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On the kinetics of the capillary imbibition of a simple fluid through a designed nanochannel using the molecular dynamics simulation approach

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ABSTRACT

A molecular dynamics (MD) approach was employed to simulate the imbibition of a designed nanopore by a simple fluid (i.e., a Lennard–Jones (LJ) fluid). The length of imbibition as a function of time for various interactions between the LJ fluid and the pore wall was recorded for this system (i.e., the LJ fluid and the nanopore). By and large, the kinetics of imbibition was successfully described by the Lucas–Washburn (LW) equation, although deviation from it was observed in some cases. This lack of agreement is due to the neglect of the dynamic contact angle (DCA) in the LW equation. Two commonly used models (i.e., hydrodynamic and molecular-kinetic (MK) models) were thus employed to calculate the DCA. It is demonstrated that the MK model is able to justify the simulation results in which are not in good agreement with the simple LW equation. However, the hydrodynamic model is not capable of doing that. Further investigation of the MD simulation data revealed an interesting fact that there is a direct relationship between the wall–fluid interaction and the speed of the capillary imbibition. More evidence to support this claim is presented.

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1. Introduction

Understanding and controlling the flow of fluids at nanoscale is currently a subject of great interest. This phenomenon, namely, fluid flow at nanoscale dimensions, has significant implications, both for our understanding of how fluids behave at very small length scales and for the design of nanofluidic devices [1]. To characterize this phenomenon, one approach is to measure the rate of penetration of the liquid into the medium, which is then modeled as a bundle of uniform capillaries. A schematic diagram of this process is shown in Fig. 1. On a macroscopic scale, a commonly used equation, i.e., the Lucas–Washburn (LW) equation, of such flow processes was proposed almost a century ago [2,3]. The LW equation relates the length of liquid penetration in a straight-line capillary *H* to the permeation time *t*, the capillary radius *R*, the viscosity and surface tension of the liquid, η and γ_{lv} , respectively, and the contact angle θ between the liquid and the capillary wall as follows:

$$H^{2} = \left(\frac{R\gamma_{lv}\cos\theta}{2\eta}\right)t\tag{1}$$

The applicability of the LW equation has been tested for modeling liquid flow in nanopores [4,5]. To derive this equation, it is assumed that the contact angle does not change during the imbibition process. However, this assumption is not correct in general since the

contact angle corresponds to the moving wetting line and its value therefore depends on the wetting-line velocity [6]. Hence, modification of the LW equation is essential to take the velocity-dependent dynamic contact angle (DCA) into account. To estimate the DCA, various models of wetting-line movement can be used, such as those based on hydrodynamics [7,8], molecular-kinetics [9,10] or phenomenology [11], in which DCA is a function of wetting-line velocity (i.e., dH/dt). In this study, we focus on the hydrodynamic and MK models since they are among top cited models in the literature.

In the context of the hydrodynamic model, the first analysis was proposed by Voinov [12]. Later treatments differ in some detail. However, they recovered an equation of essentially the same form. To our knowledge, the most complete analysis is the Cox equation [7] as follows:

$$\theta_d = \left(\theta_e^3 + 9A \frac{\eta}{\gamma_{l\nu}} \frac{dH}{dt}\right)^{1/3} \tag{2}$$

and $A = \ln (R/s)$, where R is the characteristic length of the system, s is the slip length, and θ_d and θ_e denote the dynamic and equilibrium contact angles, respectively. In the case of the capillary penetration phenomenon, the characteristic length R is the capillary radius, and the slip length s is the distance from the capillary wall that defines a region where the continuum description of fluid motion tends to break down [13]. The value of slip length should be in the order of molecular dimensions [14]. However, in practice, the quantity s is usually treated as an adjustable parameter. The modified version

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of the LW equation including the effect of the DCA on the penetration kinetics is as follows:

$$\frac{dH}{dt} = \left(\frac{R\gamma_{l\nu}\cos\theta_d}{4\eta H}\right) \tag{3}$$

The hydrodynamic model considers the dynamic wetting process to be dominated by the viscous dissipation of the liquid, assuming the bulk viscous friction is the main resistance force for the three-phase wetting-line motion. It is worthwhile to note that the hydrodynamic model does not take the characteristics of the solid surface into account, which is the main limitation of the model. Additionally, the physical meaning of the parameters in this model is not unambiguous [15].

In contrast to the hydrodynamic model, the molecular-kinetic (MK) model, which first suggested by Cherry et al. [16] and Blake et al. [9], excludes the viscous dissipation and takes the solid surface characteristics into account [17] such that the energy dissipation occurs only at the moving contact line. According to this model, the macroscopic behavior of the wetting line depends on the overall statistics of the individual molecular displacements that occur within the three-phase zone, i.e., the microscopic region where the fluid/fluid interface meets the solid surface. The velocity of the wetting line is characterized by K^0 , the natural frequency of the molecular displacements, and λ , their average length. In simple cases, λ stands for the distance between two neighboring adsorption sites on the solid surface. Assuming the driving force for the wetting line to be the out-of-balance surface tension force $\gamma_{lv}(\cos \theta_e - \cos \theta_d)$ and using the Eyring activated-rate theory for transport in liquids gives a relationship between θ_d and the velocity of the wetting line dH/dt:

$$\frac{dH}{dt} = 2K^0 \lambda \sinh\left[\frac{\gamma_{l\nu}(\cos\theta_e - \cos\theta_d)}{2nk_BT}\right]$$
(4)

where *n* is the number of adsorption sites per unit area, k_B is the Boltzmann constant, and *T* is the temperature. For small arguments of the sinh function, which occur when the driving force is small (e.g., near equilibrium, close to the critical temperature, or at high temperatures), the above equation simplifies to:

$$\frac{dH}{dt} = \frac{K^0 \lambda}{nk_B T} [\gamma_{l\nu} (\cos \theta_e - \cos \theta_d)]$$
(5)

or

$$\frac{dH}{dt} = \frac{1}{\zeta} [\gamma_{l\nu} (\cos \theta_e - \cos \theta_d)]$$
(6)

where $\zeta = nk_B T/K^0 \lambda$ is effectively the coefficient of the wetting-line friction and is a function of the liquid viscosity and the interaction between the liquid and the solid surface [18]. By combining Eqs. (6)



Fig. 1. A schematic representation of flow of a liquid through a nanochannel having the radius *R*. (Note that the time-dependent height of imbibition is showed by *H*(*t*) for the liquid, which has the viscosity and the surface tension η and γ_{tv} , respectively. In addition, ideally, the meniscus of the liquid has a parabolic profile and makes a contact angle (θ) with the tube wall.)

and (3), we obtain the desired equation for the capillary imbibition as follows:

$$\gamma_{l\nu} \left[\cos \theta_e - \frac{\zeta}{\gamma_{l\nu}} \left(\frac{dH}{dt} \right) \right] = \frac{4}{R} \eta H \frac{dH}{dt}$$
(7)

While the experimentally determined values of λ are usually in the order of molecular dimensions, those for K^0 can vary widely (usually between ~10³ and ~10¹⁰ s⁻¹) [19], and generally decrease with increasing the viscosity of liquid. Moreover, there is no definitive way of predicting the values of λ , K^0 , and ζ for a given solid– liquid system, and therefore predicting the dynamic wetting behavior from independently measured quantities. As a consequence, λ and K^0 (or ζ) are usually treated as adjustable parameters and should obtain from experimental results by the curve-fitting procedure. Another problem intrinsic to the MK model is that there is no link to the wider hydrodynamics of the system [19].

In order to study the flow behavior of fluids inside nanochannels, one can exploit the benefits of the molecular dynamics (MD) simulation approach, which serves as a powerful tool to explore the molecular details of phenomena. To our knowledge, the first analysis of the capillary imbibition at nanoscale using MD simulation was reported by Martic et al. [10,20,21]. They verified the validity of the MK model along with the LW equation to explain the dynamics of the capillary imbibition at nanoscale. Recently, a general model to demonstrate the fluid flow in nanopores has been suggested by Dimitrov et al. [22], which was used to design an artificial neural network for modeling and predicting this phenomenon in our previous work [23]. This model is also based on MD simulation. As detailed below, the kinetics of the fluid penetration through nanopores was assessed with the aid of the MD simulation code developed by Dimitrov et al. [22], and then the applicability of the hydrodynamic and MK models to derivation of the DCA was evaluated. In this investigation, we deal with the capillary imbibition of a simple fluid at a designed nanopore. In addition, an interesting result regarding the role of the wall-fluid interaction in the capillary imbibition process is presented.

2. Model and MD simulation description

In this investigation, for the sake of simplicity, we did use the dimensionless, or reduced, MD units to define all physical quantities in the MD simulation runs. The model employed in this study, as shown in Fig. 2, is comprised of a cylindrical nanotube with the radius R = 10 (or $R = 10\sigma$). The capillary wall is presented by the atoms of a triangular lattice, which has a lattice constant 1.0 in units of the fluid atom diameter 1 (or 1σ). The atoms of the capillary wall can fluctuate around their equilibrium positions at R + 1, corresponding to a finitely extensible nonlinear elastic potential (i.e., U_{FENE}) as follows:



Fig. 2. An illustration of wetting of a designed nanopore by a Lennard–Jones fluid. (Note that the fluid particles, the tube wall, and the atoms of the reservoir adhesive wall are showed in blue, brown and yellow, respectively.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$U_{FENE} = -15\varepsilon_{w}R_{0}^{2}\ln\left(1 - \frac{r^{2}}{R_{0}^{2}}\right)$$
(8)

where ε_w is the depth of the potential well, R_0 is a constant ($R_0 = 1.5$) and r is the distance between any close pair of wall atoms bound in the triangular lattice. In the above equation, ε_w is defined as $\varepsilon_w = 1.0k_BT$, where k_B stands for the Boltzmann constant and T is the temperature of the system. In addition, it is assumed that the wall atoms interact by an LJ potential as follows:

$$U_{LJ}(r) = 4\varepsilon_{ww} \left[\left(\frac{\sigma_{ww}}{r} \right)^{12} - \left(\frac{\sigma_{ww}}{r} \right)^{6} \right]$$
(9)

where ε_{ww} and σ_{ww} are the depth of the potential well and the effective molecular diameter, respectively, which are determined to be ε_{ww} = 1.0 and σ_{ww} = 0.8. Therefore, it is ensured that no penetration of fluid particles through the wall occurs. The right side of the capillary tube is closed by a hypothetically impenetrable wall, which holds the fluid particles inside the tube. Notice that for all simulation runs, the maximum wetting length was smaller than the length of the nanotube in z-direction. Therefore, we are confident that the presence of such wall does not influence the nanochannel imbibition by the fluid. The left side of the capillary tube is attached to a rectangular reservoir 40×40 involving fluid particles with periodic boundaries perpendicular to the tube axis. To avoid entry of the fluid particles into the tube before commencement of the MD simulation runs, the capillary wall is assumed to be completely hydrophobic. Therefore, the fluid particles remain in the reservoir as a stable fluid film. At time t = 0, set to be the onset of capillary filling, the hydrophobic wall-fluid interactions are changed to hydrophilic ones and then the fluid enters the tube. At the same time, the structural and kinetic properties of the imbibition process are measured at equal intervals of time. In all simulation runs, a maximum capillary length of H_{max} = 55 is used. In order to integrate the equations of motion, the Verlet algorithm [24] is employed and the temperature is kept constant using a DPD thermostat [25] with a friction parameter of ξ = 0.5, Heaviside-type weight functions, and a thermostat cutoff of $r_c = 2.5\sigma$. The integration time step δt is obtained by $\delta t = 0.01t_0$, where t_0 is the basic time unit, which is obtained by the following equation:

$$t_0 = \sqrt{\frac{m\sigma^2}{48k_BT}} \tag{10}$$

where *m* and k_BT are chosen to be 1.

Here, our simulation at NVT ensemble is restricted to a simple fluid interacting via an LJ potential with $\varepsilon = 1.4$ and $\sigma = 1.0$. However, the wall–fluid interaction is regarded as a variable parameter, which is given by an LJ potential with strength ε_{WL} . To reduce the computation time, all interactions are cut off at $r_c = 2.5\sigma$. The total number of fluid particles is 25,000, while those forming the tube are 3243.

To determine the surface tension and viscosity of the LJ fluid, following Ref. [26] for the LJ fluid (at density $\rho_l = 0.774$), it is found that $\eta \approx 6.34 \pm 0.15$. A compatible value for the viscosity is derived by applying an equilibrium MD simulation at NPT ensemble and then using the correlation function of the off-diagonal pressure tensor components and the standard Kubo relationship [24]. Here, the system is considered to be at equilibrium when the temperature and normal pressure are constant. From the flat gas-fluid interface observed in the left side of our model (see Fig. 2), it is feasible to estimate the surface tension γ_{lv} from the anisotropy of the pressure tensor components [27] as follows:

$$\gamma_{l\nu} = \int \left[p_{zz}(z) - \frac{p_{xx}(z) + p_{yy}(z)}{2} \right] dz \tag{11}$$

The above equation yields γ_{lv} = 0.735 ± 0.015 for the LJ fluid. There are some methods to calculate the surface tension of an LJ fluid. In this work, the calculated γ_{lv} value for the LJ fluid was compared to the previous studies in which the surface tension was reported between 0.4 and 0.5 [28,29]. The first effort to obtain γ_{lv} was based on the friction theory [28] in which the surface tension value is about 0.42. In the second investigation [29], the gradient theory was used in which γ_{lv} is approximately 0.5. Now, let us see why our obtained γ_{lv} value (i.e., $\gamma_{lv} = 0.735 \pm 0.015$) is different with these approaches. The liquid–liquid interaction strength (ε) is 1.4, while the temperature is expressed in reduced LI units based on the ε = 1.0. For this stronger interaction, the surface tension will be higher. If we rescale the surface tension by this larger epsilon value to correct for this, we obtain 0.735/1.4 = 0.525. We did use the same equation with Duque et al. [29] and both γ_{lv} values were given at the same temperature (i.e., T = 1). Therefore, our obtained surface tension value is in good agreement with the previous works.

As mentioned previously, the interaction strength between the fluid and the wall is considered as a variable in our MD simulations since it has been proved that this parameter has a crucial influence on the imbibition process at nanoscale. By varying this interaction strength, the wetting behavior of the test fluid can be achieved in a wide range.

3. Results and discussion

Fig. 3 shows the time evolution of the squared height of wetting. It implies that the length of imbibition depends very sensitively on the strength of the wall-fluid interaction. Since this plot is not clear for $\varepsilon_{WL} = 0.6$ and 0.8, we decided to demonstrate the time evolution of the squared wetting length for the wall-fluid interactions 0.6 and 0.8 in a separate figure (i.e., Fig. 4). Fig. 4 also shows the best fits using the simple LW equation for the wall-fluid interactions 0.6, and 0.8. The simulation results are also summarized in Table 1. This Table indicates the correlation of the squared length of imbibition as a function of time for different ε_{WL} values in terms of a statistical parameter, namely, the squared correlation coefficient (R^2). The R^2 statistic is used almost universally in judging regression equations [30]. This statistic measures the correlation between the target values and those predicted by a given



Fig. 3. Plot of the squared height of wetting as a function of the time in the case of imbibition of the designed nanopore by the Lennard–Jones fluid for the wall–fluid interactions 0.6 (\bigcirc), 0.8 (*), 1.0 (+), 1.2 (Δ), 1.4 (\square), 1.6 (\diamond), 1.8 (\mathbf{H}) and 2.0 (\triangleright).



Fig. 4. Plot of the squared height of wetting against time in the case of imbibition of the designed nanochannel by the Lennard–Jones fluid for the wall–fluid interactions 0.6 (\bigcirc), and 0.8 (*). (Note that the best fits using the simple Lucas–Washburn equation were also depicted with (+), and (Δ) for the wall–fluid interactions 0.6, and 0.8, respectively.)

Table 1

Correlation of the squared wetting length as a function of the time in the case of imbibition of a Lennard–Jones fluid into a designed nanopore for various wall–fluid interactions (ε_{WL}) in terms of the squared correlation coefficient (R^2). (Note that the equilibrium contact angle (θ_e) was a fitting parameter.)

€ _{WL}	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
R^2	0.009	0.613	0.936	0.976	0.975	0.988	0.981	0.989
θ_e (°)	n.a.	n.a.	69.322	50.781	42.336	43.912	45.607	45.665

model. The square of correlation coefficient can take on any value between 0 and 1, with a value closer to 1 indicating that the model yields a greater fitness. For a perfect correlation, we would have R^2 = 1. Here, the R^2 parameter was used in order to assess the accuracy of the squared wetting lengths measured by the MD simulation in comparison with the corresponding values calculated by the simple LW equation. As can be seen from this Table, for ε_{WL} = 0.6 and 0.8, a good correlation is not achieved. These cases yield R^2 = 0.009 and 0.613, respectively. However, for all other values of ε_{WL} , a very good relationship between the squared length of imbibition and the time, ranging from $R^2 = 0.936$ to 0.989, is obtained. Incidentally, in the latter ε_{WL} values (i.e., $\varepsilon_{WL} = 1.0-2.0$), the accuracy of the LW equation is confirmed, whereas in the former choices of ε_{WL} (i.e., ε_{WL} = 0.6 and 0.8), the simulation results do not obey the simple LW equation and a modification of this equation is needed. Notice that only the contact angle (static or dynamic) varies in the LW equation and it was a fitting parameter in this investigation, namely, correlation of the squared length of imbibition as a function of time for each ε_{WL} value. Table 1 also lists the calculated static contact angle values for ε_{WL} = 1.0–2.0. Since for ε_{WL} = 0.6 and 0.8, a good correlation was not obtained, a static contact angle cannot be ascribed to these cases. As can be seen from this Table, there is an inverse relationship between the wall-fluid interaction and the contact angle. It means that if we increase the wall-fluid interaction, the tendency of the fluid to wet the nanochannel increases. In addition, the cases $\varepsilon_{WL} \ge 1.4$ provided almost the same contact angle value (\sim 44°). The latter issue can also be understood from Fig. 3 since for the cases $\varepsilon_{WL} \ge 1.4$, all simulation data approximately fall in the same region. This implies that the same wetting behavior of the nanochannel occurs for these cases.

In what follows, the reason for this observed discrepancy between the results of MD simulation and the LW equation is

examined. First, the inertia effect in our simulations is assumed to be small since the effect of inertia, which was initially proposed by Rideal [31] and Bosanquet [32], is only significant in the early stages of penetration, or when the capillary radius is large and/or the viscosity of liquid is small. Therefore, this effect is ignored in the analysis of the simulation results. In addition, the length of the nanotube is sufficiently short to safely ignore the influence of gravity. As mentioned previously, this observed deviation from the LW equation is a result of neglecting the DCA. In order to demonstrate this fact, we should verify that the MD simulation results are in good agreement with the LW equation considering the DCA where the simple LW equation is not valid (i.e., $\varepsilon_{WL} = 0.6$ and 0.8). To this end, we employed both hydrodynamic (i.e., Eq. (2) along with the Cox equation) and MK (i.e., Eq. (6)) models to obtain the DCA and to correlate the DCA as a function of the imbibition rate using the MD simulation data. In the case of applying the hydrodynamic model, as depicted in Fig. 5, a linear relationship between the cubic dynamic contact angle and the wetting speed was observed, which is in very good agreement with the Eq. (2). In the case of employing the MK model, as demonstrated in Fig. 6, a linear relationship between the cosine of dynamic contact angle and the imbibition rate was observed, which is in very good agreement with the Eq. (6). The results of this investigation are also summarized in Table 2, where it can be seen that for $\varepsilon_{WL} = 0.6$ and 0.8, $R^2 = 0.865 - 0.931$ can be calculated. It seems that this result justifies both hydrodynamic and MK models are able to describe the kinetics of fluid penetration at nanopores where the simple LW equation tends to break down. However, further investigation provided interesting results since it was evaluated whether the fitting parameters from these correlations are reasonable or not. In the case of the hydrodynamic model, the static contact angle and the slip length were the fitting parameters. The obtained values for these parameters are also listed in Table 2. As can be seen, the static contact angle values (i.e., $\theta_e = 89.986$ and 87.595 for $\varepsilon_{WL} = 0.6$ and 0.8, respectively) are reasonable since this parameter should have a value less than 90° to obtain a spontaneous wetting of the nanochannel. Additionally, there is an inverse relationship between the wall-fluid interaction and the contact angle. However, the slip length values are not acceptable. As mentioned previously,



Fig. 5. Correlation between the cubic dynamic contact angle and the wetting speed of the nanochannel by the Lennard–Jones fluid for the wall–fluid interactions 0.6 (\odot) , and 0.8 (*).



Fig. 6. Correlation between the cosine of dynamic contact angle and the imbibition rate of the nanochannel by the Lennard–Jones fluid for the wall–fluid interactions 0.6 (+), and 0.8 (Δ).

Table 2

Correlation of the dynamic contact angle as a function of the wetting rate taken from the hydrodynamic and molecular-kinetic models in the case of imbibition of a simple fluid into a designed nanopore for various wall-fluid interactions (ϵ_{WL}) in terms of the squared correlation coefficient (R^2). (Note that the equilibrium contact angle (θ_e), the slip length (s), and the natural frequency of the molecular displacements (K^0) were fitting parameters.)

Model type	€ _{WL}	R^2	θ_e (°)	S	K ⁰
Hydrodynamic	0.6	0.931	89.986	10.730	n.a.
Hydrodynamic	0.8	0.865	87.595	12.285	n.a.
Molecular-kinetic	0.6	0.929	89.977	n.a.	9.9470×10^{10}
Molecular-kinetic	0.8	0.871	89.559	n.a.	22.7530×10^{10}

the slip length is the distance from the capillary wall that defines a region where the continuum description of fluid motion tends to break down. Since the calculated slip length values (i.e., s = 10.7297 and 12.285 for $\varepsilon_{WL} = 0.6$ and 0.8, respectively) are greater than the radius of the nanochannel (i.e., R = 10), they are not acceptable. As a result, the hydrodynamic model is not capable of modeling the kinetics of the LJ fluid at the nanochannel where the simple LW equation tends to break down. In the case of the MK model, K^0 , the natural frequency of the molecular displacements, and the static contact angle were the fitting parameters. The obtained values for these parameters are also mentioned in Table 2. Again, the static contact angle values (i.e., $\theta_e = 89.977$ and 89.559 for ε_{WL} = 0.6 and 0.8, respectively) are reasonable. Additionally, there is an inverse relationship between the wall-fluid interaction and the contact angle. Moreover, K^0 values (i.e., $K^0 = 9.9470 \times 10^{10}$ and 22.7530 $\times 10^{10}$ for $\varepsilon_{WL} = 0.6$ and 0.8, respectively) are acceptable since, as stated previously, this parameter can usually choose a value between $\sim 10^3$ and $\sim 10^{10}$ s⁻¹ and when the wall-fluid interaction increases, the K^0 value increases. This finding is also in agreement with the fundamentals of the MK model. As a consequence, the MK model is able to model the kinetics of the LJ fluid at the nanochannel where the simple LW equation tends to break down. In addition, the MK model gives better R^2 values when the wall-fluid interaction is increased since the hydrodynamic model was developed to deal only with low capillary

numbers [33]. Capillary number *Ca* is given by $Ca = \eta v / \gamma_{lv}$, where v is the velocity of imbibition.

It is interesting to say that recently we performed the same simulation procedure in the case of a polymer [34]. For this fluid, it was shown that generally the simple LW equation is a reliable model to explain the kinetics of the capillary wetting phenomenon. However, nonconformity to this equation was observed in some cases (i.e., small wall-fluid interactions) since the simple LW equation overlooks the significant effect of the DCA on this phenomenon. In addition, it was demonstrated that the LW equation together with the hydrodynamic and MK models are not able to fit the simulation results for those cases, which are not in good agreement with the simple LW equation. In order to explain this observed difference between a simple fluid and a polymer, let us compare the characteristics of both fluids. The given polymer has a higher viscosity (i.e., $\eta \approx 205 \pm 25$) than that of the LJ fluid (i.e., $\eta \approx 6.34 \pm 0.15$). Knowing that the viscosity of fluid is a measure of interaction between fluid particles [35], it can be concluded that the fluid-fluid interactions affect the imbibition of nanochannels much more than do the wall-fluid interactions where the interaction between wall and fluid is weak. Moreover, generally, it was found that higher viscosity of a fluid (i.e., higher fluid-fluid interaction) leads to slower wetting rate of nanochannels.

In what follows, we would like to demonstrate an interesting fact taken from our MD simulation results. As can be seen from Fig. 3, there is a direct relationship between the wall-fluid interaction and the speed of the capillary imbibition. This corollary is in contrast with this idea that the rate of the capillary imbibition is a nonmonotonic function of the solid-liquid interaction [18,21,36]. The latter idea, which is based on the MK model, says that the strong solid-liquid interaction will have two opposing effects: increasing the driving force for the wetting (i.e., the outof-balance surface tension force $\gamma_{lv}(\cos \theta_e - \cos \theta_d)$), but also increasing the resistance to the wetting due to reducing the general mobility of molecules within the three-phase zone. The mathematical proof of this issue and related supporting evidence can be found in the literature [18]. As a result, the maximum velocity at which a liquid can wet a solid depends in a non-monotonous way on substrate wettability [36]. The verification of this idea has been presented in the case of the imbibition at nanopores using MD simulation approach [21]. We claim that this conclusion is not correct in general. It is true as long as the LW equation associated with the MK model is able to describe the kinetics of the imbibition. As verified previously, it happens when we confront the slightly partial wetting of a given system. In all other cases, the LW equation is capable of explaining the kinetics of the imbibition. Now, let us briefly review the latter case (i.e., Ref. [21]). They performed the large-scale molecular dynamics simulations to study the details of liquid imbibition into a cylindrical pore. The intramolecular interactions were considered to be the LJ type. By changing the strength of the wall-fluid interactions, they were able to vary the wettability of the nanopore. The dynamics of liquid imbibition were followed for two pores of different radii: 50 and 70 Å. During imbibition, the distance of meniscus penetration and the relaxation of the dynamic contact angle toward equilibrium as a function of time were measured. For both cases (i.e., the pore radii 50 and 70 Å), they found the imbibition speed of the nanopore is a nonlinear function of the fluid-solid interaction. The values of the wall-fluid interaction were determined to be ε_{WI} = 0.8, 1.0, and 1.5 and it was claimed that the case ε_{WI} = 1.0 corresponds to the maximum speed of the wetting. The main flaw of this work is that the consistency of the simple LW equation has not checked. More precise assessment of the MD simulation data in this work shows that for both cases ε_{WL} = 1.0 and 1.5 complete wetting occurs since simulation data, with a good approximation, fall in the same region (see Figs. 5 and 6 in Ref. [24]). In addition,

authors reported an equilibrium contact angle 0 for both cases (see Table 2 in Ref. [24]). Consequently, this result that there is an optimum liquid to achieve the most rapid imbibition is questionable. Now, let us present more evidence to support this claim that there is a direct relationship between the wall-fluid interaction and the speed of the capillary imbibition. First, it is interesting to say that this conclusion is in consonance with the recent work of Caupin et al. [37]. They tried to find an answer for this question that what is the maximum possible capillary rise for a specific fluid? They considered the imbibition of various fluids at two different geometries, a slit pore, and a cylindrical pore and performed explicit calculations for the graphite and MgO substrates. It was found that there is a direct relationship between the maximum height of capillary rise and the fluid-surface interactions. Second, the recent computer simulations revealed that there is a direct relationship between the wall-fluid interaction and the contact angle (and consequently the speed of wetting) [38,39].

In this section, let us draw your attention to an interesting fact. The derivation of the LW equation is based on the no-slip Hagen– Poiseuille equation [40,41]. Therefore, the LW equation is not valid at the conditions where the no-slip Hagen–Poiseuille equation tends to break down. Surprisingly, this tendency has been observed in the case of the experimentally achieved fluid flow at nanoscale channels. In the following section, let us briefly review some these observations.

Fast pressure-driven flow of fluids in membranes of carbon nanotubes (CNTs) 1.6 and 7 nm in diameter has been measured by Majumder et al. [42] and Holt et al. [43], respectively. They indicated measured values of 2-5 orders of magnitude larger than those calculated by the continuum-based no-slip Hagen-Poiseuille equation. Recently, Thomas et al. [44] have reevaluated water transport through CNTs having diameters ranging from 1.66 to 4.99 nm. They found that the measured flow rates exceeded those predicted by the no-slip Hagen-Poiseuille relation. Interestingly, new experimental results for the flow of water, ethanol, and decane through carbon nanopipes with relatively large inner diameters (i.e., 43 ± 3 nm) have demonstrated that transport is enhanced up to 45 times that of theoretical predictions [45]. Not only CNTs but also other nanostructure materials have shown the contradiction between the experimental and/or theoretical predictions and those resulted from the classic equations of fluid dynamics [46-49].

As can be seen above, the classic models of fluid dynamics, including the Hagen-Poiseuille equation, often start to break down when the working length scale is reduced since in a continuum fluid, it is assumed that both static and dynamic properties change in a continuous and differentiable fashion with respect to the position in the fluid and time. Incidentally, the continuum theory formalism is independent of the nature of molecular structure and configuration [50]. Consequently, the continuum-based description of fluid flow is not applicable in a situation where reduction in the system size causes those variables (i.e., static and dynamic properties of the fluid) to vary considerably over molecular length and relaxation time scales. Even though, to our knowledge, a consensus on the exact scale where continuum models tend to break down has not yet emerged, it is obvious that the flow or diffusion at nanoscale does fall in the domain of the so-called "non-continuum fluidics" or "nanofluidics" [51,52]. Note that the employed MD simulation described in this case study does use the dimensionless, or reduced, MD units to define all physical quantities including the nanoscale dimensions. There are several reasons for doing this. One reason for using such units is related to the general notion of scaling, namely, that a single model can describe a whole class of problems. In the other words, when the properties of a given system have been measured in dimensionless units, they can readily be scaled to the meaningful physical units for each problem of interest. Therefore, one should take care of employing this MD approach in the nanoscale dimensions where the continuum models of fluid dynamics including the LW equation tend to break down.

Due to emerge of new approaches in the fabrication of the nanochannels, capillary filling in these channels have gained considerable interest in the past few years. This phenomenon is of great importance in practical applications [53]. An extensive review of the fabrication methods of the nanochannels can be found in the literature [54]. In this part of the Manuscript, let us review some capillary filling experiments in the nanochannels in which the results are in good agreement with the LW equation. Actually, we would like to mention the possible applications of the results from our MD simulation approach to these experiments. Kim et al. [55] reported experimental capillary filling of glycerin inside CNTs at room conditions. Four CNTs having different tube length. i.e., 19, 23, 32, and 37 um were employed. All tubes were estimated to have diameters of approximately 600 nm. The time needed to fill these nanochannels were varied from 0.01 to 0.36 s. The experimental observations of the capillary filling were agreed favorably with the simple LW equation. On the applications side, the Authors mentioned that these nanochannels are of interest as potential nanopipets and nanoelectrodes to probe cells with minimal intrusion and high spatial resolution and as nanopipes in biosensors. Tas et al. [56] examined the capillary filling speed of water and sodium chloride (NaCl) in nanochannels with a rectangular cross-section. The time required to fill the three channel heights (i.e., 152 ± 11 nm, 111 ± 9 nm, and 53 ± 6 nm) were less than 25 s. The measured position of the meniscus as a function of time qualitatively did follow the Washburn model. However, there was an underestimation of the capillary filling speed to that calculated using the LW equation, which was attributed to the electro-viscous effect. These experiments, as claimed by the Authors, are of practical value since in nanofluidic experiments; channels are usually filled by the capillary action. Han et al. [57] investigated the filling kinetics of different liquids in nanofabricated capillaries with rectangular cross-section having inner walls exposing silanol groups. The smallest dimension of the nanochannel cross-section was $27 \times 50 \times 73$ nm³. Ethanol, isopropanol, water, and binary mixtures of ethanol and water spontaneously filled the nanochannels. Their results confirmed the LW model in the capillary filling. The Authors suggested that nanochannels should be used as an ideal model to study mass transport mechanisms in systems where surface phenomena dominate. van Delft et al. [58] introduced a device to allow the investigation of fluid behavior inside the nanochannels without using fluorescent substances. The employed nanochannels had various heights between 6 and 20 nm. Capillary filling experiments of water and ethanol were carried out in these channels. In all case studies, the meniscus dynamics did obey the LW equation. However, a reduced filling speed was attributed to various effects such as electroviscosity, increased fluid viscosity, nanochannel deformation due to capillary-induced negative pressure, and an increasing influence of the channel roughness.

4. Conclusions

MD simulations of imbibition of a simple fluid through a designed nanopore were carried out and the following results were obtained:

(1) Generally, the simple LW equation is a reliable model to explain the kinetics of this phenomenon. However, nonconformity to this equation is observed in some cases since the simple LW equation overlooks the significant effect of the DCA on this phenomenon.

- (2) Two commonly used models to derive the DCA, namely, the hydrodynamic and MK models were proposed. The results showed that the MK model is able to justify the simulation results in which are not in good agreement with the simple LW equation. However, the hydrodynamic model is not capable of doing that.
- (3) Further investigation of the MD simulation data revealed an interesting fact that there is a direct relationship between the wall-fluid interaction and the speed of the capillary imbibition.

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