Capillary Imbibition of Binary Fluid Mixtures in Nanochannels
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ABSTRACT: Many-body Dissipative Particle Dynamics (MDPD) simulations of binary fluid mixtures imbibing cylindrical nanochannels reveal a strong segregation of fluids differing in their affinities to the pore walls. Surprisingly, the imbibition front furthest into the channel is highly enriched in the fluid with the lower affinity for the walls, i.e., the fluid less prone to enter the pore. This effect is caused by the more-wetting fluid forming a monolayer covering the walls of the pore, while the lesser-wetting fluid is expelled from the walls to the interior of the pore where the higher axial flow velocity carries it to the front. The fluids remix after cessation of the flow. Nonwetting fluids can be made to enter a pore by mixing with a small amount of wetting fluid. The imbibition depth of the mixtures scales with the square root of time, in agreement with Bell–Cameron–Lucas–Washburn theory for pure fluids.

INTRODUCTION
The flow of fluids in porous media finds many applications, e.g., in the flushing of oil from subterranean reservoirs, the cleaning of wastewater by filtering, the removal of ink spills by blotting paper, and the imbibition of ink into paper in printing processes.1−4 The latter two processes occur spontaneously, driven by the energy gain upon increasing the fluid-medium interfacial area. A seminal result describing this process is the Bell–Cameron5−7,9−15 equation for the idealized imbibition of a pure fluid into a cylindrical pore: the penetration depth of the meniscus increases with the square root of time. This process has been extensively studied using theoretical experiments16−26 and computer simulations.26 Haneveld et al.12 experimentally confirmed t1/2 BCLW scaling for deionized water imbibing even the smallest sub 10 nm nanochannels, albeit with a deviation in the prefactor. Dimitrov et al.18 demonstrated that a consistent BCLW scaling for deionized water imbibing even the smallest sub 10 nm nanochannels, albeit with a deviation in the prefactor.

The imbibition of binary fluids has attracted far less attention.27−35 Oh et al.27 observed t1/2 BCLW scaling for the imbibition of water–alcohol mixtures in pores several nanometers in height, while the prefactor to the scaling law falls short of the theoretical value by 10−30%. The latter was explained by hypothesizing that fluid molecules adjacent to the wall are immobile, thereby reducing the effective channel height. Ben Jazia et al.28 reported that the imbibition rate of ethanol–water mixtures into nanoporous networks varied from t1/2 BCLW scaling to linear scaling in time with increasing ethanol concentration, which they attributed to ethanol modifying the wetting front. Using NMR to measure imbibition, Kuijpers et al.39 recently found t1/2 BCLW scaling, though with a deviant prefactor, for a wide range of water–glycerol mixtures, which all filled the pore as homogeneous mixtures. Samin et al.30 studied the pressure-driven flow of a near-critical binary mixture into a nanochannel, elucidating the role of the Péclet number on the selectivity of the nanochannel for either component. Our objective here is to study the capillary imbibition of various binary miscible fluids in cylindrical nanochannels using a mesoscopic simulation technique, Many-body Dissipative Particle Dynamics (MDPD).37−41 The physical properties of the two components are varied, one at a time, to elucidate their impact on the imbibition process, exploiting a feature of simulations unavailable to experimental studies.

The paper is organized as follows: BCLW theory and the employed simulation techniques are described in the section Simulation Model and Methods. An overview of the simulations results of the imbibition of pure and binary fluids is presented in the section Results and Discussion. We end with a discussion and summary of the main results in the section Conclusions.
**SIMULATION MODEL AND METHODS**

**Theory.** The imbibition of a liquid in a cylindrical pore of radius \( R \), i.e., the penetration depth \( z \) as a function of the elapsed time \( t \) since the start of imbibition, see Figure 1, was first solved analytically by Bell and Cameron,\(^5\) Lucas,\(^6\) and Washburn.\(^7\) The rate of increase of \( z \) and capped by a liquid–vapor interface in the negative \( z \) direction. The few evaporated particles are confined by reflecting walls placed well outside the boundaries.

Bell and Cameron,\(^5\) Lucas,\(^6\) and Washburn.\(^7\) The rate of increase of the liquid–wall potential energy as the liquid flows deeper into the pore is equated to the rate of energy dissipation in the Poiseuille flow of the entire imbibed liquid, to obtain a differential equation for the imbibition rate \( \dot{z} \). Solving this equation yields:

\[
\dot{z}(t) = \frac{\gamma_0 R \cos \theta}{2 \eta} t + z_0^2 \tag{1}
\]

where \( \gamma_0 \) denotes the liquid–vapor surface tension, \( \theta \) the liquid–vapor–substrate contact angle, and \( \eta \) the viscosity of the liquid, while \( z_0 \) accounts for the start-up effects before this phenomenological equation dominates the imbibition. When fitting simulation data, the offset \( z_0 \) also partially absorbs deviations from BCLW due to the strongly uniform axial velocity of the meniscus, and the formally diverging dissipation rate at the moving contact line.\(^42\)\(^\text{-}45\) Upon rescaling the imbibition depth by \( L_{\text{cap}} = R/2 \) and the time by \( t_{\text{cap}} = R \eta/ (2 \gamma_0) \), the BCLW law with \( \dot{z} = z/L_{\text{cap}} \) and \( \dot{t} = t/t_{\text{cap}} \) takes the form

\[
\dot{z}^2(t) = \dot{\theta} \cos \theta + \dot{z}_0^2 \tag{2}
\]

which facilitates the comparison of the imbibition process across various liquids.

**Multibody Dissipative Particle Dynamics.** In MDPP, the force on particle \( i \) due to interactions with its neighbors \( j \) is expressed as a sum of pair forces:\(^41\)\(^\text{-}46\)

\[
\mathbf{F}_i = \sum_{j \neq i} \left( \mathbf{F}_i^C + \mathbf{F}_i^D + \mathbf{F}_i^r \right) \tag{3}
\]

with the conservative, dissipative, and random contributions marked with the superscripts \( C \), \( D \), and \( R \) respectively. The conservative force between particles \( i \) and \( j \):

\[
\mathbf{F}_i^C = A_j \omega_j(r_{ij}) \mathbf{r}_i + B_j (\mathbf{r}_i \mathbf{r}_j) \mathbf{r}_i \tag{4}
\]

combines a pairwise additive attraction with strength parameter \( A_j \) and a density dependent repulsion with strength parameter \( B_j \). The force acts along the unit vector between the two particles, \( \mathbf{r}_{ij} = (r_{ij} - \mathbf{r}_i)/r_{ij} \), with \( r_{ij} \) the position of particle \( i \) and \( r_j \) the interparticle distance. The weight-functions \( \omega_j(r_{ij}) = 1 - r_{ij}/r_k \) and \( \omega_k(r_{ij}) = 1 - r_{ij}/r_k \) decay linearly with the distance and are identically zero beyond their cutoff distances \( r_k \) and \( r_k \) respectively. The local density on particle \( i \) in the repulsive term is given by:

\[
\rho_i = \sum_{j \neq i} \omega_j(r_{ij}) \tag{5}
\]

\[
\omega_j(r_{ij}) = \frac{15}{2 \pi r_j^2} \tag{6}
\]

where the last line follows from the requirement that \( \mathbf{F}_i^C \) derives from a conservative potential, namely \( \Phi \propto \sum_i r_{ij} \), and the desire to normalize the space integral of \( \omega_j \) to unity. A conservative potential furthermore requires \( B_j \) to be independent of the particles \( i \) and \( j \).\(^47\) The existence of a stable liquid–vapor interface demands \( r_k < r_b \).\(^40\)

The dissipative force between two particles,

\[
\mathbf{F}_i^D = -D \omega_j(v_i(r_j) - v_i) \mathbf{r}_i \tag{7}
\]

with strength parameter \( D \) and weight function \( \omega_j \) is proportional to their velocity difference, \( v_j = v_i - v_i \). The random force between two particles reads:

\[
\mathbf{F}_i^r = R \sigma \mathbf{\Theta}_i \mathbf{r}_i \tag{8}
\]

with strength parameter \( R \) and weight function \( \sigma \) the Gaussian random numbers \( \mathbf{\Theta}_i \) have zero mean and unit variance, are uncorrelated in time (Markovian) and are uncorrelated between particle pairs. The dissipative and random forces are related by the fluctuation–dissipation theorem, which here takes the form,

\[
D \omega_j(v_i(r_j) - v_i) = 2 k_B T \rho_j v_i \mathbf{r}_i \tag{9}
\]

where \( k_B \) is Boltzmann’s constant, and \( T \) the temperature. Following the usual choice, \( \rho_j v_i = 1 - r_i/r_k \) with \( r_k = r_k \).

The walls confining the fluid are made by restraining particles to fixed positions by means of harmonic springs, acting on top of the aforementioned interactions. For particle \( i \) with reference position \( r_i^0 \), the additional force reads:

\[
\mathbf{F}_i^w = -k_w (r_i - r_i^0) \tag{10}
\]

with spring constant \( k_w \). The reference positions are generated as the positions in a snapshot of a bulk simulation of a liquid at the equilibrium density, followed by removal of all particles with positions outside the desired contours of the wall. Due to the softness of the conservative repulsive potential, the liquid particles may occasionally diffuse into the walls; to prevent these particles from penetrating too deeply, a purely repulsive Weck–Chandler–Andersen (WCA) potential is introduced between fluid particles and all wall particles more than \( 1.5 \sigma \) below the surface of the wall.

In the simulations and in all reported numerical values, we use the cutoff radius \( r_w \), the thermal energy \( k_B T \), and the mass of the particle \( m \) as the units of length \( \sigma \), energy \( \epsilon \), and mass, respectively. These choices imply a unit of time \( \tau = m^{1/2} \sigma / \epsilon^{1/2} \). The set of parameters common to all simulations is summarized in Table 1. The equations of motion are integrated using leapfrog Verlet. It is well-known that the actual kinetic and configurational temperatures in (MD)DPD exceed the desired temperature.\(^9\)\(^,\)\(^10\) At the selected time step of \( 0.01 \tau \), the equilibrium temperature exceeds the desired temperature by about \( 5\% \).

To simulate imbibition, the wall of a cylindrical nanopore with a radius of \( 5 \sigma \) and a length of \( 115 \sigma \), consisting of \( 52 \) \( 272 \) particles, was \"cut\" from a snapshot of a bulk fluid with an average number density of \( 6 \sigma^{-3} \). A flat substrate of \( 20 \sigma \times 20 \sigma \times 2 \sigma \) with a centered circular pore of radius \( R \), consisting of \( 3875 \) particles, was attached adjacent to the entrance of the pore, matching in size with the periodic boundary conditions in the \( x \) and \( y \) directions, see Figure 1. Reflective boundary conditions were applied in the \( z \) direction, using walls placed at \( 14 \sigma \) from the flat substrate and at \( 10 \sigma \) beyond the end of the channel, to confine the few evaporated particles. A periodically continued slab of the reference liquid, containing \( 54 \) \( 208 \) particles was also extracted from a bulk liquid snapshot, corresponding to a volume of \( 20 \sigma \times 20 \sigma \times 2 \sigma \) and \( 23 \) \( \sigma \). This slab of fluid was positioned at \( 50 \sigma \) from the flat substrate,

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Figure 1. Cross-section of a cylindrical channel (walls of gray particles) of radius \( R \), being imbibed with fluid (blue particles) entering from the reservoir on the left. The imbibition depth \( z(t) \) is measured from the entrance of the channel to the axial center of the meniscus. The fluid reservoir next to the channel is periodic in the \( x \) and \( y \) directions, bounded by a flat wall surrounding the channel at \( z = 0 \) and capped by a liquid–vapor interface in the negative \( z \) direction.
“The first three lines of the table define the units of length, energy and mass, respectively, thereby implicitly defining the unit of time as $t = m^{1/2} \sigma^{-1}$. All following parameters are given by their numerical values in these units. Lines four to nine list the parameters shared by all simulations, where the subscripts $l$ and $w$ denote liquid and wall particles, respectively. The last two lines specify parameters specific to the reference liquid.

Table 1. Summary of Simulation Parameters$^d$

| description          | symbol | value |
|----------------------|--------|-------|
| cut-off distance     | $r_{0, f}$ | $1\sigma$ |
| thermal energy       | $k_BT$ | $1\epsilon$ |
| mass of particle     | $m$ | $1m$ |
| cut-off distance     | $r_{\infty}$ | $0.75\sigma$ |
| attraction strength  | $A_{\infty}$ | $-40\epsilon/\sigma$ |
| repulsion strength   | $B_{\infty}$ | $25\epsilon a^2$ |
| friction strength    | $D_{h}$ | $6\epsilon a^2$ |
| spring constant      | $k_s$ | $12.5\epsilon a^2$ |
| time step            | $dt$ | $0.01\tau$ |
| attraction strength  | $A_{\infty}$ | $-40\epsilon/\sigma$ |
| friction strength    | $D_{h}$ | $6\epsilon a^2$ |

The equilibrium liquid—wall contact angle $\theta$ as a function of the liquid—wall interaction strength $A_{\infty}$ for $A_f = A_{\infty} = -40\epsilon/\sigma$. The error bars (enlarged by a factor of 2, denoted as $\times 2$) represent the sensitivity of the contact angle to shifting the definition of the flat “surface” of the walls by $2.5\sigma$ inward and outward. A precursor layer covers the walls for $A_{\infty} \leq -40\epsilon/\sigma$, implying a contact angle $\theta = 0^\circ$. The contact angle at $A_{\infty} = -30\epsilon/\sigma$, see inset, was estimated by eye at $90^\circ$; the fit procedure fails for a flat meniscus. The perfectly wetting reference fluid is highlighted by a deviant marker.

The imbibition simulations were continued until the precursor layer approached the end of the channel, by which time most fluid particles had entered the pore.

**System Characterization.** The liquid—vapor surface tension $\gamma_f$ is obtained by simulating a slab of liquid in a periodic simulation box of dimensions $L_x \times L_y \times L_z$. The liquid spans the length of the box in the first two directions, parallel to the slab, but the box height in the direction perpendicular to the slab well exceeds the thickness of the liquid slab, thereby effectively forming an alternating stack of liquid and vapor layers along the third direction. A small variation of the ground plane area $A_f = L_x^2$ of the box will alter the interfacial area by twice this amount, while at constant total volume $V$ this small variation will not affect the bulk liquid and vapor contributions to the total Helmholtz free energy of the system, $F_{sys}$. Combining the specifics of this system with the generic pressure expression of thermodynamics gives:

$$
\gamma_f = \frac{1}{2} \frac{\partial F_{sys}}{\partial h_{N,V,T}} = \frac{L_x^2}{2} (P_{ll} - P_l) \tag{11}
$$

where $P_{ll} = \frac{1}{2} (P_{xx} + P_{yy})$ and $P_{ll} = P_{xx}$ denote the pressures along the directions parallel and perpendicular to the slab, respectively, and where the angular brackets denote a canonical average over the Boltzmann distribution, which is evaluated in the NVT simulations as a time average. The pressures are calculated using the virial expression,

$$
P_{\alpha\beta} = \frac{1}{V} \sum_{i<j} \{ m_i u_{i\alpha} v_{i\beta} + \sum_{i<j} r_{ij\alpha} F_{ij\beta} \} \tag{12}
$$

with $\alpha$ and $\beta$ referring to the three Cartesian directions, $F_{ij}$ includes all forces acting between particles $i$ and $j$, and the second summation runs over all unique particle pairs.

The contact angle at the solid—liquid—vapor line, $\theta$, is extracted by simulating a liquid slab sandwiched between two parallel walls, with normals in the $x$ direction and separated by a height $h$, as illustrated in the inset to Figure 2. The liquid is in contact with both walls and is periodically continued by spanning the length $L_x$ of the box, but the fluid does not span the length $L_x$ of the box and therefore liquid and vapor periodically alternate along the $z$ direction. In this setup, the two liquid—vapor interfaces adopt the same equilibrium shape with one finite and one infinite radius of curvature, i.e., the interface is a segment of a cylindrical surface. The contact angle $\theta$ for partially wetting fluids is obtained as the angle between this surface and the surface of the wall, i.e., the plane used in “cutting” the wall from a liquid box. To determine the interfacial shape, all fluid particles are assigned to layers of thickness $\Delta x$ based on their elevations $x_i$ above the bottom wall. In each layer, the particles are binned in intervals of length $\Delta z$ to obtain a density profile $\rho(z)$ parallel to the wall, relative to the center of mass of the fluid at $z = 0$. The resulting density profile of each layer is fitted with the approximate theoretical density profile,

$$
\rho(z) = \frac{\rho_0}{2} \left( 1 - \tanh \frac{z - z_{fl}}{\Delta z} \right) \tag{13}
$$

where the equilibrium bulk density $\rho_0$, the location of the surface $z_{fl}$ corresponds to half the bulk density, and the width of the interface $\Delta z$ is independent fit parameters for every layer. This specific equation applies for the $z > 0$ interface, with a mirrored version applying to the $z < 0$ interface. The collection of $z_{fl}(x)$ for all layers, minus the layers within $2\sigma$ from the walls on either side to exclude a prewetting layer, is used to fit the interface with a circle segment. The contact angle is identified with the angle at which the extrapolation of this segment intersects the surface of the wall. For completely wetting liquids, i.e., liquids that spread to form monolayers covering both walls, the contact angle equals zero by definition.

The imbibition of the fluid entering a cylindrical channel is analyzed in a similar fashion. Under equilibrium conditions the meniscus will adopt two identical radii of curvature, forming a segment of a spherical surface. The fluid particles are assigned to coaxial cylindrical shells of thickness $\Delta r$, based on their distance $r$ to the central axis of the channel. In each shell, the particles are binned in intervals of length $\Delta z$ to obtain a density profile $\rho(z)$, followed by fitting with the approximate theoretical density profile of eq 13. Henceforth, the imbibition depth of the meniscus $z_{fl}$ is identified with the fitted interfacial position $z_{fl}$ for the innermost cylindrical shell, which comprises all particles within $\Delta r$ from the pore’s axis. The collection of $z_{fl}(r)$ for all shells, minus the two shells closest to the wall, is used to fit the interface with a circle segment which in turn determines the contact angle at the wall. The velocity profile of the imbibing fluid, $v(r,z,t)$, is obtained using the binning procedure described above, by determining the main axial and radial components of the particle velocities in every shell-bin combination at regular intervals in time. The time-averaging procedure, required to obtain statistically relevant velocities, is
hampered by the nonuniform motion of the imbibition front. We take advantage of the expected flow profile being proportional to the axial velocity of the meniscus, \(v_\text{m} = \dot{z}_\text{m}\) by time-averaging the normalized axial velocity,

\[
\bar{v}(r, \tilde{z}) = \left( \frac{v(r, \tilde{z} + z_a(t), t)}{v_a(t)} \right)
\]

where \(\tilde{z}\) denotes the axial position relative to the imbibition front. The radial velocity is time-averaged likewise, again by normalization with the axial velocity of the meniscus.

The viscosities of the various fluids are obtained from simulations of bulk fluid under a linear shear flow, \(\dot{\gamma}(\ell) = \gamma_\text{Lees-Edwards}\) imposed using Lees–Edwards sliding boundary conditions with a shear rate \(\dot{\gamma}\). The viscosity follows from \(\eta = (P_{\text{eff}})/\dot{\gamma}\), where the off-diagonal pressure element \(P_{\text{eff}}\) is calculated using the virial expression of eq 12, with the velocities corrected for the imposed linear velocity profile. Omission of this offset, however, hardly affects the value of the viscosity.

## RESULTS AND DISCUSSION

### Pure Liquids

The surface tension of the reference fluid was determined following the procedure outlined above. A fairly large slab of fluid was used, consisting of 17 248 particles in a periodic box measuring \(15\sigma \times 15\sigma \times 140\sigma\), to minimize finite size effects.\(^5\) The slab attained an equilibrium thickness of \(\sim 12.8\sigma\), corresponding to a number density \(\rho \approx 6.0\sigma^{-3}\). A production run of \(10^3\tau\) yielded \(\gamma_{\text{av}} = 7.29 \pm 0.03\sigma/\ell\). The contact angle \(\theta\) was obtained by computing 13 690 fluid particles between two parallel walls of \(40\sigma \times 20\sigma \times 2\sigma\), comprising 10 840 particles each and separated by \(16\sigma\), see the inset to Figure 2. Production runs at each value of the fluid–wall interaction strength, \(A_{\text{ww}}\), lasted for \(7 \times 10^5\tau\), with snapshots saved every \(2\tau\) and analyzed using a \(0.5\sigma \times 0.5\sigma\) grid. Figure 2 shows that the contact angle can be varied from zero to \(\sim 180^\circ\) by tuning the liquid–wall interaction strength. With decreasing (more negative) liquid–wall interaction strength, a precursor layer forms when, at \(A_{\text{ww}} = -40\sigma/\ell\), the interaction strength between unlike particles matches that between like particles; this is the strength henceforth used for wall interactions by the reference fluid. The viscosity was obtained from bulk simulations of 4 374 fluid particles in a \(9\sigma \times 9\sigma \times 9\sigma\) box subject to sliding Lees–Edwards boundary conditions. For shear rates around \(\dot{\gamma} \sim 0.01\tau^{-1}\), the fluid shows Newtonian behavior with a viscosity \(\eta = 7.33 \pm 0.05\sigma/\ell\).

The imbibition of the reference fluid into the cylindrical pore was analyzed by the aforementioned methods, using grid cells measuring \(\Delta r = 0.5\sigma\) by \(\Delta z = 1\sigma\), for nine independent simulations. Figure 3 confirms the expected linear increase of the squared imbibition depth with time, after the start-up effects have faded. Numerical evaluation of the slopes over the time interval \(2000\tau \leq t \leq 5500\tau\) in all nine simulations yields \((83 \pm 1)\%\) of the slope predicted by BCLW theory, see eq 1. This may indicate that inertia, slip, or the dynamic contact angle are weakly affecting the imbibition process.\(^{19,25}\) By increasing the friction coefficient, we established that quantitative agreement with BCLW theory is achieved in all simulations of fluids with \(D_{\ell} \geq 11\ell_{c}/\sigma^2\), for viscosities exceeding \(15\ell_{c}/\sigma^2\), at the expense of a substantial increase in the run time of the simulations. We nevertheless opt for the parameter values for the reference fluid collected in Table 1, as these already allow a near-quantitative study of the imbibition process at manageable computational demands.

Focusing next on the imbibition front, Figure 4(a) shows a uniform density throughout most of the fluid. The steep decline within \(\sim 1\sigma\) of the wall of the channel reflects the particulate nature of the simulated fluid. Clearly visible are the narrow width of the liquid–vapor interface, the curvature of the concave meniscus, and the tip of the meniscus adjacent to the wall. The wetting layer at the wall steadily becomes more pronounced as a precursor layer develops at the walls (this growth is not visible from the plot), while the contact angle simultaneously decreases from the initial value of about \(90^\circ\) to a final steady value of \(0^\circ\) for this completely wetting fluid. The average shape of the meniscus, depicted as a black line in Figure 4(a), is obtained by fitting the density profiles along \(z\) in concentric cylindrical shells with the theoretical profile of eq 13; the location at the center, \(z_\text{m}(0)\), defines a zero-point moving with the meniscus, thereby enabling averaging of the profiles over time. The averaged meniscus is close to hemispherical—appearing in the figure as an ellipse fragment due to the stretch (compression) in the radial (axial) directions—and barely touches the wall. The radius of curvature of the meniscus therefore nearly matches the radius of the pore, which in combination with the surface tension \(\gamma_{\text{lw}} = 7.29\sigma/\ell\) yields a capillary pressure \(P_{\ell} = 2\gamma_{\text{lw}} \cos \theta / \ell \approx 3\sigma/\ell^2\).

Having established that the imbibition rate of the completely wetting fluid almost follows the BCLW law, it appears likely that the assumption of Poiseuille flow underlying that law is also obeyed. The velocity distribution near the imbibition front is presented in Figure 4(b), where velocities at different times during the imbibition process are combined by the normalization procedure of eq 14. The axial velocities are small relative to the radial velocities, with the highest velocities reached at the pore’s center while the fluid adjacent to the wall is essentially stationary. Extracting the radial profile of the axial velocity averaged over the zone behind the meniscus, \(5\sigma \leq z \leq 15\sigma\), yields a quadratic profile, see Figure 4(c), in agreement with the expected Poiseuille flow. Extrapolation of the profile to the intersection with the wall yields a nearly vanishing slip length.

For later reference, we note that the simulations of partially wetting fluids show a modest slip at the walls (data not shown), in agreement with earlier observations.\(^{18,25}\) As long as the shape of the Stokesian imbibition flow profile is conserved and scales with \(z(t)\), the overall rate of energy dissipation due to flow is proportional to \(z(t)^3\); this loss is balanced by the potential energy gained by wetting the wall of the pore, at a
rate proportional to $\dot{z}(t)$, together giving rise to the generic $t^{1/2}$ imbibition law observed for these fluids (data not shown). Slip reduces the effective friction coefficient relative to the Poiseuille flow underlying BCLW theory, and consequently enhances the imbibition process. Dimitrov et al.\textsuperscript{18} found that the BCLW expression in eq 1 is readily corrected for slip through multiplication by $(1 + \delta/R)^{3}$, where $\delta$ denotes the slip length, thereby recovering agreement with their simulation results. For more details on the impact of wetting on the microscopic slip-stick boundary condition at a wall, we refer the reader to Barrat and Bocquet.\textsuperscript{54}

**Mixtures with Distinct Viscosities.** An appealing feature of MD PD is the possibility to study model liquids with identical thermodynamic properties but different dynamic behavior, by the expedient of changing the parameter $D_i$ determining the strengths of the friction and random forces. We supplement the reference liquid, color-code blue (b), with a liquid of higher viscosity, color-code green (g). The attractive interactions between unlike particles are set to the same strength as those between like particles, $A_{bb} = A_{gg} = A_{bg} = -40e/\sigma$ and $A_{wg} = A_{gw} = -40e/\sigma$; the repulsive interactions between particles are identical in all simulations ($B_i$ and $\rho_i$ are color blind). Consequently, the two fluids mix homogeneously at any ratio and the equilibrium thermodynamics properties of their mixtures are identical to those of the reference liquid. Notably, the fluid mixture possesses a surface tension $\gamma_f = 7.29e/\sigma^2$ and is perfectly wetting. We focus in this section on the two pure fluids and two equimolar mixtures hereof. The friction parameter of the green liquid is set at double that of the reference liquid, $D_{gg} = 2D_{bb} = 12e\tau/\sigma^3$, thereby raising the viscosity of the fluid from $\eta_g = 7.33e\tau/\sigma^3$ to $\eta_g = 17.33e\tau/\sigma^3$. Two distinct values were applied for the friction between unlike particles in the two equimolar mixtures: in the first mixture the cross term equals the friction of the blue fluid, $D_{bg} = D_{bb}$, while in the second mixture it equals the friction of the green fluid, $D_{bg} = D_{gg}$. The viscosities of these mixtures were determined as $\eta_1 = 9.33e\tau/\sigma^3$ and $\eta_2 = 14.32e\tau/\sigma^3$, respectively.

Imbibition studies on the two pure fluids and two fluid mixtures are presented in Figure 5, showing averages over 25 independent runs for each combination. As expected, the rate of penetration decreases with increasing viscosity. After the attenuation of start-up effects, all four fluids display a squared imbibition depth growing linearly with time. Notably, the quantitative agreement with eq 2 improves with increasing fluid viscosity, with the most viscous fluid (green) yielding the theoretically predicted slope of unity for a perfectly wetting fluid. By simulating even more viscous fluids (data not shown), we confirmed that the slope of unity is an upper limit. Closer inspection of the two mixtures reveals a slight enrichment by 0.3 ± 0.01% of the less viscous component (blue) over the more viscous component (green) in the pore. Comparison of the density plots in Figure 6 shows that the blue fluid is slightly more abundant than the green fluid in the region directly behind the meniscus, while the sum density in the bulk is still fairly uniform. Both liquids show almost identical density profiles near the wall. The velocity plots of both liquids are the same and are in good agreement with the expected Poiseuille profile (data not shown). The enrichment of the blue component near the meniscus gradually vanishes after discontinuation of the flow, indicating that it is of a dynamic origin.

**Mixtures with Distinct Wettabilities.** Simulations also enable the study of model fluids that differ only in their affinity to the wall. In this case, the perfectly wetting reference liquid
(blue) is mixed in equal ratio with a second liquid (red) having a lower adherence to the wall. All parameters of the red particles are identical to those of the blue particles, as are those for the red-blue interactions, except for the strength of the conservative particle–wall interaction, which is smaller (less negative) for the red particles, $A_{rw} \geq A_{bw}$. Consequently, both fluids and their mixtures share the same thermodynamic and dynamic properties, save for their liquid–wall interfacial energies and hence their contact angles. Using the previously introduced configuration of a fluid slab sandwiched between two flat walls, the contact angles were obtained for equimolar mixtures of 7197 particles in a slit of height $h = 6\sigma$. As shown in Figure 7, the contact angle steadily increases with decreasing wetting affinity of the red component, saturating at a contact angle of $\sim 45^\circ$. Even when the pure red liquid is nonwetting, which following Figure 2 occurs for $A_{rw} \geq -30\epsilon/\sigma$, the mixture remains partially wetting. The reference component is perfectly wetting and hence a blue precursor film covers the wall under all conditions, while with increasing $A_{rw}$ the red component retracts into the bulk of the fluid slab, where it is shielded from the walls by a layer of blue fluid, as illustrated by the snapshot in Figure 7. Since, by construction, the wall–vapor and liquid–vapor surface tensions are constant in these simulations, it follows from Young’s equation that the wall–liquid surface tension decreases with increasing $A_{rw}$. This result may appear counterintuitive, as the wall remains covered by a layer of perfectly wetting fluid, but is explained by the entropy reduction accompanying the formation of the blue layer covering the wall. Confining the red particles to a smaller volume, by exclusion from the walls, reduces their entropy. The accumulation of the blue particles at the walls, at the expense of their number in the bulk of the fluid, reduces their entropy as well. The effective interfacial tension of the mixture is therefore lower than the interfacial tension of the blue fluid covering the walls. Because the entropy reduction is codetermined by the fluid’s volume and its contact area with the walls, the strength of the effect will vary with the systemsize. The analysis was therefore repeated using 19 224 particles in a slit of $16\sigma$ height and for 25 256 particles at $h = 21\sigma$. The contact angles for the second and third system are nearly identical, while those of the first system—with a slit height comparable to the radius of the pore—are slightly higher. The contact angles were therefore also determined for stationary fluid mixtures inside the standard pore of radius $R = 5\sigma$ and in a larger pore of twice that radius. A good agreement is observed with the contact angles at flat walls; the small differences can be attributed to slightly deviant compositions of the fluid mixture in the interior of the pore, as the surface-to-bulk ratio varies between the systems, and might be compounded with a contribution from the contact line.

The imbibition process was simulated for three mixtures of the reference fluid with fluids of reduced wettability, with $A_{rw} = -35\epsilon/\sigma$, $-30\epsilon/\sigma$, and $-25\epsilon/\sigma$, respectively, yielding the imbibition curves of Figure 8. Like the pure fluids, the squared imbibition depth increases linearly in time. The inset shows that, as expected, the imbibition process becomes slower with decreasing wall philicity of the red component. Scaling the imbibition depth with $\cos \theta$ in the main plot, using the contact angles of Figure 7, hardly reduces the differences between the four curves, in marked deviation from BCLW theory. Inspection of the simulation data reveals two main actors contributing to this deviation. The velocity profile, as shown in Figure 9 for a mixture of the reference fluid with a nonwetting fluid, is much flatter than Poiseuille flow and shows a pronounced slip velocity at the pore wall. As discussed above for the pure fluids, slip increases the prefactor to the generic $\sqrt{t}$ scaling law beyond its value in BCLW theory. The imbibition processes in Figure 8, however, are lagging behind the predictions of BCLW theory. Inspection of the fluid composition near the imbibition front, see Figure 10, shows...
a pronounced enrichment of the wall-philic (blue) component at the walls and of the wall-phobic component (red) directly below the meniscus. Curiously, the red fluid—which as a pure fluid is nonwetting, \( \theta_{\text{rw}} > 90^\circ \), and consequently will not enter the pore spontaneously—not only enters the pore when part of a mixture but is also significantly enriched at the imbibition front (see Movie S1 in the Supporting Information, SI). While an over-representation of the red fluid in the center of the pore is to be expected, see Figure 7, the degree of enrichment is surprisingly large and far exceeds that in the equilibrium system. Note furthermore that the overall meniscus is relatively flat, with a radius of curvature equal to about 12 pore diameters and hence a corresponding decrease in the capillary pressure to \( P_c \approx 0.9 \sigma / \epsilon^3 \), relative to the pure blue fluid with the same surface tension in Figure 4.

The local enrichment of one component, and the corresponding depletion of the other component, is also clearly visible in the cross sections of the density profiles in Figure 11. Except for a small region close to the wall, the overall number density is nearly uniform at \( \rho \approx 6.0 \sigma^{-3} \). The density of the blue fluid shows a narrow peak near the wall, whereas that of the red fluid drops sharply near that peak, indicating that the wall is covered by a monolayer of blue particles; the composition of this layer is fairly uniform along the entire imbibed segment of the pore, as can be seen in Figure 11(c). Away from the walls, the density of blue (red) particles is lower (higher) than in the reservoir, essentially independent of the distance from the pore center and increasing (decreasing) with the distance from the meniscus. Averaged over the entire pore, however, the fraction blue slightly exceeds the fraction red, by \( (0.6 \pm 0.3)\% \), where the standard deviation reflects variation between independent simulations of the same system. Evidently, the segregation of the mixture near the wall and near the meniscus reduces the free energy gained by covering the pore wall, and thereby slows down the imbibition process relative to BCLW theory. A comparison of the mixture with pure fluids is provided in Figure 12. The equilibrium contact angle of \( \sim 35^\circ \) of the mixture is approximately matched by the pure fluid with a fluid–wall interaction parameter \( A_{\text{lw}} = -33 \sigma / \epsilon \), while the thermodynamic and dynamic properties of these two fluids are as much as possible equal by construction—note, however, that the differing affinities to the wall might affect the slip lengths.\(^{34} \) Despite these macroscopic similarities, the pure fluid flows more readily into the pore. Conversely, the pure fluid that matches the imbibition rate of the mixture has a contact

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**Figure 8.** Squared rescaled imbibition depth versus reduced time during the imbibition of binary equimolar mixtures of fluids differing in their wall-philicities. The interaction strength of the reference fluid (blue) with the wall is fixed at \( A_{\text{rw}} = -40 \epsilon / \sigma \), while that of the red fluid, \( A_{\text{bw}} \), is indicated in the legend. The inset shows the unscaled \( z(t) \) data over the same time range. The black line represents BCLW theory, assuming \( z_0 = 0 \).

**Figure 9.** Normalized axial velocity profile (black circles) as a function of the distance from the central axis of the pore, for a binary mixture with differing wall affinities, which differs significantly from the ideal Poiseuille profile with the same overall flux (black line). Normalized velocities in the region of 5 to 15 \( \sigma \) behind the meniscus were averaged over the time interval 2000 \( \tau \leq t \leq 10000 \), corresponding to imbibition depths 30 \( \sigma \leq z \leq 90 \sigma \) across five simulations. The axial velocities of the two components in the mixture, i.e., the completely wetting reference fluid (blue) with \( A_{\text{bw}} = -40 \epsilon / \sigma \) and the wall-phobic fluid (red) with \( A_{\text{bw}} = -25 \epsilon / \sigma \), are indicated by colored markers.

**Figure 10.** Time-averaged density fields near the meniscus during the imbibition of an equimolar mixture of (a) the reference perfectly wetting fluid (blue) with (b) a nonwetting fluid (red), for \( A_{\text{bw}} = -25 \epsilon / \sigma \). The black lines denote the average shape of the meniscus, based on the overall density.
angle of $\sim 70^\circ$, nearly double that of the mixture, while all other
dynamic and thermodynamic properties of these two fluids are
as much as possible equal by construction. A quantitative
description of the imbibition process in terms of the
macroscopic properties of the mixture remains elusive at this
point. The reduced effective interfacial tension, as represented
in BCLW theory by the contact angle, does not appear to fully
account for the actual free energy gain during imbibition.

The bigger picture that emerges from the simulations of the
mixture of a complete-wetting and a nonwetting fluid, as a
mixture of extremes, is that the former fluid preferentially
covers the wall, thereby driving the latter fluid away from
the walls to the interior of the pore. Since the axial flow velocity
increases with the distance from the wall, the nonwetting fluid
is thus propelled to the imbibition front. The monolayer of
blue particles covering the wall appears to act as a lubrication
layer for the mixture, slipping along the wall of the pore. While
the blue fluid wets the wall, the red fluid wets the blue
monolayer; the latter process likely proceeds more easily due
to the abundance (scarcity) of red (blue) particles near the
meniscus—note, however, that the blue fluid slips along the
wall while the red fluid sticks to the blue monolayer. The red
fluid will not proceed beyond the edge of the blue monolayer,
and consequently accumulates as the front. Similar behavior,
though less pronounced, is observed for mixtures with smaller
differences between the two wall affinities. The dynamics of the
imbibition process is crucial to the observed imbalance
between red and blue particles: after cessation of the
flow, i.e., when all fluid has entered the pore, the red–blue ratio at
the front starts to decrease: by a slow diffusion process, the

Figure 11. Density profiles during imbibition of a pore by a mixture of the completely wetting reference fluid (blue) and a nonwetting fluid (red), differing in their wall affinities only. $A_{bw} = -40\epsilon/\sigma$ versus $A_{rw} = -25\epsilon/\sigma$. Their number densities, as well as the overall number density (black), are plotted (a) as functions of the distances from the pore center, at three distances $\bar{z}$ behind the meniscus, see legend, and (b) as functions of the distance behind the meniscus, along coaxial lines at three distances $r$ from the center, see legend. The inset (c) shows the composition of the monolayer covering the wall, as obtained from the bin centered around $r = 4.75\sigma$.

Figure 12. Squared imbibition depth versus time during the imbibition of a binary equimolar mixtures (purple) and two pure fluids (light blue). For the particles in the mixture (purple), the interaction strengths are $A_{bw} = -40\epsilon/\sigma$ and $A_{rw} = -25\epsilon/\sigma$. The two pure liquids, with their wall interaction strengths $A_{lw}$ and contact angles indicated in the legend, match the mixture’s contact angle and imbibition rate, respectively.

Figure 13. Density profiles of an equimolar mixture of the perfectly wetting reference fluid (blue) and a nonwetting fluid (red) imbibing three cylindrical pores with radii indicated in the legend, and the corresponding overall density profile (black). The profile show (a) the variation with distance to the wall, at constant distance $\bar{z} = -2.25\sigma$ behind the meniscus, and (b) the dependence on the distance from the meniscus, along the axis of the pore. The inset (c) shows the compositions of the monolayers adjacent to the wall.
fluid reverses to a homogeneously mixed state along the length and width of the channel. The one exception is the monolayer covering the wall which, because of the favorable interaction energy, remains strongly enriched in the blue component. This nonequilibrium condition further complicates a quantitative understanding of the imbibition process.

The central role of the monolayer covering the wall suggests that the surface to volume ratio of the imbibed fluid is important to the imbibition process. The density profiles of Figure 13 were obtained by simulating the imbibition in pores with radii of 5, 7.5, and 10σ. The monolayers of blue particles covering the pore walls are almost identical in width and density in all three pores. As the pore radius increases, the formation of these layers is achieved by a smaller depletion of the concentration of blue particles away from the wall; consequently, the density of blue (red) particles near the center of the pore increases (decreases) with the pore radius. Red particles are still over-represented near the meniscus, and their excess again decreases with the distance from the imbibition front. Figure 14 shows that the imbibition curves for the three pores, after rescaling by R to remove the pore radius dependence predicted by BCLW theory, are reasonably similar. Larger pores contain more particles per unit length while the imbibition rate also increases with pore radius, and consequently a simulation at R = 10σ requires nearly six times the number of particles needed for a simulation at R = 5σ covering the same time range. Because the computation time increases correspondingly, we abstained from averaging over multiple independent runs for the larger pores. On the basis of three runs only, the contact angle is found to decrease from θ = 72° via 67° to 65° with increasing radius, at capillary pressures of 0.9e/σ, 0.8e/σ and 0.6e/σ, respectively.

The preceding observations, of a nonwetting fluid taking advantage of a completely wetting fluid to gain entry into a pore it would not have entered spontaneously, raise the question: what fraction of completely wetting fluid is needed for this effect to occur? Simulations of various mixtures of the reference fluid (blue) with a nonwetting fluid (red) differing in the wall affinity only, Anw = −25e/σ, are presented in Figure 15. Reducing the completely wetting component from 50% to 20% merely reduces the imbibition rate. Upon a further reduction to 10%, the imbibition is even slower and only starts some time after the deposition of the fluid mixture at the entry of the pore. Visualization of the process by VMD shows that the delay is caused by the slow formation of the monolayer, by blue particles diffusing randomly in an excess of red particles until they are adsorb at the walls. This delay is significantly prolonged at the lower fraction of 5% completely wetting fluid, with the imbibition again following √t scaling. Inside the channel the blue particles are always close to a wall, and visualization reveals that they are readily integrated in the monolayer; the slip velocity at the wall enables their subsequent transport deeper into the pore. This mechanism is distinct from that observed in the pure fluid, where flow in the bulk carries particles all the way to the front before they settle in a nonslip layer at the wall. Despite this marked difference, both processes follow the generic √t scaling law for the reasons discussed earlier. Imbibition was not observed at all—on a computationally accessible time scale—for a mixture containing 2% perfectly wetting fluid. It is conceivable that the formation of a blue monolayer covering the wall is no longer advantageous from a thermodynamic point of view, i.e., the energy gain might be outweighed by the accompanying entropy loss, thereby making imbibition impossible. The minimum amount of completely wetting or partially wetting fluid required to induce imbibition of a nonwetting fluid will vary with the exact properties of the two fluids, like their affinities to the wall and to each other, and is also subject to geometrical effects, like the dimensions of the fluid molecules relative to those of the pore and the area versus volume ratio of the pore. Evidently, if the fluid particles are reduced in size relative to the pore, while preserving the macroscopic properties of the two fluids, then a lower volume fraction of the completely wetting fluid suffices to form a monolayer coating the wall.

**CONCLUSIONS**

Many-body Dissipative Particle Dynamics was used to study the imbibition of fluids in cylindrical pores. Quantitative agreement with BCLW theory is observed for pure fluids and binary fluid mixtures, provided the equilibrium contact angle of the imbibing fluid is close to zero and its viscosity is sufficiently high. The imbibition of partially wetting fluids and fluid mixtures is modestly enhanced by slip at the wall. In binary mixtures of fluids differing in their affinities to the wall, the mixture partially segregates during imbibition: the wall-phile component forms a monolayer covering the wall, while the
wall-phobic component is over-represented in the center of the pore. Since the flow velocity is higher in the center, the wall-phobic component is carried—on average—further into the pore than the wall-phobic component and consequently dominates at the imbibition front. This enrichment of the wall-phobic component at the front is of nonequilibrium origin, and gradually disappears after cessation of the flow; the enrichment of the wall-phobic component at the walls is of thermodynamic origin and persists in the absence of flow. The impact of mixing a fluid with a small amount of a suitably chosen secondary fluid, or even the presence of contaminants with similar conducive properties, will probably be clearly visible in experiments as an alteration of the imbibition behavior. The biggest impact is to be expected when adding a fluid with high affinities for both the wall and the primary fluid. This combination of properties is most likely to be found in surfactants, though complicated by their concomitant impact on the meniscus. A binary liquid mixture close to its demixing critical point may also show interesting imbibition behavior. Further work is needed for a deeper understanding of the fascinating imbibition process of fluid mixtures.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at 10.1021/acs.langmuir.0c02361. Movie S1, a visualization, made with VMD, of the fluid mixture whose components differ only in their affinities to the capillary wall; the blue component is perfectly wetting, \( A_{w} = -40 \epsilon / \sigma \), while the red component is nonwetting, \( A_{w} = -25 \epsilon / \sigma \) (MPG)

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Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is part of an Industrial Partnership Programme of the Foundation for Fundamental Research on Matter (FOM), which is financially supported by The Netherlands Organisation for Scientific Research (NWO). This research program was cofinanced by Canon Production Printing (Venlo, The Netherlands). The authors thank Stefan Ludwig (UT), Herman Wijshoff (Canon), and Nicolae Tomozeiu (Canon) for stimulating discussions. An anonymous reviewer is acknowledged for suggesting the use of a near-critical mixture.

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