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Microfluidics of imbibition in random porous media

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A free-energy lattice Boltzmann approach has been used to perform simulations of liquid penetration into random porous media. We focus our study on the effects of microstructures, particularly microtopography, on liquid penetration driven by capillary force and external pressure. For this purpose we set up a model structure that consists of a network of interconnected capillaries with varying pore geometries. The results showed that the discontinuities in the solid-surface curvature, as are present as corners on the capillary surfaces, have strong influences on liquid penetration through their pinning effects and interactions with local geometry.

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I. INTRODUCTION

Liquid penetration into random porous media is a ubiquitous phenomenon in nature and is of great interest in a wide range of technical applications, such as for liquid packaging, super-absorbent polymers, inkjet printing, and oil recovery.

A great deal of work has been done on one-phase fluid flow, where, phenomenologically, Darcy's law approximately holds for a wide variety of porous media. The focus of both experimental and theoretical work has been on finding a functional relation between the permeability and structural properties of the porous media [1,2]. For example, experimental results show that the Carman-Kozeny equation provides reasonable estimates of Darcy's permeability coefficient for random packaging of spheres [3].

In two-phase flow, however, the liquid penetrates the structure also by capillary pressure caused by the curvature of the interface between the two phases. A review of the challenges in prediction of behavior of multiphase materials is given by Wang *et al.* [4]. The Lucas-Washburn equation has been used to describe such penetration behavior [5]. In its original form, the Lucas-Washburn equation assumes smooth, chemically homogeneous, and continuous cylindrical pores, the conditions of which random porous media hardly meet. Despite this, the Lucas-Washburn equation has been utilized to describe the overall behavior of liquid by introducing an effective capillary radius and length.

A natural extension of the simple Lucas-Washburn model is a capillary bundle model, which has been widely used in the engineering field to explain experimental data of mercury intrusion into porous media. Because of the obvious discrepancy in geometry of capillary bundles from real porous networks, a further extension was made by Ridgeway and other researchers [6–8] to construct a more general capillary network model. This model represents (random) porous networks as a lattice, consisting of pores and capillaries with varying sizes [6–8]. Because of its easiness of incorporating size distributions, it has been commercialized and used for interpreting mercury porosimetry data. An important feature of these models is, however, that local geometry is represented

by a sole factor, (effective) capillary radius, and the fluid-solid interface interaction by (static) contact angle, the latter, which is generally a function of flow conditions (capillary number), and thus varies with the characteristic flow speed in the system [9–11].

Mark *et al.* used a multiscale approach to calculate the fluid penetration in paperboard [12]. The macroscale model was based on Darcy's law and mass conservation, where the permeability and capillary pressure must be calculated as a function of saturation level from a microscopic model. On that level, instead of directly solving the two-phase flow problem, a pore morphology model was used [13]. The pore morphology model determined the fluid-gas interface geometry by inserting different sizes of spheres in the porous media and thus provides the capillary pressure through the Young-Laplace equation.

Hyvluoma *et al.* used the so-called Shan-Chen lattice Boltzmann model to simulate two-phase fluid flow in a random porous medium, which consisted of a 3D reconstruction of a sample of paperboard, based on x-ray microtomography [14]. They found that, in spite of a rather small system size as compared with the heterogeneities in the structure, the simulated behavior was described well by the Lucas-Washburn equation. However, one drawback of this method is that the static contact angle cannot be known beforehand but instead must be obtained from the simulation itself.

Although these studies have been able to describe successfully the effective behavior of liquid penetration in an entire porous medium, they tend to provide very little information on microfluidics in the porous media, namely the deformation of the fluid interface and complex interactions with local geometry. Curved channels, size variations of pores, roughness of surfaces that can appear as sharp edges or corners, and blocked or dead-end pores, all these features can significantly affect the liquid penetration behavior.

In this work, we focus on the effects of microstructures, particularly microtopography, on liquid penetration driven by capillary forces and external pressure. For this purpose we set up a model structure that consists of a network of interconnected capillaries. We use a lattice Boltzmann method for binary fluids [15,16] together with a wetting boundary condition [17–19] to solve the dynamic equations for this two-phase microfluidic problem.

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II. THEORY

A. Governing equations

In this study we consider the penetration of liquid into random porous structures as a binary flow problem, that is, the flow of liquid and gas. To describe the binary fluid system we have used a diffuse interface model developed by Cahn and Hilliard. In the Cahn-Hilliard model, it is assumed that the local free-energy density of a binary fluid is a function of composition and composition gradient. To take wetting surfaces into account, Cahn introduced a surface energy term [19]. Assuming that the solid surface-fluid interfacial energy is a function of only the fluid composition at the solid surface, the equilibrium properties of such a solid-binary fluid system can be described by a free-energy functional [15,19,20]:

$$\Psi = \Psi_b + \Psi_s$$

$$= \int_V \left[\psi_b(C) + \frac{\kappa}{2} \partial_\alpha C \partial_\alpha C \right] dV + \int_S \psi_s(C) dS, \quad (1)$$

where $\psi_b(C)$ is the bulk free-energy density, and $\psi_s(C)$ is a surface free-energy density function. C is the order parameter and is a measure of the amount of phase, i.e., the concentration. The gradient term in Eq. (1) represents the contribution from the fluid-fluid interface. κ is a constant related to the surface tension, and α represents the Cartesian coordinates. In order to model the immiscibility of the two fluids, ψ_b is taken to be [15]

$$\psi_b = \frac{1}{3} \rho \ln \rho + A \left(-\frac{1}{2} C^2 + \frac{1}{4} C^4 \right), \quad (2)$$

where ρ is the average fluid density and A is a constant. This choice of bulk free-energy density has a double-well structure with minima at $C = \pm 1$, corresponding to the two stable phases of the fluids.

At equilibrium, the concentration profile both at the solid surface and in the bulk must minimize the total free energy, Eq. (1). In other words, from the calculus of variations, the concentration profile C must first satisfy

$$\frac{\partial \Psi}{\partial C} = \frac{\partial \psi_b}{\partial C} - \kappa (\partial_\alpha^2 C) = \mu_{\text{chem}} = \text{const.} \quad (3)$$

and, second, the natural boundary condition [20]:

$$\partial_\perp C = \frac{1}{\kappa} \frac{d\psi_s}{dC}, \quad (4)$$

where μ_{chem} is the chemical potential, and $\partial_\perp C$ denotes the derivative in the direction normal to the solid surface and into the fluid domain. The choice of Eq. (2) for ψ_b , and setting the right-hand side of Eq. (3) to zero, yields an interface with surface tension, σ , and interface width, ξ [15]:

$$\sigma = \sqrt{8\kappa A/9}, \quad \xi = \sqrt{\kappa/A}. \quad (5)$$

The choice of surface free-energy density function, $\psi_s(C)$, is, however, not arbitrary but is very important for accurately capturing the physics of wetting [17]. It was shown that in order for ψ_s to satisfy Eqs. (3) and (4), a cubic function is necessary and the following expression can be found [17]:

$$\psi_s(C) = \sqrt{\frac{\kappa A}{2}} \cos \theta \left(\frac{1}{3} C^3 - C \right) + \text{const.} \quad (6)$$

The implication of this is significant. With this choice of surface free-energy density, the boundary condition, Eq. (4), states that the gradient of the order parameter C , in the normal direction to the solid surface, must be zero when $C \pm 1$. In other words, at the boundary facing one of the two stable phases, there should not be any concentration gradient. In contrast, a linear choice of ψ_s always gives a variation in the concentration at the boundary, even when the boundary faces a pure phase, creating an artificial “film” on the surface. Elimination of this spurious variation in the concentration was shown in Ref. [17]. This enables simulations of a larger range of contact angles and also capillary intrusion, even with relatively low resolution of the capillaries, at a high accuracy. This is of particular importance in the simulation of capillary intrusion into porous media, where each pore would require high resolution and, thus, high computational cost. This “film” should be distinguished from a physical precursor film created near the contact line [21].

The dynamics is governed by the continuity equation, the Navier-Stokes equations, and the convection-diffusion equation [15,16]:

$$\partial_t \rho + \partial_\alpha (\rho u_\alpha) = 0, \quad (7)$$

$$\partial_t (\rho u_\beta) + \partial_\alpha (\rho u_\beta u_\alpha) = -\partial_\alpha P_{\alpha\beta} + \partial_\alpha [\nu \rho (\partial_\beta u_\alpha + \partial_\alpha u_\beta)], \quad (8)$$

$$\partial_t C + \partial_\alpha (C u_\alpha) = M \nabla^2 \mu_{\text{chem}}, \quad (9)$$

where $\mathbf{u}$ is the velocity, M is the mobility, and ν is the kinematic viscosity.

The thermodynamic properties of the system enter the hydrodynamic description through the chemical potential μ_{chem} and the pressure tensor $P_{\alpha\beta}$. The pressure tensor can be found from the free-energy functional and is given by [15,16]

$$P_{\alpha\beta} = p \delta_{\alpha\beta} + \kappa \partial_\alpha C \partial_\beta C, \quad (10)$$

where

$$p = p_0 - \kappa C \partial_\alpha^2 C - \frac{\kappa}{2} \partial_\alpha C \partial_\alpha C, \quad (11)$$

$$p_0 = \frac{1}{3} \rho + A \left(-\frac{1}{2} C^2 + \frac{3}{4} C^4 \right). \quad (12)$$

III. NUMERICAL MODEL

A. The lattice Boltzmann algorithm

In this work, we use a lattice Boltzmann numerical scheme [15] to solve the above equations, together with a wetting boundary condition, for diffuse interface models [17,18]. The lattice Boltzmann method solves the Navier-Stokes equations by following the evolution of particle velocity distribution functions on a fixed regular lattice. Interfaces between the two fluids are modeled through a scalar phase field, and the model makes specific tracking of surfaces unnecessary and, therefore, there are no assumptions of the specific shape of the interface.

We use the binary free energy lattice Boltzmann model, first developed by Swift *et al.* [22] and later extended by Briant *et al.* [15] and Pooley *et al.* [16]. The binary free energy lattice Boltzmann model includes two particle distribution functions, $f_i(\mathbf{r}, t)$ and $g_i(\mathbf{r}, t)$, where $\mathbf{r}$ denotes the position in the lattice

and i is the lattice direction. In this work, we use a two-dimensional lattice with directions denoted $\mathbf{e}_0 = (0,0)$, $\mathbf{e}_{1,3} = (\pm 1,0)$, $\mathbf{e}_{2,4} = (0,\pm 1)$, $\mathbf{e}_{5,7} = (\pm 1,\pm 1)$, and $\mathbf{e}_{6,8} = (\mp 1,\pm 1)$. The distribution functions are updated in two steps: a collision step,

$$\begin{aligned} f_i^*(\mathbf{r},t) &= f_i(\mathbf{r},t) - \frac{1}{\tau_f} [f_i - f_i^{\text{eq}}], \\ g_i^*(\mathbf{r},t) &= g_i(\mathbf{r},t) - \frac{1}{\tau_g} [g_i - g_i^{\text{eq}}], \end{aligned} \quad (13)$$

and a streaming step,

$$\begin{aligned} f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) &= f_i^*(\mathbf{r},t), \\ g_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) &= g_i^*(\mathbf{r},t), \end{aligned} \quad (14)$$

where Δt is the time step, f_i^{eq} and g_i^{eq} are the equilibrium distribution functions, and τ_f and τ_g are the relaxation parameters, which will be described later in the paper.

$f_i(\mathbf{r},t)$ is related to macroscopic fluid density ρ and momentum $\rho \mathbf{u}$, and $g_i(\mathbf{r},t)$ is related to the order parameter C :

$$\rho = \sum_i f_i, \quad (15a)$$

$$\rho \mathbf{u} = \sum_i f_i \mathbf{e}_i, \quad (15b)$$

$$C = \sum_i g_i, \quad (15c)$$

where $\mathbf{e}_i$ denotes the lattice velocity vector.

The equilibrium distribution functions f_i^{eq} and g_i^{eq} can be written as [15,23]

$$\begin{aligned} f_i^{\text{eq}}(\mathbf{r}) &= A_i + B_i e_{i\alpha} u_\alpha + C_i u^2 + D_i e_{i\alpha} e_{i\beta} u_\alpha u_\beta \\ &\quad + G_{i\alpha\beta} e_{i\alpha} e_{i\beta}, \end{aligned} \quad (16)$$

$$g_i^{\text{eq}}(\mathbf{r}) = H_i + K_i e_{i\alpha} u_\alpha + J_i u^2 + Q_i e_{i\alpha} e_{i\beta} u_\alpha u_\beta. \quad (17)$$

The coefficients are derived by enforcing constraints on the moments of the equilibrium distribution functions. In order for the collision step to retain the correct conservation laws, the first two moments of the equilibrium distribution functions are constrained by [15,23]

$$\sum_i f_i^{\text{eq}} = \rho, \quad (18)$$

$$\sum_i f_i^{\text{eq}} e_{i\alpha} = \rho u_\alpha, \quad (19)$$

$$\sum_i g_i^{\text{eq}} = C, \quad (20)$$

$$\sum_i g_i^{\text{eq}} e_{i\alpha} = C u_\alpha. \quad (21)$$

Higher-order moments of f_i^{eq} and g_i^{eq} were chosen such that the evolution scheme correctly describes the dynamics of a binary fluid [15,23]:

$$\begin{aligned} \sum_i f_i^{\text{eq}} e_{i\alpha} e_{i\beta} &= P_{\alpha\beta} + \rho u_\alpha u_\beta + \nu (u_\alpha \partial_\beta \rho + u_\beta \partial_\alpha \rho + u_\gamma \partial_\gamma \rho \delta_{\alpha\beta}), \end{aligned} \quad (22)$$

$$\sum_i f_i^{\text{eq}} e_{i\alpha} e_{i\beta} e_{i\gamma} = \frac{\rho}{3} (u_\alpha \delta_{\beta\gamma} + u_\beta \delta_{\alpha\gamma} + u_\gamma \delta_{\alpha\beta}), \quad (23)$$

$$\sum_i g_i^{\text{eq}} e_{i\alpha} e_{i\beta} = \Gamma \mu_{\text{chem}} \delta_{\alpha\beta} + C u_\alpha u_\beta, \quad (24)$$

where ν is the kinematic viscosity of the fluid and Γ is a diffusion coefficient. A set of coefficients for Eqs. (16) and (17) can be found in Refs. [15,17].

The relaxation parameters τ_f and τ_g are related to the kinematic viscosity, ν , and mobility, M , through

$$\nu = \frac{1}{3} (\tau_f - \frac{1}{2}), \quad (25)$$

$$M = \Gamma (\tau_g - \frac{1}{2}). \quad (26)$$

In our simulations the mobility was chosen as $M = 0.5$, the grid resolution as $1 \mu\text{m}$ per 2 lattice units, and the interface width as $\xi = 1$. These parameter values have been shown to give accurate results for droplet-spreading and capillary-rise problems in a previous study [17].

B. Boundary conditions

Figure 1 shows a simulation set-up used for this study. We first consider an inlet-outlet boundary condition. Here, we follow the approach by Briant *et al.* and Zou and He [23,24]. Consider a boundary node situated on the x axis at the inlet of the system in Fig. 1. After streaming, f_0, f_1, f_3, f_4, f_7 , and f_8 are known, while f_2, f_5 , and f_6 are unknown. The unknown components are solved for using Eqs. (15a) and (15b), together with the constraint of the boundary condition; $\rho_{\text{in}} = \rho$ is taken as constant at the boundary, and $u_y = 0$ and $f_2 = f_4$, for symmetry. This yields

$$f_5 = f_7 - \frac{1}{2} (f_1 - f_3) + \frac{1}{6} \rho_{\text{in}} u_x, \quad (27)$$

$$f_6 = f_8 + \frac{1}{2} (f_1 - f_3) + \frac{1}{6} \rho_{\text{in}} u_x, \quad (28)$$

$$u_x = 1 - \frac{[f_0 + f_1 + f_3 + 2(f_4 + f_7 + f_8)]}{\rho_{\text{in}}}. \quad (29)$$

FIG. 1. Schematic of the simulation setup. Black areas represent the liquid phase, white areas represent the gas phase, and gray areas represent solid surfaces.

The same approach was used for the g components. This boundary condition also allows us to monitor the pressure at the inlet and the outlet.

Next we consider a no-slip boundary condition, $\mathbf{u} = 0$ at solid walls. We again follow the same approach as Briant *et al.* and Zou and He [23,24]. Consider a boundary node situated on the y axis at the solid wall on the left-hand side in Fig. 1. Components f_0, f_2, f_3, f_4, f_6 , and f_7 are determined by the streaming step, but f_1, f_5 , and f_8 are unknown. From symmetry, we obtain $f_1 = f_3$, while f_5 and f_8 were determined from Eqs. (15a) and (15b):

$$f_5 = f_7 - \frac{1}{2}(f_2 - f_4), \quad (30)$$

$$f_8 = f_6 + \frac{1}{2}(f_2 - f_4). \quad (31)$$

The same approach is used to find the components of g .

In addition to satisfying the no-slip boundary condition, the order parameter must also satisfy the wetting boundary condition given by Eqs. (4) and (6). This was done by implementing an additional condition on the order parameter [17]. For simplicity we show the one-dimensional case. To avoid numerical stability issues and improve accuracy the total discretized free energy close to the solid boundary was minimized to find a wetting boundary condition. The total discrete free energy is given by

$$\begin{aligned} W_{\text{tot}} &= W_s + W_b \\ &= W_s + \frac{1}{3}\rho_0 \ln \rho_0 + A \left(-\frac{1}{2}C_m^2 + \frac{1}{4}C_m^4 \right) \\ &\quad + \frac{\kappa}{2} \left(\frac{C_1 - C_0}{\Delta x} \right)^2, \end{aligned} \quad (32)$$

where W_s is the discrete surface free-energy density, W_b is the discrete free energy in the bulk, C_0 is the value of C at the wall node, C_1 is the value of C at the first fluid node, and $C_m = (C_0 + C_1)/2$. ρ_0 is the density, and the derivative dC/dx was approximated by $(C_0 - C_1)/\Delta x$. To avoid energy minima outside the interval $-1 < C < 1$, caused by numerical fluctuations, W_s must be chosen appropriately: for contact angles less than 90° , we take

$$W_s = k \left(\frac{1}{3}C_0^3 - C_0 \right) \text{sgn}(1 + C_0), \quad (33)$$

and for angles larger than 90° ,

$$W_s = k \left(\frac{1}{3}C_0^3 - C_0 \right) \text{sgn}(1 - C_0), \quad (34)$$

where $k = \sqrt{\kappa A/2} \cos \theta$. Minimizing the discrete form of the total free energy with respect to C_0 gives

$$\frac{\partial(W_s + W_b)}{\partial C_0} = 0. \quad (35)$$

Solving Eq. (35) for C_0 , we have the value for the order parameter at the wall node, which is inserted to Eqs. (16) and (17) to obtain the equilibrium distribution functions. Such a value of C_0 is considered to be a “target” value for the equilibrium. The actual value of the order parameter on the other hand is calculated by Eq. (15c) as usual. Hence, the order parameter is conserved at the collision step.

A major challenge when dealing with numerical simulations of patterned structures is to correctly handle boundary conditions at corners or discontinuities in curvature on solid

surfaces. Above we have described (Sec. III B) the discretization of the wetting boundary condition for a flat surface. The wetting boundary condition Eq. (4) defines the concentration value in the normal direction from a flat surface. At corners, no unique direction exists, but there are two possible directions from the neighbors. In this case, we solve Eq. (35) in each direction at the corner and then take the average value as the boundary value at corners.

IV. RESULTS

A. Two-phase flow in porous media

We have performed simulations of liquid penetration into a random porous structure (Fig. 1) by varying the pressure ratio ($p_{\text{in}}/p_{\text{out}}$) between the inlet and outlet of the system and the contact angle (θ) of the solid surfaces. The surface tension was 0.073 N/m and the viscosity of the liquid phase was set to about ten times that of the gas phase. Initially the bottom part of the system is filled with the liquid phase while the porous structure is filled with the gas phase. The liquid is then allowed to penetrate the structure through capillary forces, with and without external pressure. The percentage of penetrated liquid into the structure is recorded as a function of time.

In Fig. 2 the percentage of penetrated liquid into the structure is shown as a function of square root of time for different external pressures, $p_{\text{in}}/p_{\text{out}} = 1, 1.0006, 1.006$ and different contact angles, $\theta = 20^\circ$ and $\theta = 60^\circ$. In a majority of the cases tested, the penetration of the liquid into the structure stops and the $\theta = 60^\circ$ and $p_{\text{in}}/p_{\text{out}} = 1$ case gives the least penetration. In some cases the penetration curves exhibit a series of bumps, suggesting that in some places in the structure the penetration slows down and later accelerates.

Figures 3 and 4 show snapshots of the liquid penetration for the two cases: $\theta = 60^\circ$ and $p_{\text{in}}/p_{\text{out}} = 1$, in which only capillary forces are present, and $\theta = 20^\circ$ and $p_{\text{in}}/p_{\text{out}} = 1.006$ in which both capillary forces and external pressure determine the penetration. It can be seen in Fig. 3 that the liquid fronts stop and the contact lines are pinned by the geometry of the solid structure. It is also clear from Fig. 3(d) that the contact lines are pinned by high curvature points in the structure and also in those places where the pores become wider. It can also be seen that at the time when the liquid front stops (is pinned), the curvature of the interface between the two phases is lost, as the interface continues to minimize its surface. A loss of the curvature of the interface obviously implies that capillary pressure is no longer driving the liquid front further. However, as seen in Fig. 4, with the additional external pressure, the penetration further progresses.

It is also noted that in both Figs. 3 and 4, so-called dead-end capillaries don't seem to be penetrated by liquid. Figure 5 shows the relative pressure field at $t = 0.001 \text{ s}$ and $\theta = 20^\circ$ for the case when external pressure is not present. The relative pressure is defined as the ratio of the pressure to the pressure at the inlet (or outlet). A marked difference is seen in the pressure distribution between the open and dead-end capillaries in the structure. In the open capillaries, a pressure increase is limited to just in front of the liquid-gas interface, whereas an increase in the pressure is clearly visible in the typical dead-end capillaries. This pressure increase is

FIG. 2. The percentage of penetrated liquid as a function of square root of time for the three different pressure ratios. (a) $\theta = 20^\circ$; (b) $\theta = 60^\circ$.

obviously another mechanism that creates a resistance to liquid penetration. This has also been seen by Phan *et al.* [25].

These results suggest that there are certain microstructural features that are unique to random porous media but that are not present in typical Lucas-Washburn analyses. These are (1) “corners” or high-curvature points on solid surfaces, i.e., a point where a sharp change in the direction of the surface normal occurs, in the form of surface roughness or irregular shapes, and (2) branching and varying-width capillaries. As seen in the above results, these features seem to have very

significant impact on the liquid penetration behavior. Next, we look at how these properties can influence the penetration behavior in more detail.

B. Pore geometry and pinning behavior

To investigate the effect of high-curvature points and pinning behavior on liquid penetration, we have performed simulations using a test geometry, as seen in Fig. 6. This geometry represents, in a small-scale, a discontinuity of

FIG. 3. $p_{in}/p_{out} = 1$, $\theta = 60^\circ$. (a) $t = 0.002$ s, (b) $t = 0.02$ s, (c) $t = 0.04$ s, (d) $t = 0.08$ s.

FIG. 4. $p_{\text{in}}/p_{\text{out}} = 1.006$, $\theta = 20^\circ$. (a) $t = 0.002$ s, (b) $t = 0.02$ s, (c) $t = 0.04$ s, (d) $t = 0.08$ s.

curvature on a solid surface, such as a surface roughness in the form of a sharp edge or a high-curvature point, but in a larger scale, the geometry represents a pore that is widening or is branching. In this set-up, we can vary the contact angles, θ_1 and θ_2 , independently. The angle θ_1 controls the angle ψ (Fig. 6), the maximum possible angle that the liquid pinned at the discontinuity can achieve before it passes the discontinuity.

When the liquid passes the high-curvature point (Fig. 7), it should move from the contact angle θ to the angle $\psi_{\text{max}} = 180^\circ - \psi_{\text{discontinuity}} + \theta$ [21]. Applying this to the case in

FIG. 5. The relative pressure field at $t = 0.002$ s for $\theta = 20^\circ$. No external pressure, $p_{\text{in}} = p_{\text{out}}$. The relative pressure is defined as the ratio of the pressure to the pressure at inlet (or outlet).

FIG. 6. Schematic of system used to test the behavior of the contact angle at high-curvature points. θ_1 is the contact angle of the solid surface on the left-hand side and θ_2 is the contact angle of the solid surface on the right-hand side.

FIG. 7. Possible contact angle values at a high curvature point.

Fig. 6, we find the condition for the liquid to be pinned as

$$\psi - \psi_{\max} \leq 0. \quad (36)$$

Although the above consideration is for an equilibrium state, it may be a good approximation to describe the pinning behavior of the liquid near a high-curvature point. We tested this condition in the setting in Fig. 6, where the contact angle on the left solid surface θ_1 was set to 20° and the contact angle on the right solid surface θ_2 was varied between 30° and 70° . The results are given in Table I. “No” indicates that the contact line is not pinned. ψ_{flat} is the angle when the interface is assumed to be flat (Fig. 6).

The deviation in the results from the flat interface case is obviously due to the fact that the interface in the simulations is not flat so that the angle ψ can exceed $\psi_{\max}$ at a slightly smaller angle than ψ_{flat} .

These results show not only the very strong effect of the high-curvature points present on the solid surface but also the effect of widening channels on pinning. We will elaborate this latter effect in the next section.

C. Effect of varying capillary width

To further investigate the effect of different geometric structures on the liquid penetration into random porous media, we have performed simulations of individual capillaries with varying width. We use two different types of capillary, narrow-to-wide and wide-to-narrow; see Fig. 8. The equilibrium contact angle in both cases was set to be $\theta = 20^\circ$.

Figure 9 shows the results for the two different types of capillary. The Lucas-Washburn solutions for the cases of the two different uniform diameters are also shown in the same graph. (We have taken into account the viscosity of the gas phase and the dynamic contact angle.) In the case of the narrow-to-wide capillary it is clear that the liquid front stops when it reaches the wider part of the capillary. However, in the case of the wide-to-narrow capillary the liquid front continues to move into the narrower part and even accelerates its movement. The reason for the behavior for the narrow-to-wide capillary can be easily explained by

TABLE I. Results from simulations using the test geometry, as seen in Fig. 6. “No” indicates that the contact line is not pinned.

$\psi = \psi_{\text{flat}}$	θ_2	$\psi_{\max}$	Flat interface	Simulation
160°	30°	120°	No	No
160°	40°	130°	No	No
160°	50°	140°	No	No
160°	60°	150°	No	Yes
160°	70°	160°	Yes	Yes

FIG. 8. Capillaries with varying width.

the argument in the previous section. As given in Sec. IV B, pinning will occur if

$$\psi - \psi_{\max} \leq 0. \quad (37)$$

In the case of Fig. 8, $\psi_{\max} = 110^\circ$ as the contact angle is $\theta = 20^\circ$ and $\psi_{\text{discontinuity}} = 90^\circ$. From the symmetry of the pore geometry, the maximum possible $\psi = 90^\circ$. Therefore, as the interface minimizes its interface and forms a straight line between the two corners, penetration stops. In the case of the wide-to-narrow capillary, the contact line must also pass a corner but in the opposite direction. For this situation, the curvature of the interface is always maintained (or even increased) and, therefore, the penetration continues. The same behavior has been reported by Mehrabian *et al.* [26] who studied in detail the hydrodynamics of the curvature of the fluid-fluid interface as it passes narrowing and widening channels and also the effect of corners on the contact line.

It is to be noted that in the case of the wide-to-narrow capillary [Fig. 9(b)], the liquid penetration is initially slower than that predicted by the Lucas-Washburn equation for the corresponding diameter (wide), suggesting that there is a resistance to penetration caused by the finite viscosity of the gas phase that creates an increased resistance as it passes the narrow part of the capillary.

In Fig. 10, the case of narrow-to-wide capillary is presented for different external pressures between the inlet and outlet of the system: $p_{\text{in}}/p_{\text{out}} = 1, 1.0006, 1.006$, for $\theta = 20^\circ$. Again, the Lucas-Washburn solutions for the two different diameters are also shown in the same graph as a reference. It is obvious that as the external pressure increases to a critical level, the liquid front can pass from the narrow to the wide part of the capillary.

This critical pressure may be estimated by considering the static equilibrium, at which the liquid front, under the influence of external pressure, is about to spread to the new surface (Fig. 11):

$$p_{\text{out}} + p_{\text{cap}} = p_{\text{in}}, \quad (38)$$

FIG. 9. Liquid penetration as a function of time in capillaries with varying width. (a) narrow-to-wide; (b) wide-to-narrow.

where p_{cap} is the capillary pressure resulting from the curved interface and given by

$$p_{\text{cap}} = \frac{2\sigma \sin \theta_b}{d}, \quad (39)$$

where σ is the surface tension, d is the diameter of the capillary, and $\theta_b = \psi - 90^\circ$ where ψ is the angle according to Fig. 6. To fulfill the condition $\psi > \psi_{\text{max}}$, the critical pressure ratio should be $(\frac{p_{\text{in}}}{p_{\text{out}}})_{\text{critical}} > 1.0015$. The simulations in this study indeed showed that the contact line was unable to pass to the narrow-to-wide part for $\frac{p_{\text{in}}}{p_{\text{out}}} = 1.0006$, but able to pass for $\frac{p_{\text{in}}}{p_{\text{out}}} = 1.006$.

However, it should be noted that this static analysis consistently underestimates the critical pressure in the dynamic case (simulation). As additional pressure develops in the back of the liquid front when the liquid front starts decelerating, the actual critical pressure required for overcoming this pinning effect, without any delay, becomes much higher than that estimated from the static analysis. (In the previous case, $\frac{p_{\text{in}}}{p_{\text{out}}} \approx 1.005$ instead of 1.0015.) This suggests not only a need for the direct simulation method but also poses a fundamental question of

effective capillary models used for explaining imbibitions in random porous networks.

V. CONCLUDING REMARKS

In this work, we have used a free-energy lattice Boltzmann approach to perform simulations of liquid penetration into random porous media. For this purpose we set up a model structure that consists of a network of interconnected capillaries of varying size and shape. We varied the contact angle of the solid surfaces and external pressure differences. Among the structural features that are unique to random porous media, as compared with smooth straight cylinders used in the Lucas-Washburn models, “corners” or high-curvature points on solid surfaces showed critical effects on the penetration behavior of liquid, through their pinning effects and complex interactions with local geometries. Without this feature, the random porous media with nonstraight channels but with slowly varying surface curvature may not differ greatly from those effective models based on the Lucas-Washburn equation. It is important to note that there are also some challenges in the simulations performed in this study for liquid penetration into random porous media. One is the two-dimensional implementation

FIG. 10. Liquid penetration as a function of time in the narrow-to-wide capillary with different pressure ratios between the inlet (p_{in}) and outlet (p_{out}).

FIG. 11. The liquid front under influence of external pressure as it is about to spread to the new surface.

of the lattice Boltzmann method. Although the formulation presented here is for a general three-dimensional case, the implementation was made in two dimensions because of the computational cost associated with three-dimensional simulations. This limits quantitative predictions of the penetration behavior. This is because isolated pores in two dimensions are often interconnected in three dimensions and, thus, a permeability estimate based on a two-dimensional structure tends to give a lower value. Therefore, the results obtained here are still of a semiquantitative nature. The second challenge is more general, commonly existing in the multiphase lattice Boltzmann methods. In the free-energy lattice Boltzmann model we have used, the immiscible fluids are described by a simplified form of the two-well bulk free-energy function. This results in the two fluids having the same density. In addition, the viscosity ratio between the fluids is relatively

low because of high gradients at interfaces that result in numerical instabilities. More recent implementations of the lattice Boltzmann model have attempted to solve these issues, but at an increased computational cost and complexity of the numerical scheme. This study is limited to a creeping flow range and, therefore, the effects of inertia and, thus, density ratio play a very little role to the phenomena studied here. For the viscosity ratio, we took ten as a compromise between numerical stability and accuracy. In order to expand the application range of the lattice Boltzmann scheme, these points must be further developed. However, it should also be noted that in our simulation we changed the viscosity ratio within a limited range and were able to confirm that the effect does not affect our major conclusion; i.e., the local geometry near the contact point has a significant effect on wetting dynamics and, thus, local capillary force.

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