

Capillary Displacement of Viscous Liquids in Geometries with Axial Variations

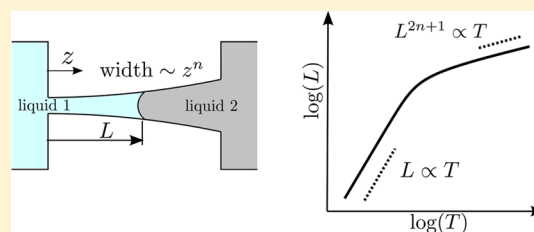
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ABSTRACT: Axial variations in geometry and presence of viscous displaced fluid are known to alter the diffusive-dynamics of capillary imbibition of a wetting liquid. We here show that the coupled effect of axially varying capillary geometry and finite viscosity of the displaced fluid can lead to significant variations in both short and long time dynamics of imbibition. Based on a theoretical model and lattice Boltzmann simulations, we analyze capillary displacement of a viscous liquid in straight and diverging capillaries. At short times, the imbibition length scales proportionally with time as opposed to the diffusive-dynamics of imbibition of a single wetting liquid. Whereas, at long times, geometry-dependent power-law behavior occurs which qualitatively resembles single liquid imbibition. The distance at which the crossover between these two regimes occurs depends strongly on the viscosities of the imbibing and the displaced liquid. Additionally, our simulations show that the early time imbibition dynamics are also affected by the dynamic contact angle of the meniscus.



INTRODUCTION

Capillary driven flows are ubiquitous to a wide variety of processes, including enhanced oil recovery,¹ groundwater pollution,² tissue drug delivery,³ and fabrication of ceramics.⁴ These processes leverage the interfacial tension at the interface separating two immiscible fluids to imbibe a fluid in narrow capillaries or porous media while displacing the residing fluid.⁵ Spontaneous imbibition depends primarily on the differential wettability of the capillary surface for imbibing fluid. Besides the surface wettability, the dynamics of imbibition depends on the interfacial tension, fluid properties, and the geometry of capillary.

The dynamics of capillary imbibition of a single liquid wetting a straight capillary was first described by Washburn.⁶ Washburn assumed a quasi-static liquid–gas meniscus shape which leads to a constant suction pressure across the meniscus. By balancing the suction pressure with the viscous stresses, Washburn⁶ showed that the position of the liquid–gas meniscus l depends on time t as $l^2 = Dt$, where the coefficient D depends on the interfacial tension, liquid viscosity, and capillary diameter. The square-root dependence of imbibition length l on time t results from the continuing increase in hydraulic resistance of the liquid-filled capillary during imbibition, proportional to the imbibition length l .

Several extensions of Washburn's model have been reported to account for the effects of capillary geometry on the imbibition rate: cross-section shape,^{7,8} step changes in capillary cross-section,^{9,10} patterned cross-section,¹¹ and continuous monotonous variation in capillary cross-section.^{12,13} These studies show that meniscus displacement can deviate significantly from the Washburn law ($l^2 \propto t$) due to geometric

variations. For example, using a lubrication approximation based model and validation experiments, Reyssat et al.¹² showed that power-law variation in capillary radius leads to diffusive dynamics ($l \propto \sqrt{t}$) for short times, but shape-dependent dynamics ($l \propto t^\beta$) at longer times; the exponent $\beta \neq 1/2$ depends on the capillary shape.

The majority of reported models for capillary imbibition, including those mentioned above, are limited to the case of a single liquid invading an initially empty capillary. However, in several physical processes, such as enhanced oil recovery¹ and groundwater pollution,² a higher wetting liquid imbibes into a capillary or a porous medium and displaces the residing liquid. In such processes, both the imbibing liquid and the displaced liquid contribute to the hydraulic resistance of the capillary and hence affect the dynamics of imbibition. Hultmark et al.¹⁴ explained the deviation from Washburn law due to viscosity of displaced fluid in a straight capillary using analytical solutions to a one-dimensional (1D) model and validation experiments in long capillaries. In their experiments, even though the viscosity of displaced gas was low compared with the imbibing liquid, long length of the capillary led to appreciable viscous resistance due to the displaced gas. Hultmark et al. concluded that the deviations from Washburn equation at early times can be explained due to viscous resistance of the displaced fluid. Similar results were obtained by Chibbaro et al.¹⁵ in an earlier study of capillary displacement of viscous liquids using lattice Boltzmann simulations. Recently, Walls et al.¹⁶ experimentally

Received: July 28, 2016

Revised: September 20, 2016

Published: September 21, 2016



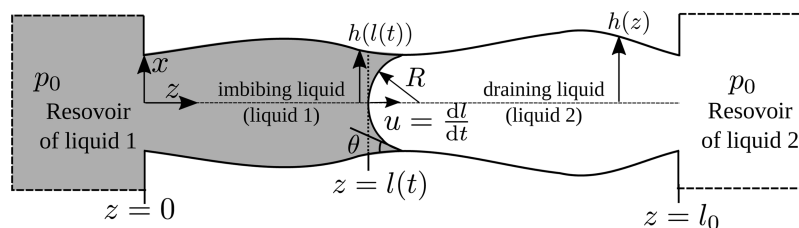


Figure 1. Schematic illustrating multiphase imbibition in a capillary with axially varying cross-section. Initially, at $t = 0$, the meniscus separating immiscible liquids 1 and 2 is at $z = 0$. At later times t , liquid 1, which is higher wetting, imbibes into the capillary until $z = l(t)$ while displacing liquid 2. The meniscus makes a contact angle θ with the capillary wall and its radius of curvature R depends on $h(z)$, which is the local half-width (2D) or radius (3D) of the capillary. The suction pressure across the meniscus results in a mean flow speed u which is equal to the interface speed.

demonstrated that the viscosity of displaced fluid can significantly affect the early imbibition dynamics in vertical, straight capillaries. All these studies on capillary displacement of a viscous fluid^{14–16} are limited to straight capillaries. In practical applications, spatial variations in porosity of the medium can lead to a change in the hydraulic resistance of the porous medium through coupled effects of geometric variation and the finite viscosity of displaced liquid. While, the individual effects of geometric variation¹² and viscosity of displaced liquid during capillary imbibition^{14–16} have been discussed previously, we know of no study focusing on their coupled effects.

In this paper, we consider capillary displacement of viscous liquids in capillaries with axially uniform and varying cross-sectional area. We present a quasi 1D model based on the lubrication approximation along with its analytical solutions to describe the dynamics of imbibition of a wetting liquid displacing a less-wetting liquid in capillaries with axially varying cross-section. In particular, we analyze the meniscus displacement in straight and power-law-shaped capillaries for different viscosities of the two liquids. Our analytical model yields scaling of imbibition length with time, physical properties of liquids, and geometric parameters. As is common to most mathematical models for imbibition,¹² our theoretical model for capillary displacement of viscous liquids is based on the assumption of quasi-static meniscus shape, and hence, it does not account for the dynamic nature of the meniscus.^{17,18} Therefore, we supplement our analytical solutions with LBM simulations for capillary displacement in axially varying geometries to account for the dynamic change in the meniscus during imbibition.

■ QUASI 1D MODEL FOR MULTIPHASE IMBIBITION

We here present a quasi-1D model to describe spontaneous capillary imbibition of a liquid while displacing the residing liquid due to the relative difference in their surface wettability. We begin by simultaneously considering two-dimensional (2D) and three-dimensional (3D) capillaries of lengths l_0 , symmetrical about z -axis, with arbitrary varying half-width (2D) and radius (3D). The half-width (2D) or radius (3D) of the capillary at an axial location z is given by $h(z)$, as shown in Figure 1. Initially, the capillary is filled with liquid 2 which has relatively less affinity to the capillary surface. The capillary is in contact with reservoirs of liquid 1 on the left and liquid 2 on the right, both of which are at equal pressure p_0 . At $t = 0$, liquid 1 starts displacing liquid 2 from the left inlet ($z = 0$). At later times ($t > 0$), the location of the meniscus is given by $z = l(t)$, where $l(t)$ is meniscus displacement from $z = 0$, termed as the imbibition length. Here, we limit our discussion to horizontal capillaries where gravity does not affect the imbibition dynamics.^{16,19}

The speed of the meniscus is equal to the area-averaged flow speed u at the location of the meniscus, $dl/dt = u(z = l(t))$. Under the lubrication approximation ($dh/dz \ll 1$),¹² the volume flow rate per unit width $q(t)$ for 2D capillary and volumetric flow rate $Q(t)$ for 3D capillary, along with the flow speeds $u = q(t)/(2h)$ and $u = Q(t)/(\pi h^2)$ respectively, depend on pressure p as

$$-\frac{dp}{dz} = \frac{3\mu_1 q(t)}{2h(z)^3} \quad (2D) \quad (1a)$$

$$-\frac{dp}{dz} = \frac{8\mu_1 Q(t)}{\pi h(z)^4} \quad (3D) \quad (1b)$$

where μ_i denotes the viscosity of liquid $i = 1, 2$. Next, we integrate eq 1 between $z = 0$ and $z = l_0$ to get

$$p_+ - p_- = q(t) \left(\int_0^{l(t)} \frac{3\mu_1}{2h(z)^3} dz + \int_{l(t)}^{l_0} \frac{3\mu_2}{2h(z)^3} dz \right) \quad (2D) \quad (2a)$$

$$p_+ - p_- = Q(t) \left(\int_0^{l(t)} \frac{8\mu_1}{\pi h(z)^4} dz + \int_{l(t)}^{l_0} \frac{8\mu_2}{\pi h(z)^4} dz \right) \quad (3D) \quad (2b)$$

where $p_+ = p(z = l + 0)$ and $p_- = p(z = l - 0)$ denote the pressures in front and behind the meniscus at $z = l(t)$, respectively. The pressure drop across the meniscus ($p_+ - p_-$) is given by the Young–Laplace equation as, $p_+ - p_- = \gamma/R$ for a 2D capillary and $p_+ - p_- = 2\gamma/R$ for an axisymmetric 3D capillary. Here, γ is the interfacial tension and R is the radius of curvature of the meniscus (see Figure 1). For a quasi-static meniscus, the radius of curvature R depends on the half-width or radius of the capillary as $R = h/\cos \theta$, where θ is the contact angle that the meniscus makes with the surface.⁵ As shown in Figure 1, we have defined θ with reference to liquid 1, such that, for $\theta < 90^\circ$ liquid 1 displaces liquid 2 and vice versa for $\theta > 90^\circ$. For analytical simplicity, we neglect the dynamic nature of the meniscus and assume that the contact angle θ remains constant throughout the imbibition process; we capture the dynamic effects in our LBM simulations.

Under the aforementioned assumptions, eq 2 simplifies to

$$\frac{c\gamma}{h(l(t))} = q(t) \left(\int_0^{l(t)} \frac{3\mu_1}{2h(z)^3} dz + \int_{l(t)}^{l_0} \frac{3\mu_2}{2h(z)^3} dz \right) \quad (2D) \quad (3a)$$

$$\frac{c\gamma}{h(l(t))} = Q(t) \left(\int_0^{l(t)} \frac{8\mu_1}{\pi h(z)^4} dz + \int_{l(t)}^{l_0} \frac{8\mu_2}{\pi h(z)^4} dz \right) \quad (3D) \quad (3b)$$

where $c = \cos \theta$ for a 2D capillary and $c = 2 \cos \theta$ for a 3D capillary. The left-hand side of this equation takes into account varying pressure jump across the meniscus due to variation in geometry. Whereas, the terms in parentheses on the right-hand side of eq 3 take into account the effect of time-varying hydraulic resistance of the capillary during imbibition. Finally, knowing the flow rates $q(t)$ or $Q(t)$ from eq 3, the meniscus location can be obtained by solving $dl/dt = u = q(t)/2h(l(t))$ or $dl/dt = u = Q(t)/\pi h(l(t))^2$. That is

$$\frac{dl}{dt} = \frac{c\gamma}{3\mu_1 h(l(t))^2} \left(\int_0^{l(t)} \frac{dz}{h(z)^3} + \frac{\mu_2}{\mu_1} \int_{l(t)}^{l_0} \frac{dz}{h(z)^3} \right)^{-1} \quad (2D) \quad (4a)$$

$$\frac{dl}{dt} = \frac{c\gamma}{8\mu_1 h(l(t))^3} \left(\int_0^{l(t)} \frac{dz}{h(z)^4} + \frac{\mu_2}{\mu_1} \int_{l(t)}^{l_0} \frac{dz}{h(z)^4} \right)^{-1} \quad (3D) \quad (4b)$$

These equations describe the imbibition of liquid 1 and the displacement of liquid 2 in an arbitrarily shaped capillary with half-width (2D) or radius (3D) $h(z)$. We compare the analytical solutions of our model with computationally less-intensive 2D LBM simulations.

Equation 4 suggests that the imbibition rate depends on the relative viscosities of two liquids and the geometry of capillary. To elucidate the effect of viscosity of liquids and capillary geometry on the displacement of interface, we construct analytical solutions of eq 4 for various capillary geometries. First, we revisit the problem of capillary displacement of a viscous liquid in a straight capillary to eliminate the geometric effects and focus on the effect of varying viscosity ratio μ_2/μ_1 of the liquids. We then analyze the coupled effects of geometric variation and viscosity of the displaced liquid through the example of imbibition in power-law-shaped diverging capillaries.

We note that, in our analysis we have neglected the inertial effects as they are usually limited to very short times.^{14–16} For example, if the imbibing and draining liquids have comparable density and viscosity, inertial effects are important for $t \ll \rho_1 h^2/\mu_1$.^{14,15} For typical values of $h = 10 \mu\text{m}$, $\rho_1 = 1000 \text{ kg m}^{-3}$ and $\mu_1 = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$, $\rho_1 h^2/\mu_1 = 0.1 \text{ ms}$. Whereas, the time scale over which imbibition dynamics is governed by the balance of viscous and interfacial tension effects is given as $\mu_1 l_0^2/(c\gamma h)$. For typical values of $\gamma = 0.05 \text{ N m}^{-1}$ and $l_0/h \sim 1000$, viscous effects dominate over much long times of order 100 ms. The assumption of negligible inertial effects is validated by our LBM simulations. However, we note that the current model is not valid if the density of the liquid is so high or the viscosity is so low that the time scale $\rho_1 h^2/\mu_1$ is large enough for inertial effects to become dominant.

Imbibition in Straight Capillary. For a straight capillary with $h(z) = h_0$, eq 4 describing the dependence of imbibition length on time simplifies to the equation derived previously by Hultmark et al.¹⁴ and Walls et al.¹⁶ That is

$$\tilde{L}^2 + \frac{\mu_2}{\mu_1} \tilde{L}(2 - \tilde{L}) = \frac{2}{3} \tilde{T} \quad (2D) \quad (5a)$$

$$\tilde{L}^2 + \frac{\mu_2}{\mu_1} \tilde{L}(2 - \tilde{L}) = \frac{1}{4} \tilde{T} \quad (3D) \quad (5b)$$

where $\tilde{L}$ and $\tilde{T}$ denote dimensionless length and time, defined as

$$\tilde{L} = \frac{l}{l_0} \text{ and } \tilde{T} = \frac{c\gamma h_0 t}{\mu_1 l_0^2} \quad (6)$$

In Figure 2a we show the dependence of imbibition length $\tilde{L}$ on time $\tilde{T}$, given by eq 5, for varying relative viscosities of

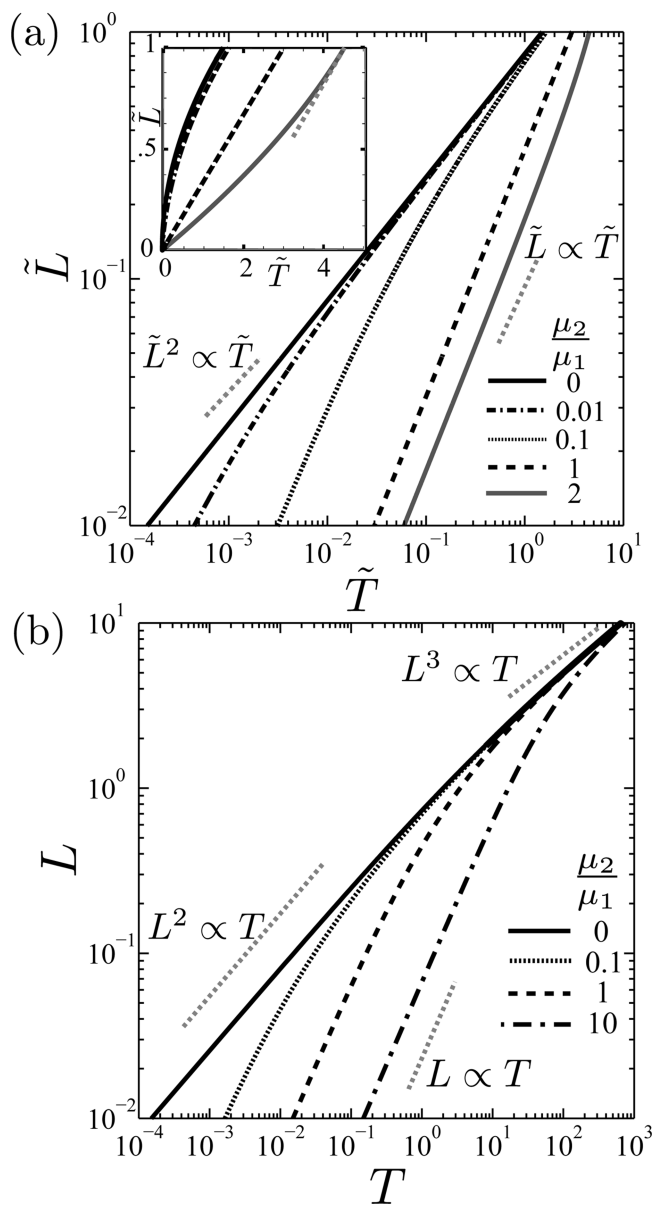


Figure 2. Effect of viscosity of displaced liquid on imbibition in (a) straight 2D capillary and (b) 2D wedge, predicted by the quasi-1D model. (a) log–log plot of dimensionless imbibition length $\tilde{L}$ and time $\tilde{T}$ for a straight capillary at varying viscosity ratios (μ_2/μ_1). When $\mu_2/\mu_1 = 0$, the imbibition dynamics follows the Washburn equation ($\tilde{L}^2 \propto \tilde{T}$). However, the Washburn equation does not hold for finite viscosity ratios. The inset shows the same data on a linear scale. The imbibition time increases with an increase in viscosity of the displaced liquid (liquid 2). (b) For imbibition of a single wetting liquid ($\mu_2/\mu_1 = 0$) in a wedge, $L^2 \propto T$ at short times ($T \ll 1$). Whereas, for finite viscosity ratios, $L \propto T$ at short times ($T \ll 1$). The long time dynamics ($L^3 \propto T$) does not depend on the viscosity of displaced liquid as the hydraulic resistance is primarily governed by the imbibing liquid (liquid 1) for long imbibition lengths. For all these calculations, we assumed that the meniscus makes a contact angle of 0° with the capillary wall.

liquids μ_2/μ_1 . We can identify several limiting cases from the results presented on the log–log plot shown in Figure 2a for a 2D capillary. First, for the case of relatively small viscosity of the displaced fluid ($\mu_2/\mu_1 \ll 1$), eq 5 reduces to the Washburn equation ($\tilde{L}^2 \propto \tilde{T}$) for a wetting liquid imbibing into an empty capillary.⁶ Next, for the limiting case of two liquids having equal viscosity ($\mu_2 = \mu_1$) wherein the hydraulic resistance of the capillary remains constant, eq 5 yields a linear relationship between imbibition length and time, $\tilde{L} = \tilde{T}/3$ for a 2D capillary and $\tilde{L} = \tilde{T}/8$ for a 3D capillary. Whereas, for liquids with unequal viscosity but with a finite viscosity ratio μ_2/μ_1 , eq 5 suggests that $\tilde{L} \propto \tilde{T}$ only for short imbibition times ($\tilde{T} \ll 1$) or imbibition lengths. Similar variation was observed in the experiments of Hultmark et al.¹⁴ This is because, for short imbibition length, the hydraulic resistance of the capillary is dominated by liquid 2 as it fills the majority of capillary. Therefore, constant capillary pressure leads to a constant imbibition rate. Similarly, toward the end of imbibition ($\tilde{L} \approx 1$), hydraulic resistance of the capillary is dominated by liquid 1 and hence the viscosity of liquid 2 has no effect on the imbibition rate. Consequently, the imbibition rates or the slopes of $\tilde{L}$ versus $\tilde{T}$ curves in the inset of Figure 2a are identical for different viscosity ratios μ_2/μ_1 toward the end of imbibition.

In general, the results presented in Figure 2a indicate that the imbibition time increases with an increase in the viscosity ratio μ_2/μ_1 as the displaced liquid (liquid 2) with higher viscosity leads to higher overall hydraulic resistance of the capillary and thus lower flow rate. As shown in the inset of Figure 2a, the meniscus displacement shows supralinear variation with time when the displaced liquid has lower viscosity than the imbibing liquid ($\mu_2 < \mu_1$) and sublinear variation when the displaced liquid has higher viscosity than the imbibing liquid ($\mu_2 > \mu_1$).

Imbibition in Power-Law-Shaped Capillaries. Next, we analyze the effect of geometric variation on capillary displacement of a viscous liquid. As an example case of diverging capillaries, we here consider a generalized diverging capillary with power-law variation in half-width $h(z)$ for a 2D capillary and radius $h(z)$ for a 3D capillary

$$h(z) = h_0 + \alpha z^n, \quad \alpha > 0 \quad (7)$$

Here h_0 is the half-width or radius of the capillary inlet. The dimensions of the geometric parameter α depend on the exponent n . As noted by Reyssat et al.,¹² lubrication approach requires $n \geq 1$. Substituting this geometric profile in eq 4 describing multicomponent imbibition in axially varying capillary, and introducing dimensionless imbibition length L and time T

$$L = \left(\frac{\alpha}{h_0}\right)^{1/n} l \quad \text{and} \quad T = \frac{c\gamma h_0}{\mu_1} \left(\frac{\alpha}{h_0}\right)^{2/n} t \quad (8)$$

we obtain

$$\frac{dL}{dT} = \frac{1}{3(1+L^n)^2} \left(\int_0^L \frac{dZ}{(1+Z^n)^3} + \frac{\mu_2}{\mu_1} \int_L^{L_0} \frac{dZ}{(1+Z^n)^3} \right)^{-1} \quad (9a)$$

$$\frac{dL}{dT} = \frac{1}{8(1+L^n)^3} \left(\int_0^L \frac{dZ}{(1+Z^n)^4} + \frac{\mu_2}{\mu_1} \int_L^{L_0} \frac{dZ}{(1+Z^n)^4} \right)^{-1} \quad (9b)$$

Here, $L_0 = l_0(\alpha/h_0)^{1/n} = \Delta h/h_0$ denotes the relative difference between the exit and inlet widths (or radii) of the capillary. We note that, introducing dimensionless length L and T yields a single governing equation (eq 9) for imbibition in power-law-shaped capillaries of various inlet widths (or radii), exponent n , and geometric parameter α .

Imbibition in a Wedge ($n = 1$). For a qualitative description of geometric effects on capillary displacement of a viscous liquid, we first consider the case of a 2D wedge and 3D cone, with linearly varying width or radius ($n = 1$). Solving eq 9, while ignoring the dynamic nature of the interface, yields

$$T = \frac{3}{2} \left(\frac{\mu_2}{\mu_1} - 1 \right) L + \frac{1}{2} \left(1 - \frac{\mu_2}{\mu_1} \frac{1}{(1+L_0)^2} \right) ((1+L)^3 - 1) \quad (2D) \quad (10a)$$

$$T = \frac{8}{3} \left(\frac{\mu_2}{\mu_1} - 1 \right) L + \frac{2}{3} \left(1 - \frac{\mu_2}{\mu_1} \frac{1}{(1+L_0)^3} \right) ((1+L)^4 - 1) \quad (3D) \quad (10b)$$

When the displaced liquid has negligible viscosity compared with the imbibing liquid ($\mu_2/\mu_1 \ll 1$), eq 10 reduces to that obtained by Reyssat et al.¹² for imbibition of a single wetting liquid. In Figure 2b we present the variation of imbibition length in 2D wedge with time predicted by eq 10a on a log–log plot. From eq 10 and the corresponding results presented in Figure 2b, we observe that, for a single wetting liquid invading a diverging capillary, diffusive dynamics ($L^2 \propto T$) prevail for short times ($T \ll 1$) for 2D and 3D capillaries. Whereas, for long times ($T \gg 1$), $L^3 \propto T$ for a 2D capillary and $L^4 \propto T$ for a 3D capillary. The crossover between these two regimes occurs for $L \simeq 1$ or $l \simeq l_0 h_0/\Delta h$. Note that, due to the finite length of the capillary, the crossover between these regimes is observable only when $L_0 = \Delta h/h_0 \gtrsim 1$.

To elucidate the effect of finite viscosity ratio μ_2/μ_1 on imbibition dynamics, we consider the case of a long diverging capillary with $L_0 = \Delta h/h_0 \gg 1$. Under this assumption, eq 10 simplifies to

$$L^3 + 3L^2 + \frac{3\mu_2}{\mu_1} L = 2T \quad (2D) \quad (11a)$$

$$2L^4 + 8L^3 + 12L^2 + \frac{8\mu_2}{\mu_1} L = 3T \quad (3D) \quad (11b)$$

When the viscosity of displaced liquid is comparable to the viscosity of the imbibing liquid, eq 11 and the corresponding results presented in Figure 2b suggest that, $L \propto T$ for short times ($T \ll 1$) for 2D and 3D capillaries. This $L \propto T$ behavior is in contrast to the diffusive-dynamics ($L^2 \propto T$) for single wetting liquid at short times predicted by Reyssat et al.¹² The change in short-time dynamics due to the presence of draining liquid occurs because, the overall hydraulic resistance of the capillary, which is dominated by liquid 2 during the initial stage of imbibition does not change appreciably. Moreover, the

change in capillary pressure due to varying width or radius is negligible for short times. Consequently, for short times, the imbibition rate is constant and $L \propto T$ for 2D and 3D capillaries.

Whereas, at long times ($T \gg 1$), eq 11 predicts that the imbibition dynamics is similar to that for single wetting liquid with $L^3 \propto T$ for a 2D capillary and $L^4 \propto T$ for a 3D capillary. This is because, for a diverging capillary, the overall hydraulic resistance of the capillary is governed by the liquid residing in the regions with narrow cross-section. Consequently, the displacement dynamics is governed by the imbibing liquid once the imbibing liquid penetrates sufficient length to dominate the hydraulic resistance. The imbibition length at which the crossover between $L \propto T$ and $L^3 \propto T$ (or $L^4 \propto T$) regimes takes place for a 2D (or 3D) capillary depends on the viscosity ratio, as shown in Figure 2b. For comparable viscosities of two liquids, the crossover between the two regimes occurs at $L \simeq (3\mu_2/\mu_1)^{1/2}$ for a 2D capillary and $L \simeq (4\mu_2/\mu_1)^{1/3}$ for a 3D capillary. Although, the long time dynamics of capillary displacement of a viscous liquid in a diverging capillary is qualitatively similar to that for a single wetting liquid, drainage of second liquid leads to quantitative differences. As shown in Figure 2b, an increase in relative viscosity of liquid 2 compared with liquid 1, μ_2/μ_1 , leads to an increase in imbibition time.

Asymptotic Limits for Generalized Power-Law-Shaped Capillary ($n \geq 1$). The governing equation eq 9 can be solved analytically for any value of $n \geq 1$. The analytical solutions are however tedious for $n > 1$; for example, see Reyssat et al.¹² for solution for $n = 2$ for a single wetting liquid. However, it is possible to obtain the asymptotic limits corresponding to short and long times for general value of n .

At short times where $L \ll 1$, eq (9) can be simplified by noting that $(1 + L^n) \simeq 1$ and

$$\int_0^L \frac{dZ}{(1 + Z^n)^{d+1}} + \frac{\mu_2}{\mu_1} \int_L^{L_0} \frac{dZ}{(1 + Z^n)^{d+1}} \simeq \frac{\mu_2}{\mu_1} \int_0^\infty \frac{dZ}{(1 + Z^n)^{d+1}} \quad (12)$$

where $d = 2$ or 3 is the dimension of the capillary. These integrals for $d = 2$ and 3 converge for the lubrication approximation, which requires $n \geq 1$. Therefore, we get¹²

$$A(n) = \int_0^\infty (1 + Z^n)^{-3} dZ = \frac{\pi (2n - 1)(n - 1)}{2 n^3 \sin(\pi/n)} \quad (13)$$

$$B(n) = \int_0^\infty (1 + Z^n)^{-4} dZ = \frac{\pi (3n - 1)(2n - 1)(n - 1)}{6 n^4 \sin(\pi/n)} \quad (14)$$

Thus, for short times where $L \ll 1$, eq 9 yields

$$L \approx \frac{\mu_1}{3\mu_2 A(n)} T \quad (2D) \quad (15a)$$

$$L \approx \frac{\mu_1}{8\mu_2 B(n)} T \quad (3D) \quad (15b)$$

Hence, the short time imbibition behavior is given by $L \propto T$ for power-law-shaped 2D and 3D capillaries with $n \geq 1$. This is in contrast to the diffusive dynamics, $L^2 \propto T$, for a single wetting liquid. We note that the $L \propto T$ behavior at short times does not correspond to the inertial regime, described by Das et al.,²⁰

resulting from the balance of inertia and surface tension effects. In the current case, the $L \propto T$ results due to constant hydrodynamic resistance of the channel, dominated by the viscous draining fluid, at small times. As discussed above based on scaling arguments, the inertial effects are usually limited to times which are much smaller than the time scale over which early viscous regime dominates.^{14–16}

At long times where $L \gg 1$, eq 9 can be simplified by noting that $(1 + L^n) \simeq L^n$ and

$$\int_0^L \frac{dZ}{(1 + Z^n)^{d+1}} + \frac{\mu_2}{\mu_1} \int_L^{L_0} \frac{dZ}{(1 + Z^n)^{d+1}} \simeq \int_0^\infty \frac{dZ}{(1 + Z^n)^{d+1}}, \quad d = 2, 3 \quad (16)$$

Thus, in the limit of $L \gg 1$, eq 9 simplifies to

$$A(n)L^{2n} \frac{dL}{dT} \approx \frac{1}{3} \quad (2D) \quad (17a)$$

$$B(n)L^{3n} \frac{dL}{dT} \approx \frac{1}{8} \quad (3D) \quad (17b)$$

which yields the power laws

$$L^{2n+1} \approx \frac{2n+1}{3A(n)} T \quad (2D) \quad (18a)$$

$$L^{3n+1} \approx \frac{3n+1}{8B(n)} T \quad (3D) \quad (18b)$$

Therefore, at long times, the imbibition dynamics depend upon the shape of the capillary. Note that the long time power laws are same as those obtained by Reyssat et al.¹² for a single liquid imbibition. This is because, at long times the displaced fluid does not contribute appreciably to the hydraulic resistance of the capillary. The imbibition length at which the crossover between the short and long time limits occurs can be obtained by equating the imbibition times in eqs 15 and 18. The crossover length is given by $L \simeq ((2n+1)\mu_2/\mu_1)^{1/(2n)}$ for a 2D capillary and $L \simeq ((3n+1)\mu_2/\mu_1)^{1/(3n)}$ for a 3D capillary.

LATTICE BOLTZMANN SIMULATIONS

So far in our analysis, we have assumed a quasi-static meniscus which depends on the surface wettability and the local cross-section of the capillary. However, in practice, the viscous stresses acting on a moving meniscus change its curvature and hence the capillary pressure. To capture the dynamic nature of the meniscus, we supplement the analytical solutions with simulations based on the lattice Boltzmann method (LBM). The LBM has developed into a powerful technique for simulating transport processes for applications involving interfacial dynamics owing to its excellent numerical stability and constitutive versatility.²¹ The earliest of lattice Boltzmann models was proposed by Higuera et al.^{22,23} by introducing a collision matrix in the lattice Boltzmann equations. The model was later simplified by Qian et al.²⁴ wherein they introduced single relaxation time to replace the collision matrix. Ever since, LBM has grown into a powerful tool for various applications such as multiphase flows, phase change heat transfer, and microfluidics. The readers can refer to the earliest of the reviews on LBM by Benzi et al.²⁵ for details description of single phase lattice Boltzmann equations. The wide range of simulations which are possible using LBM can be found in the recent review of Aidun and Clausen.²⁶

Table 1. Description and Results of Simulation Cases for Capillary Displacement of an Equal-Viscosity Liquid in Straight Capillaries

cases	$l_0(\mu\text{m})$	$h_0(\mu\text{m})$	h_0/l_0	θ_d	$\tilde{u}_{\text{fit}}$	$\tilde{u}$	Ca	Re
A	50	1.5	0.03	17	0.32	0.30	9.12×10^{-3}	0.97
B	50	2.5	0.05	31	0.29	0.27	1.35×10^{-2}	2.36
C	75	3.75	0.05	36	0.27	0.27	1.31×10^{-2}	3.40
D	100	5	0.05	38	0.26	0.26	1.28×10^{-2}	4.42
E	100	3	0.03	25	0.30	0.29	8.46×10^{-3}	1.74

We performed LBM simulations of multi-liquid capillary imbibition based on a pseudopotential multicomponent LBM.²⁷ The pseudopotential multicomponent model inherently captures the dynamic nature of the interface due to the presence of microscopic interfacial forces between solid–liquid and liquid–liquid interfaces. This model has been applied previously to successfully capture interface dynamics in straight capillaries: liquid–gas interface^{28,29} and liquid–liquid interface.¹⁵ We validated our LBM solver using the Laplace test, wherein the pressure drop across interface is compared with that predicted by the Laplace law. Moreover, we verified our LBM solver with the results of Chibbaro et al.¹⁵ capillary displacement of a viscous liquid in a straight capillary. In order to check the grid independence on the simulation results, we performed the simulation of imbibition in straight channel by doubling the lattice points while maintaining the same length, fluid viscosities, and interfacial tension. We quantified the interfacial velocity for simulations performed on high and low resolution grids and found that the difference in interfacial velocities was 3.5%.

For all the simulations reported in this paper liquid 1 (dynamic viscosity $\mu = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$, density 1000 kg m^{-3}) fully wets ($\theta = 0^\circ$) the capillary wall under equilibrium conditions. The interfacial tension between liquids 1 and 2 is taken as 0.035 N m^{-1} and both liquids have same density and viscosity. The pseudopotential model used in the current work has few limitations due to spurious currents and diffusive interface as shown by Diotallevi et al.³⁰ However, in the present simulations we have chosen both liquids with identical densities, which minimizes the interface diffusion and spurious currents at the interface.

Effect of Dynamic Contact Angle on Imbibition in Straight Capillaries. To highlight the deviations in predictions of our quasi 1D model due to the dynamic contact angle, we first performed a series of simulations for capillary displacement of a viscous liquid in a 2D straight capillary. In general, the dynamic contact angle depends primarily on the capillary number¹⁸ $Ca = \mu u/\gamma$, that is, the ratio of viscous to capillary forces. As shown previously,^{31,32} the dynamic contact angle increases with an increase in the capillary number. In addition, the relative local slip l_s/h_0 , where l_s denotes the slip length at the three-phase contact line,³³ can have a secondary effect on the dynamic contact angle. To capture the effects of capillary number and relative local slip on imbibition dynamics, we performed simulations for five cases described in Table 1. In cases A and B, we varied the width of the capillary while keeping the length fixed. Cases A and B were chosen because, from eq 5a, the imbibition rate and capillary number change appreciably with a change in capillary width. Therefore, cases A and B highlight the role of capillary number on dynamic contact angle. Whereas for cases B, C, and D, we kept the aspect ratio h_0/l_0 constant while varying the length and width of the capillary. We note that when the aspect ratio h_0/l_0 is kept

constant, the imbibition rate and capillary number does not change according to eq 5a. Therefore, cases B–D highlight the importance of relative local slip on the dynamic contact angle. Lastly, in case E we kept the length similar to case D and aspect ratio of case A to evaluate the coupled effect of capillary number and relative local slip on the dynamic contact angle and imbibition dynamics.

In Figure 3, we present the variation of imbibition length $\tilde{L}$ on imbibition time $\tilde{T}$ predicted by our LBM simulations for

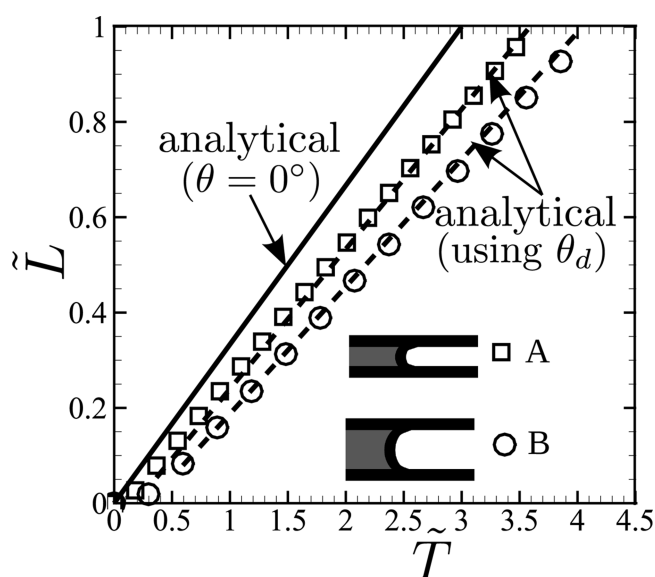


Figure 3. Comparison of imbibition dynamics in 2D straight capillary predicted by LBM simulations and 1D model for cases A and B. LBM simulations (data points) and 1D model (solid and dashed lines) predict proportional increase of dimensionless imbibition length $\tilde{L}$ with time $\tilde{T}$ for capillary displacement of viscous liquids in a straight capillary at equal viscosities. The simulated imbibition rate differs from the model predictions with equilibrium contact angle (solid line). Using simulated dynamic contact angle in the 1D model (dashed lines) yields excellent agreement with simulations.

cases A and B. Our simulations accurately capture the linear dependence of imbibition length $\tilde{L}$ on imbibition time $\tilde{T}$. However, a comparison of LBM results with theoretical predictions of eq 5a in Figure 3 suggests that the 1D model overpredicts the imbibition rate, $\tilde{u} = d\tilde{L}/d\tilde{T} = 1/3$. This deviation can be explained by the dynamic contact angle of the interface. In the current case, for example, the static contact angle of the meniscus is zero as we have chosen liquid 1 which fully wets the surface. However, as shown in the insets of Figure 3, the dynamic contact angle of the meniscus is nonzero during imbibition. Consequently, the pressure difference across the interface in the simulations is lower and hence the imbibition is slower compared with that predicted by the 1D model, eq 5a. For the same reason, when we extract the dynamic contact

angles (θ_d) from our simulation data and use them in the 1D model for 2D straight capillary, eq 5a, we observe excellent agreement between simulations and analytical solutions as shown in Figure 3.

Similar to the results shown in Figure 3 for cases A and B, LBM simulations predict linear dependence of imbibition length on time for cases C–E. In Table 1, we report the simulated imbibition rates $\tilde{u}$ for different geometric configurations along with those predicted by analytical solution after accounting for the dynamic contact angle, $\tilde{u}_{fit}$. We also report the corresponding capillary number Ca and Reynolds number, $Re = \rho u h_0 / \mu_1$. Comparison of data for cases A and B and cases D and E shows that the dynamic contact angle increases appreciably with an increase in the capillary number. Whereas, for cases B–D for which the capillary number remains unchanged, the dynamic contact angle increases with an increase in capillary width. Because the capillary number is same for cases B–D, we attribute this variation in dynamic contact angle to the change in the relative local slip (l_s/h_0);³³ wetting force, that governs the slip velocity or length, is constant for all the cases. Due to the relative local slip velocity the capillary number based on the interface displacement rate overpredicts the viscous stresses. Hence, for a fixed capillary number, higher relative local slip leads to lower viscous stresses and therefore lower dynamic contact angle. We note that the variation of dynamic contact with the relative local slip is in good agreement with the predictions of Cox³³ for spreading. Because the cosine of dynamic contact angle ($\cos \theta_d$) has a logarithmic dependence on the relative local slip,^{33,34} the effect of relative local slip on dynamic contact angle is weaker than that of the capillary number. Therefore, in the subsequent simulations for axially varying geometries, we directly attribute the change in dynamic contact angle to the capillary number.

In addition to the dynamic contact angle, the imbibition rate is also affected by the pressure loss at the capillary entrance as discussed by Waghmare and Mitra.³⁵ In our LBM simulations for straight capillaries, this entrance pressure drop was relatively small (5%) compared to the pressure drop across the liquid–liquid interface. Therefore, even without accounting for the entrance pressure losses, predictions of our analytical model presented in Figure 3 and Table 1 compare well with the simulation data.

Imbibition in Power-Law Geometries. We performed another set of simulations for imbibition in a 2D wedge ($n = 1$) with linearly diverging width. We performed simulations for four different geometries having two different wedge angles: (i) wedge angle of 4° and inlet half-widths of 1.5 and 9.6 μm and (ii) wedge angle of 8° and inlet half-widths of 1.5 and 2.5 μm . The length of capillaries was chosen such that $L_0 = \Delta h/h_0 > 10$. For these simulations, we maintained a viscosity ratio of unity ($\mu_2/\mu_1 = 1$). In Figure 4a we report the interface position l as a function of time t for simulations of imbibition in a wedge. Among the capillaries with same wedge angle, the imbibition rate is higher in capillaries with larger initial width due to reduced hydraulic resistance.

Next, we nondimensionalized the simulated imbibition length l and time t presented in Figure 4a using the analytical scaling given by eq 8 to compare the simulations with the analytical solution given by eq 11a. The log–log plot of dimensionless length L versus dimensionless time T is shown in the inset of Figure 4a along with the analytical solution (solid line). The simulation data for various wedge angles and inlet widths collapse onto a single curve. While the simulation data

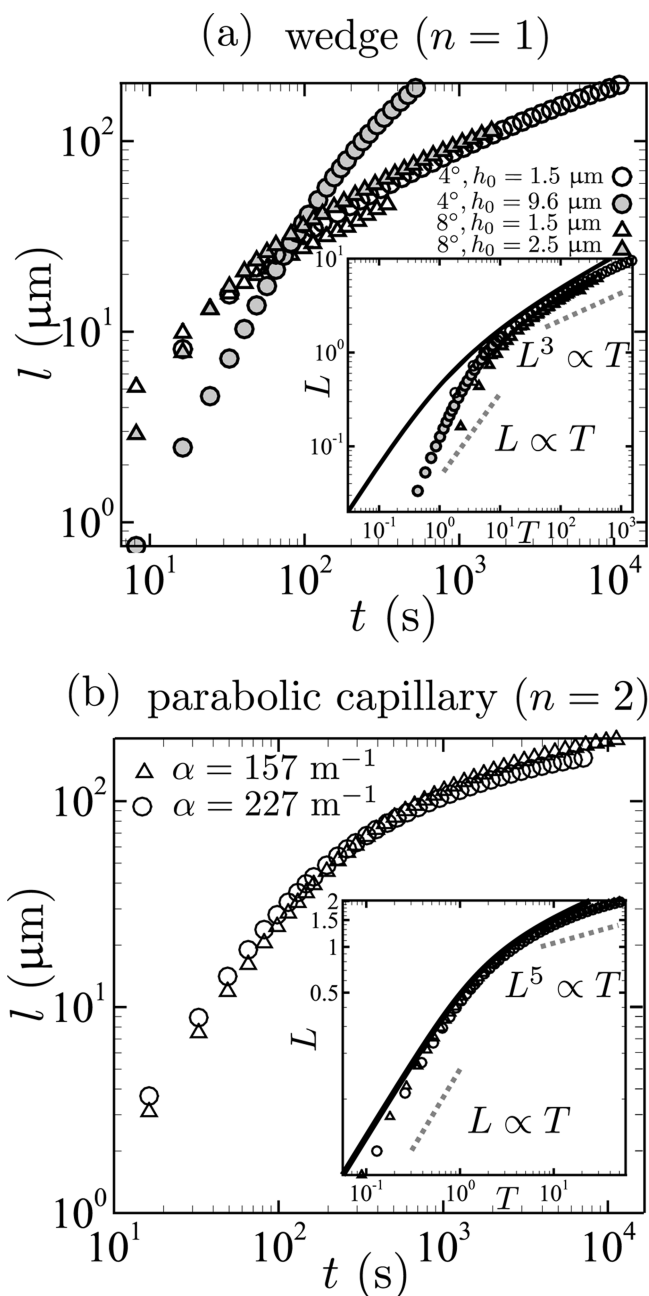


Figure 4. Imbibition length versus time predicted by LBM simulations for (a) 2D wedge with linearly varying width ($n = 1$), and (b) 2D parabolic capillary ($n = 2$). log–log plots of imbibition length l and time t for capillary displacement of a viscous liquid having equal viscosity as the imbibing liquid. When the same data are plotted using dimensionless imbibition length L and time T , it collapses onto a single curve as shown in insets. The simulated data compares well with the corresponding analytical (solid line).

shows the expected $L^3 \propto T$ at long times, we observe deviation from analytical solution at short times. The deviation from the analytical solution can again be attributed primarily to the dynamic change in meniscus shape, which is pronounced at small times due to large interface speed.^{33,34}

Lastly, we performed simulations for imbibition in a 2D parabolic capillary ($n = 2$) with imbibing and displaced liquid having equal viscosity. We performed simulations for two geometries having same initial half-width of $h_0 = 1.5 \mu\text{m}$ but different values of geometric parameter $\alpha = 157$ and 227 m^{-1} .

Figure 4(b) shows the variation of imbibition length versus time. The inset of Figure 4(b) shows the same data using dimensionless length and time along with the analytical solution (solid line). Unlike the case for imbibition in a wedge ($n = 1$), the simulation data for parabolic capillary ($n = 2$) shows good agreement with the analytical solution at all times. In particular, the simulation data shows the expected $L \propto T$ behavior at short times and $L^5 \propto T$ behavior at long times. We note that compared with $n = 1$, the deviation between simulations and analytical solution is relatively less for $n = 2$.

Similar to the case of straight capillaries, the deviations between the simulation results and those predicted by the quasi 1D model in Figure 4 can be explained primarily based on the variation of dynamic contact angle with the capillary number. From eq 8, we note that the capillary number Ca for power-law-shaped capillaries depends on the imbibition rate as,

$$Ca = h_0 \left(\frac{\alpha}{h_0} \right)^{1/n} \frac{dL}{dT} \quad (19)$$

In our simulations, the hydraulic resistance of the capillary remains constant over time as both liquids have equal viscosity. Due to the diverging width of the capillary, the imbibition rate dL/dT and hence the capillary number decreases with time. Consequently, the dynamic contact angle approaches the equilibrium contact angle over time. Therefore, in Figure 4 the deviation in simulation predictions and analytical solution, which assumes a quasi-static interface, reduces with time. Moreover, at short times, reduction in dynamic contact angle over time causes the meniscus to further accelerate. Consequently we observe that in Figure 4 the imbibition rate at short times is faster than that predicted by the quasi 1D model.

For our simulation cases, the factor $h_0(\alpha/h_0)^{1/n}$ in eq 19 does not vary significantly for $n = 1$ and 2. Because the parabolic capillary has a narrower width than the wedge near the entrance, the hydraulic resistance is higher for the parabolic capillary ($n = 2$) compared with the wedge ($n = 1$). As a result, the imbibition rate and capillary number in our simulations for parabolic capillary are lower compared with that in the wedge. We therefore observe lower deviations between the simulations and analytical solutions for the case of $n = 2$ as shown in Figure 4. In addition to the variation in contact angle, our simulations also predict entrance pressure loss³⁵ at the capillary inlet, which we have neglected in our quasi 1D model. The entrance pressure loss is significant only for the case of imbibition in a wedge ($n = 1$) at short times, when the imbibition rate is high. This is another reason for deviation in theoretically predicted and simulated scaling of imbibition length with time at short times for $n = 1$.

CONCLUSION

We have analyzed the coupled effects of geometric variation and viscosity of displaced liquid on the dynamics of capillary displacement of a viscous liquid. We modeled capillary displacement of a viscous liquid in straight and power-law shaped capillaries using a quasi-1D model based on lubrication approximation. We also validated our quasi-1D model with LBM simulations based on the pseudopotential multicomponent model. Based on the analytical solutions of the quasi-1D model and LBM simulations, we have shown that for a general power-law-shaped diverging capillary, when a viscous liquid

displaces another viscous liquid during imbibition, the dimensionless imbibition length and time scales follow $L \propto T$ at short times and $L^{2n+1} \propto T$ (2D) or $L^{3n+1} \propto T$ (3D) at long times. This short time behavior differs significantly from the diffusive-dynamics of single wetting liquid imbibing into a power-law-shaped capillary.¹² However, the long time behavior of capillary displacement of a viscous liquid in diverging capillaries is qualitatively similar to single liquid imbibition. This is because, for long imbibition lengths, the imbibing liquid occupies the narrow sections of capillary and dominates the hydraulic resistance. Because the narrow sections of the capillary dominate the hydraulic resistance, for long diverging capillaries, the entrance region over which the viscous effects of displaced fluid are felt does not depend on the length of capillary.

While the predictions of our quasi-1D model agree qualitatively with LBM simulations, quantitative differences exist as the quasi-1D model does not account for the dynamic contact angle of meniscus. However, using dynamic contact angles predicted by LBM simulations in the quasi 1D model yields excellent agreement with simulations data. Although, our analysis is limited to capillaries, we expect that qualitative conclusions of the current work would also apply to random porous media with gradual spatial variations in porosity.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

S.K. thanks DST INSPIRE fellowship for providing necessary funds for carrying out this research.

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