 15: The variation of tortuosity corresponding to the sorption isotherms i.e. both adsorption and desorption, for $T = 0.4, 0.6, 0.7, 0.8$ and $0.9$ and $y = 1.5$ in all cases. Tortuosities for the adsorption branches all follow $\alpha \sim \phi^{-1.43}$, whilst those from the desorption branches follow this law only for $\phi < 0.6$. Colour online.

or increased fluid-solid interaction strength. If one examines these morphologies, the reason for the departure from the power law behaviour are clear. Fig. 16 shows the morphologies at nearly identical filling fractions for the adsorption and desorption isotherms, with (a) and (c) showing the adsorption branch and (b) and (d) the desorption branch at $y = 1.5$ and $T = 0.8$. The adsorption mechanism has already been discussed and involves the formation of a liquid layer that coats the aerogel strands. As the filling fraction increases, the gaps between proximate groups of gel strands are bridged. The process is completed by a major final condensation event which fills the large void. The desorption process is quite different. Three possible mechanisms for desorption were proposed in [19]: (i) cavitation, which consists of the appearance of gas bubbles in the bulk of the filled material and occurs at values of $T/T_c$ close to 1, (ii) a percolation transition with the invasion of the whole sample by a self-similar vapour domain, and (iii) a depinning transition leading to the passage of a self-affine gas-liquid interface. Both (ii) and (iii) rely on the presence of a physical interface between the gel and the gas reservoir, whose implementation in this work follows was described previously. Figs. 16(c) and (d) show how these different mechanisms effect the adsorbed fluid shape at virtually identical filling fractions. In the desorption case there is clearly a depinning transition associated with the gas reservoir interface as opposed to the more uniform film in the adsorption case. These different morphologies naturally give rise
FIG. 16: Morphologies of the adsorbed fluid film for the sample 2-D DLA cluster where (a) and (c) are the adsorption branch and (b) and (d) the desorption branch for $y = 1.5$ and $T = 0.8$. Colour online.

to different tortuosities. However at the lower filling fractions shown in Figs. 16(a) and (b), when the hysteresis in the sorption isotherms is no longer present, the adsorbed fluid shape is largely the same regardless of whether it has been obtained from adsorption or desorption, and so at lower filling fractions the adsorption and desorption tortuosities agree.

3.5. Numerical and predicted scaling

Having the values of $D_f$ and $D_w$ for the adsorbed fluid allows the comparison of the numerical scaling with the scaling exponent predicted by equation (1). These results are shown in fig. 17. The agreement between the predicted exponents and numerical exponents is generally good, especially for the DLA clusters, where the prediction is even sensitive to small changes in the numerical exponent of different DLA clusters. The maximum percentage difference between the predicted and numerical exponents for the DLA clusters is 7.6%. This is a promising result, as it suggests that the method is capable of determining the different microstructure of different realisations of the same family of stochastic fractals. The agreement of the numerical and predicted exponents for the deterministic fractals is
FIG. 17: Comparison of the numerically observed and predicted exponents for the unsaturated model. (x) 2-D deterministic fractals, (+) 2-D DLA clusters, (,) 3-D deterministic fractals, (Δ) 3-D DLA clusters. The straight line Predicted $\epsilon = $ Numerical $\epsilon$ again guides the eye.

less impressive, although still in general good, with the exception of one fractal (fractal 10), where there is a disagreement of 58%.

Excluding this point, the agreement between the predicted and numerical exponents is good over a wide range of the value of the exponent. Due to the limited number of deterministic fractals considered, it is difficult to say whether the predictions are more accurate for the 2-D or 3-D cases but it appears that the agreement in 3-D is better as in the saturated case. This observation, in tandem with the better agreement for the stochastic fractals, suggests that the predicted exponent is more accurate for highly porous materials. In general, the predicted exponent is an overestimate, and in the few cases where the numerical exponent is greater than the predicted one, it is by a relatively small amount when compared to the magnitude of the overestimation of the predicted exponent in some cases i.e. there are more points further underneath the line Predicted $\epsilon = $ Numerical $\epsilon$ in fig. 17. Currently, we have no explanation for this.

4. CONCLUSIONS

It has been shown that a lattice gas model of adsorption combined with a simple finite element method describes accurately the variation of tortuosity with liquid filling fraction in fractal materials. This defractalisation process is a way of characterising fractal materials
over all length scales as smaller length scales are removed as the filling fraction increases. It was shown that the pertinent geometric disorder can be captured using a local mean field theory model. The scaling of tortuosity of the 3-D DLA cluster with filling fraction obtained is in very close agreement with that obtained for aerogel in [10]. The value of the exponent changes for different realisations of the DLA cluster and also for different fractals and was shown to be independent of the model parameters $y$ and $T$. The exponent is the same for desorption and adsorption when the sorption isotherms coincide, i.e., in regions where no hysteresis is observed. The numerically calculated exponent also showed good agreement with the predicted values using equation (1), especially for the DLA clusters. The exponent $\epsilon$ is an important characteristic as it measures the impact of different length scales on the tortuosity of the material and is a measure of the multiscale nature of materials, which can be accessed experimentally. Further work is needed to understand why the predicted exponent is always an overestimate and what other fractal characteristics may be needed to more accurately predict $\epsilon$. The authors are grateful to A. I. Golov, S. Babuin and C. Ashton for many fruitful discussions. Both authors would like to acknowledge support under EPSRC grant number GR/S27559/01.