A grey free-energy multi-phase lattice Boltzmann model with effective transport and wetting properties

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The paper shows that it is possible to combine the free energy lattice Boltzmann approach to multi-phase modelling of fluids involving both liquid and vapour with the partial bounce back lattice Boltzmann approach to modelling effective media. Effective media models are designed to mimic the properties of porous materials with porosity much finer than the scale of the simulation lattice. In the partial bounce back approach, an effective media parameter or bounce back fraction controls fluid transport. In the combined model, a wetting potential is additionally introduced that controls the wetting properties of the fluid with respect to interfaces between free space (white nodes), effective media (grey nodes) and solids (black nodes). The use of the wetting potential combined with the bounce back parameter gives the model the ability to simulate transport and sorption of a wide range of fluid / material systems. Results for phase separation, permeability, contact angle and wicking in grey media are shown. Sorption is explored in small sections of model multi-scale porous systems to demonstrate two-step desorption, sorption hysteresis and the ink-bottle effect.

I. INTRODUCTION

Numerical simulation of multi-phase fluids in porous media is challenging. In addition to the problem of adequately describing each phase of the fluid and the complex geometry, a numerical algorithm is required to track interfaces between the fluid phases. Lattice Boltzmann methods have the advantage of coping with complex geometries and tracking the creation, movement and annihilation of interfaces automatically. Consequently, they have grown in popularity and have been used successfully to simulate fluids in a wide variety of applications [1–5].

Several conceptually different algorithms have been developed to describe multi-phase and multi-component fluids within a lattice Boltzmann framework [6–10]. The algorithms differ in terms of the accuracy with which they describe the fluid and the range of physical parameters, *e.g.* density and viscosity ratios of the different phases or components, over which they are numerically stable. Much research has addressed these issues leading to significant improvements. Substantive reviews are now available [11–15]. However, these improvements have come at considerable computational cost and have limited the application of multi-phase (specifically liquid and gas) methods to relatively simple systems. This is a critical limitation as many potentially interesting applications of multi-phase methods concerning wetting and sorption in porous media deal with systems with large representative elementary volumes and/or pore sizes spanning multiple length scales.

An approach to reducing computational cost when modelling multi-scale porosity is to use an effective media

framework. The first lattice models incorporating effective media properties were developed as early as the 1990s [16–21] but they started gaining traction only recently [22–30]. In these models, in addition to lattice nodes assigned to be either fluid space or solid, some nodes are assigned effective media properties. Typically they represent material with porosity on a scale finer than the simulation lattice. In the partial bounce back approach, they are described by a parameter that controls effective transport properties. These models have been used to study the speleogenesis of 2D carbonate aquifers [31] and the permeability of 3D sandstone [32] and cement paste [27, 33]. However, all these studies were necessarily restricted to a single-phase fluid.

The authors are unaware of lattice Boltzmann models that combine effective media and multi-phase methods except their own, [34] and those of Pereira [35] very recent attempts to do this using the Shan Chen [7] multi-phase model. Here we extend that work to the free energy model [8] with the significant advantage that we are able, unlike with Shan-Chen as previously implemented, to separate transport and wetting. This paper introduces this combination creating a new model with both effective transport and effective wetting properties for two phase liquid-gas fluid systems. The paper is arranged as follows. In section II, the standard lattice Boltzmann algorithm, the free energy method for two-phase fluids, wetting of surfaces and the effective media approach are all recapped. Section III describes the main novelty of this paper: the combining of the free energy and effective media approaches and the introduction of the new concept of *effective wetting* additional to *effective transport*. This gives significant control of the properties of the simulated system. Implementation and validation of the new algorithm are discussed in section IV. Opportunities afforded by the combined method are demonstrated in section V on sections of model porous media containing solids, pores, and effective media and incorporating both effective transport and effective wetting.

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II. THE LATTICE BOLTZMANN METHOD

A. General framework

In lattice Boltzmann (LB) methods, at each node of a discrete lattice mesh, the fluid is represented by a density distribution of Q fluid elements each with a defined lattice velocity performing consecutive propagation and collision steps. The standard LB method is encapsulated in:

$$f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) - f_i(\mathbf{r}, t) = \Delta t \sum_{j=1}^Q S_{ij} (f_j(\mathbf{r}, t) - f_j^{eq}(\mathbf{r}, t)) + F_i(\mathbf{r}). \quad (1)$$

Here $\mathbf{r}$ is a lattice node and Δt is the simulation time step. The functions f_i represent the density of fluid at position $\mathbf{r}$ and time t moving with velocity $\mathbf{e}_i$ such that $\Delta t \mathbf{e}_i$ is a lattice vector. The first term on the RHS of Eq. 1 is the collision operator in which S_{ij} is the collision matrix of rate terms that serves to relax the fluid towards an equilibrium distribution $f_j^{eq}(\mathbf{r}, t)$ that encapsulates the physics of the problem. In a single relaxation time implementation, as here, $S_{i,j} = \delta_{i,j}/\tau$. Lastly, F_i represents movement of mass density in direction i in response to external force that describes, for example, gravity or interfacial tension.

In the absence of external forces, the macroscopic density $\rho(\mathbf{r}, t)$ and momentum $\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)$ are calculated from the distribution functions as:

$$\rho(\mathbf{r}, t) = \sum_{i=1}^Q f_i(\mathbf{r}, t) \quad (2)$$

and

$$\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) = \sum_{i=1}^Q f_i(\mathbf{r}, t)\mathbf{e}_i \quad (3)$$

where $\mathbf{u}(\mathbf{r}, t)$ is the macroscopic velocity.

The no-slip boundary condition can be approximated with the bounce back rule [36]. If a fluid element hits a solid boundary following the propagation step, its momentum is reversed so that:

$$f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) = f_{\tilde{i}}(\mathbf{r}, t) \quad (4)$$

where $\tilde{i}$ is the direction opposite to i : $\mathbf{e}_{\tilde{i}} = -\mathbf{e}_i$.

B. Free energy approach for two phase fluids

The physics of a two phase (liquid - gas) fluid enters the LB algorithm by inclusion of a discrete version of the pressure tensor in the equilibrium function. The description here follows references [8, 37, 38] that start with an expression for the total free energy written as

$$\Psi = \int_V \left[\psi(T, \rho) + \frac{\chi}{2} (\nabla \rho)^2 \right] dV \quad (5)$$

where $\psi(T, \rho)$ is the free energy density of the bulk fluid, T is temperature and V is volume. The constant χ determines the surface tension between the liquid and vapour phases. Using this free energy, the pressure tensor has been shown to be

$$P_{\alpha\beta} = \xi \left\{ \left[p - \chi \left(\rho \nabla^2 \rho + \frac{1}{2} |\nabla \rho|^2 \right) \right] \delta_{\alpha\beta} + \chi \partial_\alpha \rho \partial_\beta \rho \right\} \quad (6)$$

where p is the bulk fluid pressure and α and β run over x , y and z . The constant ξ is a pressure scaling factor introduced by Wagner and Pooley [39], to improve the numerical stability of the simulation without affecting the equilibrium behaviour. A van der Waals equation of state expressed in reduced units is used to link the pressure to the density, *viz*:

$$p = \frac{\rho}{3 - \rho} - \frac{9}{8} \theta_c \rho^2. \quad (7)$$

where $\theta_c = T_c/3T$ is the reduced critical temperature and the critical density is taken as $\rho_c = 1$. Assuming that $\Delta x = \Delta t = 1$, it follows that the equilibrium function is given by

$$f_i^{eq}(\mathbf{r}, t) = \omega_i \left[\rho(\mathbf{e}_i \cdot \mathbf{u}) + \frac{3}{2} \rho(\mathbf{e}_i \cdot \mathbf{u})^2 - \frac{1}{2} \rho(\mathbf{u} \cdot \mathbf{u}) + \frac{3}{2} \lambda [2(\mathbf{e}_i \cdot \mathbf{u})(\mathbf{e}_i \cdot \nabla \rho) + (\mathbf{e}_i \cdot \mathbf{e}_i - 1)(\mathbf{u} \cdot \nabla \rho)] \right] + \xi \left[\begin{aligned} &\omega_i^p p - \chi \omega_i^t \rho \nabla^2 \rho \\ &- \chi \sum_{\alpha=x,y,z} \omega_i^{\alpha\alpha} \partial_\alpha \rho \partial_\alpha \rho \\ &+ \chi \sum_{\alpha,\beta=x,y,y,z,z,x} \omega_i^{\alpha\beta} \partial_\alpha \rho \partial_\beta \rho \end{aligned} \right]. \quad (8)$$

The coefficients ω_i are the lattice dependent weights and the coefficients $\omega_i^{p,t,\alpha\alpha,\alpha\beta}$ are other weights as explained in literature [40]. The term involving λ ensures Galilean invariance [41]. The parameter λ is given by

$$\lambda = \left(\tau - \frac{1}{2} \right) \left(\frac{1}{3} - \frac{dp}{d\rho} \right). \quad (9)$$

Lastly, χ is related to the interfacial width, ϖ , [39], and interfacial tension, γ , [42], through

$$\chi = \frac{\varpi^2}{2} \left(\frac{\theta_c}{\theta} - 1 \right) \quad (10)$$

and

$$\gamma = \frac{4}{3} \sqrt{\frac{16\chi}{3}} \left(1 - \frac{\theta}{\theta_c} \right)^{\frac{3}{2}} \quad (11)$$

respectively.

C. Two phase fluids and solid interfaces

Wetting of solid surfaces is introduced to the LB free energy framework by adding a term to the free energy to account for the fluid interaction with the solid surface, S . Following Cahn and Briant *et al.* [38, 43], the additional term is written in terms of the surface fluid density as

$$\Psi_s = \int_S \Phi(\rho) dS \quad (12)$$

where

$$\Phi(\rho) = -\phi\rho. \quad (13)$$

The constant ϕ is the wetting potential. Within the simulation, this translates to a boundary condition for the surface normal gradient of the fluid density,

$$\nabla_n \rho = -\frac{\phi}{\chi}. \quad (14)$$

The contact angle ϑ is determined by

$$\cos(\vartheta) = \frac{(1 + \Omega)^{\frac{3}{2}} - (1 - \Omega)^{\frac{3}{2}}}{2}. \quad (15)$$

where Ω is related to the wetting potential through

$$\phi = \Omega \left(1 - \frac{\theta}{\theta_c}\right) \frac{\sqrt{2\chi}}{\chi}. \quad (16)$$

D. Single phase fluids and effective media

In effective media approaches, a multi-scale problem is addressed by assigning effective meso-scale properties to numerical nodes that encapsulate the fluid dynamics within the underlying microstructure of the node that is not explicitly resolved. Hitherto, these methods are limited to a single phase fluid. There are two main classes of lattice Boltzmann solvers that incorporate effective media: force-adjusted and partial bounce back methods [16–30]. We chose to follow the partial bounce back method of Walsh *et al.* [26] that combines computational simplicity with an ability to accurately link the partial bounce back fraction to the permeability. Without loss of generality, we describe the method for a single-relaxation-time collision operator and with $\Delta x, \Delta t$ and τ set to unity. In this case, and in the absence of external forces, Eq. 1 is reduced to:

$$f_i(\mathbf{r} + \mathbf{e}_i, t + 1) = f_i^{eq}(\mathbf{r}, t). \quad (17)$$

In the partial bounce back method, an effective media parameter $\sigma(\mathbf{r})$ is introduced which combines Eq. 17 with the bounce back step as described in Eq. 4 so that, in every step of the simulation and at every node, a fraction $(1 - \sigma)$ of the fluid propagates forward in the i direction

while the remainder is bounced back in the $\tilde{i}$ direction. The master equation of the algorithm becomes:

$$f_i(\mathbf{r} + \mathbf{e}_i, t + 1) = [1 - \sigma(\mathbf{r})] f_i^{eq}(\mathbf{r}, t) + \sigma(\mathbf{r}) f_{\tilde{i}}(\mathbf{r}, t). \quad (18)$$

The parameter σ is sometimes referred to as “solid fraction” although, as Walsh *et al.* have observed, this is a misnomer: it is simply a parameter that controls the permeability. Equation 18 recovers Eq. 17 in regions of bulk fluid where $(\sigma(\mathbf{r}) = 0)$ and Eq. 4 in the case of solid boundaries where $(\sigma(\mathbf{r}) = 1)$.

Since this section considers transport properties of single phase fluids in saturated media, the equilibrium distribution functions are the widely known functions [44]:

$$f_i^{eq}(\mathbf{r}, t) = \omega_i \rho \left[1 + 3(\mathbf{u}^* \cdot \mathbf{e}_i) + \frac{9}{2}(\mathbf{u}^* \cdot \mathbf{e}_i)^2 - \frac{3}{2}(\mathbf{u}^* \cdot \mathbf{u}^*) \right]. \quad (19)$$

where it is assumed that $\Delta x = \Delta t = 1$ and $\mathbf{u}^*$ is the equilibrium velocity that is equal to the macroscopic velocity $\mathbf{u}$ in absence of external forcing. Note that there is a factor 3 difference in the weights ω_i between Eqs. 8 and 19.

Walsh *et al.* [26] derived the intrinsic permeability of homogeneous partially-permeable media for which $\sigma(\mathbf{r}) = \sigma \forall \mathbf{r}$ as a function of the fluid kinematic viscosity ν and the effective media parameter σ as [45]

$$\kappa(\sigma, \nu) = \frac{1 - \sigma}{2\sigma} \nu. \quad (20)$$

Finally we note that a weakly-permeable node, for which $0 < \sigma < 1$, is commonly labelled a grey node. Similarly fluid nodes are labelled white ($\sigma = 0$) and solid nodes black ($\sigma = 1$). Given how concise this notation is, we use it in the following sections.

III. THE COMBINED MODEL AND EFFECTIVE MEDIA WETTING

In this section, the free energy model presented in section IIB including wetting, section IIC, is extended to include effective media through partial bounce back, section IID. On one level, this is very simple. The equilibrium function for the multiphase method, Eq. 8, is used within the partial bounce back rule, Eq. 18, of the effective media method. The novel step and difficulty lies in defining the fluid density gradient within grey nodes and at interfaces between grey nodes and either bulk-fluid or solid nodes in order to ensure sensible wetting behaviour.

Consider first nodes in regions of homogeneous grey-ness. Our approach is to consider that there is both a fluid-fluid interaction operating at the resolved (meso) length scale of the node spacing and a local fluid-solid interaction operating at the unresolved (micro) scale of the effective media within the node. Analogous to Eq. 12, we envisage a further term added to the free energy at grey nodes to represent the microscale interaction of the

fluid with the solid of the effective medium at the microscale. The extra term is justified by considering that, at least according to one interpretation, the effective media is microporous so that any given node may be considered as comprising a mixture of pure fluid and pure solid. It therefore has internal interfaces and any microscopic fluid element is surrounded by solid either side within the node. Given that there is both a fluid-fluid and a fluid-solid interaction within the node, and following Eq. 14, the modulus of the gradient of fluid density either side of the node is increased by a constant ϕ_{gg} . The constant ϕ_{gg} serves as an internal wetting parameter for the unresolved porosity of the effective media. However, note the notation. With reference to Eq. 14, for a fluid-solid interface, *i.e.* white-black node pairs, the constant χ is rolled into the the gradient between them, now written

as ϕ_{wb} , so that $\phi = \chi\phi_{wb}$. Likewise a different χ is associated with grey nodes and is rolled into ϕ_{gg} , the additional gradient between two grey nodes. A numerical scheme to calculate the density gradient at the central grey node of three consecutive grey nodes is presented in the second line of Table I, along with the trivial case for a string of white, *i.e.* bulk fluid, nodes as shown in the top line. The grey node density gradient is unchanged compared to the bulk fluid density gradient. However, the second derivative is affected. It is increased by $2\phi_{gg}$ as shown by the entries in the third column of the Table. The constant ϕ_{gg} is quite distinct from σ which serves to control the permeability (transport properties). The provision of these two parameters enables a variety of different wetting and transport scenarios to be modelled within the effective media nodes.

TABLE I: Density gradient boundary rules. The subscripts $[-, 0, +]$ refer to three consecutive nodes. The gradients are evaluated at the central node.

colour at nodes x_-, x_0, x_+	$\frac{\partial \rho}{\partial x}$	$\frac{\partial^2 \rho}{\partial x^2}$
white, white, white	$\frac{1}{2}(\rho_+ - \rho_-)$	$\rho_+ + \rho_- - 2\rho_0$
grey, grey, grey	$\frac{1}{2}[(\rho_+ + \phi_{gg}) - (\rho_- + \phi_{gg})]$ $= \frac{1}{2}(\rho_+ - \rho_-)$	$(\rho_+ + \phi_{gg}) + (\rho_- + \phi_{gg}) - 2\rho_0$ $= \rho_+ + \rho_- - 2\rho_0 + 2\phi_{gg}$
white, white, black	$\frac{1}{2}(\rho_0 - \rho_- + \phi_{wb})$	$\phi_{wb} + \rho_- - \rho_0$
white, white, grey	$\frac{1}{2}(\rho_0 - \rho_- + \phi_{wg})$	$\phi_{wg} + \rho_- - \rho_0$
grey, grey, black	$\frac{1}{2}(\rho_0 - \rho_- - \phi_{gg} + \phi_{gb})$	$\phi_{gb} + \rho_- - \rho_0 + \phi_{gg}$
grey, grey, white	$\frac{1}{2}(\rho_+ - \rho_-)$	$\rho_+ + \rho_- - 2\rho_0 + 2\phi_{gg}$

The remaining issue is to decide how to treat interfaces between white, grey and black nodes. Two further interface gradients between white and grey and between grey and black nodes, analogous to ϕ_{wb} , are necessarily introduced: ϕ_{wg} and ϕ_{gb} . If just one grey level is assumed, then there are 27 permutations of three consecutive white, grey or black nodes in one dimension of which there are 4 that offer distinct types of single interfaces that serve to illustrate the approach taken. These are listed in the first column of the remaining rows of Table I. The second and third columns present numerical expressions for the first and second derivatives of the density gradient of the central node. The case of the trio white-white-black follows directly from Eq. 14. White-white-grey is handled in a directly analogous fashion. The case of grey-grey-black is slightly more complex. On the righthand side, the gradient is ϕ_{gb} while on the left the modulus is augmented by ϕ_{gg} . The centre node gradient is the average of the two. The anomaly is the three node set grey-grey-white. By analogy with grey-grey-black, we might expect $(\rho_0 - \rho_- - \phi_{gg} + \phi_{gb})/2$.

However, here it is treated exactly the same as grey-grey-grey, a rule that is not symmetric with the white-white-grey interface. The reason is that we consider the internal wetting of the microporous effective media within a node to dominate the wetting of the “external surface” contacting the space beyond, in the next node. These rules were followed in this work. The extension to two or more dimensions is obvious. Moreover, optimised stencils to calculate the gradients in regions of homogeneous media using information in all surrounding nodes have been published by Pooley and Furtado [40] and were used where appropriate in this work.

Before moving on to the implementation and results, we consider that one might attempt to harmonise the wetting rules into a simple symmetric numerical scheme that can be applied at any sequence of nodes irrespective of colour and we explain why we did not do this. Apparently simple and obvious rules to do this are:

$$\frac{\partial \rho}{\partial x} = [[(1 - \sigma_+)\rho_+ + \sigma_+\phi_{0+}] - [(1 - \sigma_-)\rho_- + \sigma_-\phi_{0-}]]/2 \quad (21)$$

and

$$\frac{\partial^2 \rho}{\partial x^2} = [(1 - \sigma_+) \rho_+ + \sigma_+ \phi_{0+}] + [(1 - \sigma_-) \rho_- + \sigma_- \phi_{0-}] - (2 - \sigma_+ + \sigma_-) \rho_0 \quad (22)$$

where $\phi_{0+,0-}$ are variously ϕ_{ww} , ϕ_{wg} etc. Such a scheme is symmetric in all cases and reproduces some of the results in Table I. The main problem, however, is that this approach has the effect of weakening the fluid-fluid interaction in the effective media nodes because the fluid-fluid contribution to the gradient is scaled by $(1 - \sigma)$. We did not consider this desirable because we did not want to link the wetting behaviour to the transport parameter sigma. Hence we did not explore the symmetric approach further in this work.

IV. IMPLEMENTATION AND RESULTS

A. Implementation

This section demonstrates the effective wetting lattice Boltzmann model. The code developed comprises a coupling of two previous codes written by the authors in the course of previous published work: first, a standard free energy lattice Boltzmann algorithm for two phase fluids, as discussed in section II B; and second a lattice Boltzmann model for single phase fluids incorporating effective transport properties, as discussed in section II D. The two codes were previously validated against the published results of others [5, 27, 33]. In the case of the free energy model code, it was shown that the contact angle varied as expected with the surface normal fluid density gradient. The measured pressure decrease across the interface of a spherical vapour drop was seen to vary inversely with the drop radius. The measured interfacial tension was within 6% of the expected value. Phase separation was seen to occur as expected in a fluid with periodic boundary conditions and in a fluid confined by solid walls. The model was shown to capture capillary rise and ink-bottle effect phenomena. In the case of the effective media code, it was shown that the model recovers the behaviour of a standard isothermal LB algorithm when the effective media parameter is restricted to $\sigma = 0$ or 1. The accuracy of the model was tested by computing the permeability of square pipes and of arrays of overlapping impermeable spheres. It was further tested by calculating the permeability of homogeneous media and comparing the results with those predicted by Eq. 20 and by calculating the permeability of regular arrays of overlapping permeable spheres. The code was used to calculate the permeability of media composed of layered structures, each layer characterized by a different effective media parameter (and hence different permeability) setup either in series or in parallel. In all the tests, the simulation results were in very good agreement with expectation and theory as shown in the references.

What follows here are the tests and results now carried out using the combined code for the new combined model. The description is subdivided into results discussing: (i) phase separation inside systems of uniform grey nodes where it is shown that the distribution of vapour in homogeneous grey nodes is independent of both the permeability parameter, σ and the internal wetting of the unresolved grey node porosity, ϕ_{gg} though that when regions of grey nodes are surrounded by black solid nodes the regions of liquid and gas depend in logical fashion on the relative sign and magnitude of the wetting potentials ϕ_{gg} and ϕ_{gb} ; (ii) permeability that shows that the permeability of fully saturated mixed white-grey-black systems varies with σ but is independent of ϕ_{gg} ; (iii) contact angle that shows that the contact angle of liquid-vapour and fluid-material interfaces depends in a coherent way on all the different wetting parameters ϕ_{gg} , ϕ_{wg} , ϕ_{gb} and ϕ_{wb} but is independent of the permeability parameter σ ; (iv) wicking in grey nodes that shows that the sorptivity is dependent on *both* the permeability, σ and internal wetting of the grey nodes, ϕ_{gg} as expected and (v) sorption isotherm cycles that show that the model naturally leads to sorption hysteresis cycles for systems comprising uniform grey nodes. The last section goes on to consider sorption in a more complex porous system with the ink-bottle effect.

B. Results

All the following simulations were carried out at one of two reduced temperatures $\theta/\theta_c = 0.96$ or 0.98 yielding co-existence bulk liquid and gas densities of $\rho_{bulk-liq} = 1.41$ and $\rho_{bulk-gas} = 0.62$ and $\rho_{bulk-liq} = 1.29$ and $\rho_{bulk-gas} = 0.727$ respectively. The pressure scaling factor was set to $\xi = 0.5$ and 1 respectively, in the former case to improve numerical stability. The parameter χ describing the liquid - vapour interfaces was calculated using Eq. 10 to return an interface width $\varpi = 1$, *i.e.* $\chi = 0.0208$ and 0.0102 respectively. The simulations were considered to have converged when the maximum density variation per 5000 time steps was smaller than 10^{-6} or better.

1. Phase separation inside grey nodes

To test the liquid-vapour phase separation in grey nodes, simulation boxes of size $(L_x, L_y) = (21, 21)$ or $(50, 50)$ with a constant value of σ and periodic boundary conditions were initialized with a random fluid density distribution in the range $\rho = 1 \pm 0.05$, close to the critical density $\rho_c = 1$. The reduced temperature was set to 0.96 . Phase separation occurred as expected and as previously observed for the standard free energy algorithm applied to pure white systems. The separated fluid distribution was observed to be independent of the value of the imposed internal wetting potential ϕ_{gg} or

of the permeability parameter σ . As evidence, the top left image of Fig.1 is for $\sigma = 0.1$ and $\phi_{gg} = 0$. It shows the separating phases just 100 cycles after the random initialisation. The top right image shows how the separation pattern has further developed after 1000 cycles. ϕ_{gg} is the only wetting parameter operative in homogeneous grey nodes. After 100 cycles there are clear areas of liquid and gas but the equilibrium distribution is not reached. The lower two images show what happens when σ is doubled to 0.2 (left) and when ϕ_{gg} is set equal to 0.1 (right). In each case, the random initial distribution was seeded with the same seed and essentially the same pattern evolves. The differences are that when σ is doubled, the pattern takes $\sqrt{2}$ times as long to evolve as transport is slower (see sections below). The image is therefore shown after 1410 cycles. Also, the phase separation is *slightly* “weaker” than when $\sigma = 0.1$. The liquid density is decreased marginally and the image is qualitatively less “sharp”. However, without a formulae for the pressure in the effective media, this cannot be elaborated further. Similarly, when $\phi_{gg} = 0.1$, the phase separation is slightly “stronger” than when it is zero. The liquid density is increased marginally and the image is more “sharp”.

FIG. 1: Evolution of fluid separation for a random distribution of density around 1 in homogeneous grey nodes with $\sigma = 0.1$ and $\phi_{gg} = 0$ after 200 (top left) and 1000 (top right) cycles. The system size is $(L_x, L_y) = (50, 50)$. Bottom left shows the evolution for the same starting distribution with $\sigma = 0.2$ after 1410 cycles and bottom right with $\phi_{gg} = 0.1$ after 1000 cycles.

When the simulation boxes are surrounded by impermeable solid walls, the results of the phase separation, *i.e.* where the liquid condenses and which phase wets the solid boundaries in equilibrium, depends on an interplay between the wetting potentials ϕ_{gb} and ϕ_{gg} . As a baseline for discussion, the top left image of Fig. 2 shows the equilibrium fluid distribution for a solid box surrounding white nodes. The wetting potential $\phi_{wb} = 0.18$ and as a result liquid wets the walls and a gas bubble forms at the centre. In the remaining 3 images, the white nodes and replaced with grey nodes. Lower left image shows what

happens for $\sigma = 0.1$ with $\phi_{gb} = 0.18$ and $\phi_{gg} = 0$. As expected, liquid continues to wet the walls. It still does so if ϕ_{gg} is made positive, top right image. However, the situation is reversed by making ϕ_{gg} negative. The bottom right image is for $\phi_{gg} = -0.9$ where it is seen that gas wets the walls. One expects gas wetting walls for negative ϕ_{gb} . Generally this is true. However, if ϕ_{gg} is additionally made positive, then it is not. As an example, the top right image is for $(\phi_{wb}, \phi_{gg}) = (-0.18, 0.09)$. Thus it is seen that the relative magnitude and sign of the two wetting parameters determines whether the liquid preferentially wets the unresolved internal porosity of the grey nodes or the resolved external solid (black) surface.

FIG. 2: Equilibrated fluid distribution for white nodes bounded by a square of black nodes (top left). The system size is $(L_x, L_y) = (21, 21)$. It was seeded with $\rho = 1$. $\phi_{wb} = 0.18$ so the walls are liquid wetting. In the remaining maps, the white nodes are turned grey, with $\sigma = 0.1$ and $(\phi_{wb}, \phi_{gg}) = (-0.18, 0.09)$ (top right); $(0.18, 0)$ (bottom left); and $(0.18, -0.9)$ (bottom right).

2. Grey node permeability

A 3D system of $(L_x, L_y, L_z) = (72, 9, 9)$ nodes with periodic boundary conditions in y and z was created. The region $1 < x \leq 9$ was designated a white inlet channel and the region $64 < x \leq 72$ was designated a white fluid outlet channel. Pressure and velocity boundary conditions [46] were established in slices $x = 1$ and $x = 72$ meaning that constant pressure was maintained in slice $x = 1$ and constant velocity $\mathbf{u} = u_x \mathbf{i}$ in slice 72. The space $9 < x \leq 63$ was filled either uniformly with grey nodes or a cubic lattice of overlapping grey spheres of radius 27.5 nodes on lattice centres separated by 9 nodes with the interstitial space white. The spheres have an ideal grey fraction of 80.6% and an actual grey fraction 76.4% due to digitisation. A surface rendering of the spheres is shown in the inset to Fig. 3. For tests the reduced temperature was $\theta/\theta_c = 0.98$, the inlet density was set to either $1.2\rho_{bulk-liq}$ or $0.2\rho_{bulk-gas}$ and the out-

let speed was 2×10^{-5} lu/tu. The wetting parameters were set as $\phi_{gg} = \phi_{wg} = 0.133$.

FIG. 3: The measured permeability of homogeneous grey nodes (squares) as a function of σ together with a fit according to Eq. 20. Other parameters are given in the text. The measured permeability (circles) of the cubic lattice of grey spheres (inset). Additional data evaluated for other values of the wetting parameters at $\sigma = 0.2$ and 0.8 are shown as diamonds and are just visible underneath the spheres. The inset is a surface rendered image of the chain of 6 overlapping grey spheres along the x -axis with inlet and outlet chambers either end. The structure is periodic in y and z .

Fig. 3 shows the measured permeability of the homogeneous grey nodes as a function of σ . The data points, squares, fall well on the theoretical line predicted by Eq. 20 confirming that the analysis of Walsh *et al.* carries over to the new combined model. For the fit, the viscosity, ν , is taken as $1/6$ as is normal for lattice Boltzmann with $\Delta x = \Delta t = \tau = 1$. The permeability of the overlapping grey spheres with white interstitial spaces is shown by the other curve of data points, circles. The permeability is everywhere greater than for the homogeneous grey nodes, reflecting the presence of the white channels through the matrix. For low σ , tending to 0, the system approaches uniform material and is little different to homogeneous (light) grey nodes. This is reflected in the permeability that tends towards the earlier theory curve. For increasing σ , tending towards 1, the system behaves increasingly like solid (black) spheres for which the theoretical permeability is expected to be in the range 0.023 ± 0.006 lu² (dependent on the assumed grey fraction, 76 or 80%) [47] in good agreement with the simulation.

Also included in the plot are 4 permeability data points for the matrix of grey spheres evaluated for other values of the wetting parameters $\phi_{gg} = \phi_{wg} = 0.05, 0.1$ and 0.2 at $\sigma = 0.2$ and another 4 for $\sigma = 0.8$, diamonds. The permeability values are the same to a high degree of accuracy showing that, so long as the grey nodes are saturated, the permeability depends only on σ , and not on the wetting parameter, ϕ_{gg} . A wide variety of scenarios can be envisaged with partially saturated (mixed liquid and gas) systems of mixed white and grey nodes leading

to measures of effective permeability. However, these are beyond the scope of the current work.

3. Contact angle

The contact angle made by liquid drops on black, grey and random mixed patterned black and grey surfaces was systematically studied. Simulations have been carried out in both 2D and 3D on systems of minimum size $(L_x, L_y) = (40, 120)$ and $(L_x, L_y, L_z) = (20, 40, 40)$ respectively, but, for patterned surfaces, as large as $(100, 1500)$ and $(30, 60, 60)$ with the intent of ensuring adequate statistics for the random pattern beneath the drop. The reduced temperature is 0.98 . In every case the system comprised white nodes, save for the surface. Although for a black surface, a thickness of 1 pixel suffices, for a grey surface this is not the case. The grey nodes can absorb fluid. Hence, due to the finite interface width of the fluid, 3 pixel layers of surface were always used. Moreover, since there are periodic boundary conditions, the fluid can permeate through grey surfaces and coalesce on both sides of that surface even if the system is initiated with a drop on only one side. Contact angles have been estimated from the gradient of tangents of arcs of circles fit to interface data points. The error in the angle is estimated from the spread of values recovered from fittings to different sets of interface points.

The first test was to show that equation 15 continues to describe the situation for black nodes, in part as a further test to validate the code. Fig. 4 shows experimental measurements of the contact angle, ϑ , for 2D liquid drops as a function ϕ_{wb} together with a fit calculated from Eq. 15. Good agreement between theory and experiment is observed showing that, in the limit of white and black nodes only, the model as coded reduces to the standard free energy model. It is evident that, for the parameters of this simulation, the theory is well approximated by $\vartheta = \arccos(\phi_{wb}/0.2)$.

FIG. 4: Cosine of the measured contact angle, $\cos(\vartheta)$, for a liquid drop equilibrated on a black surface as a function of ϕ_{wb} and a fit to the data according Eq. 15.

Fig. 5 shows four drops equilibrated on grey surfaces for $\sigma = 0.1$. The parameters are $(\phi_{wg}, \phi_{gg}) = (0.225, -$

FIG. 5: Drops equilibrated on a grey ($\sigma = 0.1$) surface for, from top, $(\phi_{wg}, \phi_{gg}) = (0.225, -0.133)$, $(0.525, -0.133)$, $(-0.525, 0.133)$ and $(-0.225, 0.133)$. Liquid shows as light colours, as indicated by the scale bar. The grey surface shows as the 3 rows of nodes at the bottom of each image, gas filled in the top two cases, liquid in the lower two. Note that the shape (hemispherical) but not volume of the seed drop was constant between simulations

0.133), $(0.525, -0.133)$, $(-0.525, 0.133)$ and $(-0.225, 0.133)$ respectively. The simulations were initiated with a hemispherical drop on the surface. The drop shown in the top row of the figure corresponds to a dewetting situation whereas that in the second corresponds to wetting. The third and fourth rows are similarly dewetting and wetting respectively. The difference is that within the top pair the grey surface has equilibrated saturated with gas whereas in the lower pair the surface has equilibrated with liquid. By varying the two parameters ϕ_{wg} and, ϕ_{gg} it is possible to model a wide variety of scenarios. It can be surmised that ϕ_{gg} characterises actual material-fluid interaction, *i.e.* wetting, of the unresolved internal porosity of the grey nodes since changing its sign causes the substrate to change from gas to liquid filling. This is developed further below, under wicking. On the other hand, ϕ_{wg} characterises the external surface-fluid interaction since increasing ϕ_{wg} increases the wetting of the drop on the external grey surface. These ideas are elaborated in the following sections.

Fig. 6 shows the measured contact angle at the external grey node surface as a function of ϕ_{wg} for different values of ϕ_{gg} . Data sets are shown for $\phi_{gg} = \pm 0.133$ and ± 0.067 and also $\phi_{wg} = 0$. Open symbols are drawn for situations in which the surface equilibrates gas filled and closed symbols in which it equilibrates liquid filled. Notice that, broadly, negative ϕ_{gg} corresponds to gas filling, positive to liquid filling. Within these two classes, the data clusters into two clear groups, with a clear dependence on ϕ_{wg} and a much weaker dependence

on ϕ_{gg} . We presume that this is because the equilibration of a drop on a surface depends on the *difference* in interfacial energies between the liquid-substrate, liquid-gas and gas-substrate. Due to the fluid-fluid term in the potential, the interfacial energy at the resolved surface of grey nodes (*i.e.* the external surface) depends not only on ϕ_{wg} but also on whether the grey nodes are liquid or gas filled. The case, $\phi_{gg} = 0$ is different and interesting. Now, by varying ϕ_{wg} it is possible to equilibrate with the substrate either gas or liquid filled. There is a clear discontinuity in the external surface contact angle close to $\phi_{wg} = 0$. Away from this, the contact angle trends fall into line with the previous data sets. We find that different spatial configurations of fluid can be equilibrated for the same total fluid content in a very small region of parameter space close to $\phi_{gg} = \phi_{wg} = 0$ dependent on the starting distribution of fluid. This ambiguity is presumed to be related to either or both of (i) the finite simulation cell size and (ii) the adsorption-desorption hysteresis described in the next section.

FIG. 6: Cosine of the measured contact angle, $\cos(\vartheta)$, for a liquid drop equilibrated on a grey surface as a function of ϕ_{wg} . The data points are for $\phi_{gg} = 0.133$ (solid squares), 0.067 (solid diamonds), 0 (solid and open circles), -0.067 (open diamonds) and -0.133 (open squares). Open symbols indicate the substrate equilibrates gas filled, closed liquid filled. The solid line is based on Eq. 15 but with ϕ_{wb} substituted by ϕ_{wg} . The dashed lines are the same curve displaced ± 0.333 along ϕ_{wg} axis.

As yet we do not have a theory to relate ϕ_{wg} and ϕ_{gg} to external contact angle. However, we note the solid and dashed lines in the figure. The solid line is the contact angle evaluated using Eq. 15 save that we substitute ϕ_{wg} for ϕ_{wb} . The two dotted lines show it displaced by $\pm 1/3$ along the ϕ_{wg} axis. The functional form fits the data moderately well, though we stress that we have no justification for this at present save that the shift might result from the additional surface energy term difference associated with liquid or gas filling within the substrate.

We have duplicated many of the simulations just reported for other values of σ , the permeability parameter. Within measurement error, we have failed to find any significant dependence of the contact angle on σ . As

FIG. 7: The contact angle on a grey surface for $\phi_{wg} = -0.225$ and $\phi_{gg} = 0.133$ as a function of σ .

an example, Fig. 7 shows the example of $(\phi_{wg}, \phi_{gg}) = (-0.225, 0.133)$.

Finally in this section, we explore the case of the contact angle of a drop of liquid in free space (white region) sitting on a surface randomly populated with grey and black nodes and how this varies with the fraction of grey nodes, s , in the surface and compare the results with a Cassie-Baxter type theoretical analysis according to which the cosine of the apparent contact angle, ϑ_{eff} is a weighted average of the contact angle on grey and black surfaces, viz:

$$\cos(\vartheta_{eff}) = s \cos(\vartheta_{grey}) + (1 - s) \cos(\vartheta_{black}) \quad (23)$$

FIG. 8: Equilibrated liquid drops on a surface that is randomly 0.7:0.3 (top) and 0.3:0.7 (bottom) grey:black. The surface occupies the bottom three rows of nodes. Black nodes show black. Liquid shows light. Notice that not all grey nodes in the surface are fully saturated with liquid.

Fig. 8 shows drops on mixed surfaces that are 0.3:0.7 ($s = 0.3$) and 0.7:0.3 ($s = 0.7$) grey:black. The simulation cell is $(L_x, L_y) = (120, 40)$ nodes, $\phi_{gg} = \phi_{gb} = 0.1$, $\phi_{wg} = \phi_{wb} = -0.133$ and $\sigma = 0.1$. A contact angle is established and is measurable in each case. Fig. 9 shows the effective contact angle for these parameters as a function of s , the fraction of grey nodes, in the mixed grey-black surface. For $s = 0$ the surface is entirely black.

FIG. 9: A plot of the effective contact angle of a liquid drop on a randomly mixed surface of grey (fraction s) and black nodes. The parameters are $\phi_{wb} = \phi_{wg} = -0.133$ and $\phi_{gg} = \phi_{gb} = 0.1$. The solid line is a fit based on Eq. 23.

For $\phi_{wb} = -0.133$ the contact angle is predicted to be 135° by Eq. 15. Empirically, it is measured as $143 \pm 1^\circ$ quite independent of system size and this value is used in subsequent analysis. As s increases, so the effective contact angle decreases. For $s = 1$ it is $35 \pm 1^\circ$. The error bars are the standard error for repeated simulations on different random surfaces leading to statistical variation. The solid line fit to the data results from the application of Eq. 23.

4. Wicking in grey nodes

A 3D system of $(L_x, L_y, L_z) = (100, 3, 3)$ nodes with periodic boundary conditions in all directions was created. Nodes with $x \leq 50$ were made white (bulk fluid) and with $x > 50$ grey (semi-permeable). The reduced temperature was set to 0.98. A slug of fluid of density equal to $\rho_{bulk-liq}$ 25 nodes long was placed in the bulk fluid region in contact with the grey interface, ($25 < x \leq 50$). Vapour at density $\rho_{bulk-liq}$ filled the remaining white and grey volumes. The parameter ϕ_{wg} was set equal to zero. No external forces act on the fluid. Dependent on the wetting of the unresolved porosity of the grey nodes, determined by ϕ_{gg} , there is a capillary force that draws the liquid out of the white nodes and into the grey nodes.

The position of the liquid front is plotted as a function of root time for the specific case of $\sigma = 0.1$ and $\phi_{gg} = 0.1596$ in Fig. 10. The figure shows that the front moves linearly with the square root of time as expected from the Lucas Washburn equation modified adapted for wicking in a porous medium [48] until the moment that the back of the slug enters the grey volume. Notice that the liquid / vapour interface width means that the apparent width of the equilibrated slug in the grey nodes is slightly greater than 25 lu. Initial equilibration of the interface also accounts for the slight offset at zero time. The gradient of the plot is a measure of the sorptivity.

FIG. 10: The position of the liquid front as it is drawn into homogeneous grey nodes by capillary action (wicking) as a function of root time for the specific case of $\phi_{gg} = 0.1596$ and $\sigma = 0.1$

FIG. 11: Sorptivity as a function of ϕ_{gg} (a) and the root of the cosine of grey node internal contact angle calculated on the basis of Eq. 15 but substituting ϕ_{gg} for ϕ_{wb} (b) for $\sigma = 0.1$ (circles), 0.2 (squares) and 0.3 (triangles). The solid lines are linear fits to the data.

The sorptivity is plotted in the upper part of Fig. 11 as a function of ϕ_{gg} for different values of σ . Notice that the sorptivity varies non-linearly with ϕ_{gg} . The white-black contact angle is given by Eq. 15 and for the parameters of these simulations it is very well approximated by $\theta_{wb} = \arccos(\phi_{wb}/0.2)$. Empirically, we find that if we write $\theta_{gg} = \arccos(\phi_{gg}/0.2)$, then the sorptivity varies linearly with the square root of $\cos(\vartheta_{gg})$, lower part of Fig. 11. The sorptivity also varies linearly with the square root of the permeability, $\kappa^{0.5}$, calculated using Eq.

FIG. 12: The data of Fig. 11 as a function of the square root of the permeability calculated on the basis of Eq. 20

20 as $\sqrt{(\sigma - 1)/12\sigma}$, as shown in Fig.12. Thus within the combined model there is independent control of the sorptivity in grey nodes both through the permeability and wetting parameters according to the Lucas-Wasburn equation, *viz*:

$$S \propto (\kappa \cos(\vartheta_{gg}))^{0.5} \quad (24)$$

We suggest that this is strong justification for recognising that ϕ_{gg} corresponds to an internal wetting parameter for the unresolved porosity of the grey nodes.

5. Sorption isotherm of the grey nodes

The wetting behaviour of grey nodes was studied by measuring water sorption isotherms of homogenous systems comprised of grey nodes ($\sigma(\mathbf{r}) = \sigma \forall \mathbf{r}$) at $\theta/\theta_c = 0.96$. Adsorption and desorption isotherms are normally obtained by measuring the equilibrated water content by mass of a real system as a function of the relative humidity (RH) of the surrounding environment. To model adsorption and desorption using the lattice Boltzmann algorithm, test structures of L^3 grey nodes were put in contact with a vapour source of $L^2 \times \alpha$ white nodes where α is the source width. Due to the periodic boundary conditions, the source was in contact with the test structure from two sides. The source width α was set equal to $(\varpi + 3)$ where ϖ is the width of the liquid – vapour interface defined in Eq. 10 and made equal to 1. The maximum environment relative humidity, $\text{RH} = 100\%$, corresponds to the coexistence density of the bulk gas, $\rho_{\text{bulk-gas}}$. To model the isotherms, the grey nodes are initially saturated with liquid ($\rho = \rho_{\text{bulk-liq}}$) and the source is initialised to 100% RH ($\rho = \rho_{\text{bulk-gas}}$). Once the system is equilibrated while holding the centre of the source at 100% RH, the RH of the source centre is progressively reduced (here in 3 % steps) and the system re-equilibrated at each RH step. Afterwards, the RH is progressively increased back to 100%. At each RH step,

the convergence is considered to be achieved when the relative mass change per 5000 time steps is less than 10^{-5} . Finally, the isotherms are obtained by plotting the average density in the system as a function of the relative humidity. The size of the systems was $L^3 = 10^3$ and the effective media parameter of the grey nodes was set to $\sigma_g = 0.01$. Figure 13 shows the desorption and adsorption curves for different numerical values of the internal wetting potential ϕ_{gg} ranging from 1.6 to 38.

FIG. 13: Mass of adsorbed fluid per node *vs.* RH for homogeneous grey systems with $\sigma_g = 0.01$ and different values of internal wetting potential ϕ_{gg} . In (a) $\phi_{gg} = 0.27$ and data points are shown explicitly. In (b) ϕ_{gg} ranges from 0.07 (sorption curves transition between 90 and 100 % RH) through 0.13, 0.20, 0.27, 0.53, 0.80, 1.07 (curves transition between 20 and 40 % RH) down to 1.6 for which the transition is not seen.

As described above, regardless of the internal wetting potential, the grey nodes are initially saturated with liquid so that their initial density is $\rho_{bulk-liq} = 1.41$. Figure 13(b) shows that as the internal wetting potential ϕ_{gg} is increased, so the amount of liquid adsorbed at equilibrium by grey nodes, when the external RH is 100%, also increases. This is consistent with expectation from the definition of the internal wetting potential. Moreover, the system with the highest wetting potential retains the liquid fluid for longer when the surrounding RH is de-

creased and starts adsorbing the liquid fluid earlier when the surrounding RH is increased. All the tested systems show considerable hysteresis. For the lowest value of internal wetting potential, $\phi_{gg} = 0.07$, the potential was not large enough to allow the fluid to condense when the RH of the source was increased back to 100%. For the highest value of internal wetting, $\phi_{gg} = 1.6$, the system held the liquid water down to the smallest tested RH, 7%. For $\phi_{gg} = 0$, the algorithm recovers the standard free energy model without grey nodes. In this case, because of the periodic boundary conditions in two of the spatial directions, the system is effectively infinite, empties at 100% RH and does not refill.

Figure 14 shows the effect of varying multiple parameters while keeping the internal wetting potential constant at $\phi_{gg} = 0.267$. First, the internal wetting was verified to be independent of the effective transport properties of the grey nodes. This was confirmed by varying the intrinsic permeability of the grey nodes by a factor 891 ($\sigma_g = 0.01$ to $\sigma_g = 0.9$). The result is as expected, since the isotherms are obtained at mass equilibrium and should be independent of the transport properties. Second, the isotherms were verified to be independent of the size of the system. This was tested by increasing the size of the system by 16 times from $10 \times 10 \times 10$ to $10 \times 40 \times 40$. The results shown in Fig. 14 show that the grey nodes display intrinsic sorption behaviour that is only dependent on the wetting potential ϕ_{gg} . Looking ahead, this parameter may yet be linked to a characteristic pore size.

FIG. 14: Mass of adsorbed fluid per grey node *vs.* RH for a homogeneous system of $\phi_{gg} = 0.267$ and $\sigma_g = 0.01$ as in Fig. 13(a) (light dash line) showing the effects of changing effective media permeability ($\sigma_g = 0.9$, dashed line) and of increasing the system size 16 fold (dotted line). Within measurement error, the curves are identical.

V. APPLICATION TO A POROUS MEDIUM

Here we demonstrate how the model captures the dynamics of two phase fluids in media containing solids,

pores and effective media. Although the model was implemented and validated in 3D, the examples shown in this section are limited to 2D to ease the visualization of the results. Two 2D pseudo-random systems of size 67×30 containing open pores, impermeable solids, and low-permeability effective media were created. Figure 15 shows an exemplar system, system A, and a modified version of it, system B, that has the grey nodes replaced by solid nodes. The white nodes are the same. The systems were put in contact with a vapour source at a varying RH as discussed in section IV B 5. Applying the new combined method to system B returns the results of the regular free energy model.

FIG. 15: (a) System A: a 2D porous medium containing pores (white), solids (black), and effective media (grey). (b) System B: a modified version of system A where the grey nodes are considered impermeable solids with no internal wetting. Both systems are connected to a vapour source from the LHS.

The isotherms of both systems were modelled. The grey nodes were assigned a wetting potential $\phi_{gg} = 0.267$ and an effective media parameter $\sigma_g = 0.01$. The sorption isotherms were shown to be independent of the permeability of the grey nodes in section IV B 5. Choosing a low value of σ allows faster transport and hence faster convergence of the algorithm. The interface wetting potentials were set to $\phi_{wb} = \phi_{wg} = \phi_{gb} = 0.267$. The isotherms are shown in Fig. 16. There are two important observations. The first and most important is that system A with grey nodes empties of liquid in two distinct stages (Fig. 16(a)) whereas system B without grey nodes empties in just one (Fig. 16(b)). For system A, the first drying stage ($\sim 100 - 85\%$ RH) corresponds to loss of liquid from the pores and the second ($\sim 85 - 75\%$ RH) to loss from the grey nodes; evidenced by separately plotting the average density of fluid in white and grey nodes, Fig. 17.

The second observation is that the amount of fluid adsorbed in the pores, that is the white nodes, of System A (Fig. 17) is very similar to the amount in system B (Fig. 16b). The small differences that do exist can be attributed easily to the presence of grey nodes in system A. As an example, at 75% RH, the average adsorbed fluid per white node in system B is slightly more than it is system A. This is explained by reference to Figs. 18 and 19 that show the fluid distributions in systems A and B respectively at critical values of the RH through the desorption-adsorption cycle. There is a liquid-saturated pore in the right-bottom corner of structure B which is

FIG. 16: Sorption isotherm loop of systems (a) A and (b) B. The isotherms are plotted as the average fluid density per system node excluding solid nodes. System B has more solid nodes than system A and hence contains proportionally less fluid overall.

FIG. 17: Sorption isotherm loop of system A split into two parts representing white (solid lines) and grey (dashed lines) nodes. The isotherms are plotted as the average fluid density per node of that colour.

isolated and cannot empty (Fig. 19). In contrast, the same pore does empty in system A. It does so by means of fluid transport through the grey nodes (Fig. 18). This

FIG. 18: (Colour on-line) The equilibrium fluid distribution in system A at selected values of the RH during a full desorption-adsorption cycle. From top left down to bottom right, the RH values are 100, 85, 84, 78, 76 (desorption), 76 (adsorption), 86, 94, 96 and 100 %. Liquid ($\rho > 1$) is shown in dark shades of blue, gas ($\rho < 1$) in light blue and solids in black. Note there is a small density difference between the liquid in white and grey nodes at high values of RH.

FIG. 19: (Colour on-line) The equilibrium fluid distribution in system B at selected values of the RH during a full desorption-adsorption cycle. From top left down to bottom right, the RH values are 100, 86, 85 (desorption), 85 (adsorption), 98 and 100 %. Liquid ($\rho > 1$) is shown in dark blue, gas ($\rho < 1$) in light blue and solids in black.

specific pore illustrates the ink-bottle effect [49] where, during desorption, a pore can be blocked from emptying (at the RH expected from the Kelvin equation) until a direct liquid-free access to the vapour source is provided. However, in this case, the pore is not blocked by liquid in explicitly resolved smaller-sized pores. Rather, it is blocked by liquid retained in grey nodes that is held there by the internal wetting potential of those grey nodes (Fig. 18).

VI. CONCLUSIONS

In this paper, a new lattice Boltzmann model for two phase fluids in effective media has been proposed, implemented and validated. In addition to black and white nodes representing solids and pores, the model includes grey nodes with effective media properties. Grey nodes

are described by *two* independent parameters. The first is the partial bounce back parameter σ_g . It links the intrinsic permeability κ to fluid transport properties in the effective media. The second, new, parameter, is the internal wetting potential ϕ_{gg} . It relates to the equilibrium fluid sorption properties of the effective media. Empirical evidence of how it could link to the contact angle of the fluid with the walls of unresolved porosity has been offered through wicking tests in particular. The model allows control of the wetting properties that occur at interfaces of different material type: pores and effective media; pores and solids; and effective media and solids, through a series of interface wetting potentials analogous to the wetting potential of the standard free energy model. Multiphase fluid transport and sorption in real porous media is clearly a complicated function of many parameters including meso and micro-scale geometry; physical-chemical properties and hold-up. Within the model as currently conceived, physical-chemical properties are the domain of wetting (χ and ϕ_{gg}); meso-scale geometry is resolved at the level of the simulation node size; micro-scale geometry is sub-resolution and subsumed within the effective media (χ and σ). This micro-porosity includes issues of hold-up. However, it is unlikely that these parameters alone will ultimately be sufficient to describe the most heterogeneous real systems for which one can imagine that even more complex schemes will be required. As it stands, we have rolled χ and ϕ_{gg} together into a single parameter giving us just *two* principal free model parameters. If it were felt that the local sub resolution microstructure influenced the fluid behaviour independent of single phase permeability then this restriction could be broken giving *three* parameters. Alternatively the local gradient conditions could be varied as suggested at the end of section III.

The model was demonstrated in section V where it was used to study fluid dynamics in pseudo-random porous media comprising pores, solids, and grey regions with both effective transport and wetting properties. The simulations readily captured a two-step isotherm (Fig. 16(a)). This would not be possible in a regular LB simulation without explicitly resolving pores of two distinct sizes - a more computer memory and processor time intensive process. The simulations also illustrated the ink-bottle effect during desorption (Fig. 18), showing how effective media correctly allows delayed emptying of otherwise isolated pores. This was a consequence of the grey nodes, but is also a manifestation of hold up. Overall, the work opens the door to future applications of effective media lattice Boltzmann models to study, amongst others things, the dynamics of two phase fluids in complex three-dimensional multi-scale microstructures such as, in our case, cement paste, or the rehydration of food powders.

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