Effect of Electric Field on Liquid Infiltration into Hydrophobic Nanopores

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ABSTRACT: Understanding the variation of nanofluidic behavior in the presence of an external electric field is critical for controlling and designing nanofluidic devices. By studying the critical infiltration pressure of liquids into hydrophobic nanopores using molecular dynamics (MD) simulations and experiments, important insights can be gained on the variation of the effective liquid—solid interfacial tension with the magnitude and sign of electric field, as well as its coupling with the pore size and the solid and liquid species. It is found that the effective hydrophobicity reduces with the increase of electric intensity and/or pore size, and the behavior is asymmetric with respect to the direction of the electric field. The underlying molecular mechanisms are revealed via the study of the density profile, contact angle, and surface tension of confined liquid molecules.

INTRODUCTION

In a confined nanoenvironment, owing to the unique solid—liquid interfacial characteristics, the liquid infiltration and transport exhibit many interesting phenomena.1−3 Nanotubes can be spontaneously filled with liquids only when the surface tension of the liquid is low enough to allow internal wetting.4 Otherwise, an external pressure is required to force a nonwetting liquid to infiltrate a hydrophobic nanoporous material, and during this process, the external work will be in part converted to solid—liquid interfacial tension and in part dissipated via friction during nanofluidic transport.5 The performance of such a nanoporous energy absorption system (NEAS) is critically affected by the infiltration pressure6 (at which the capillary resistance of the nanopore walls is overcome), which can be adjusted by tuning the effective hydrophobicity of the system. Several strategies have been proposed to control the nanofluidic infiltration and flow behavior by modifying the solid—liquid interfacial characteristics, such as adjusting the nanopore structure,7 surface treatment,8 adding the gas9 or ion10 phase, and/or applying an external pressure,11 thermal field,12 or electric field.13 Among these approaches, the electrical control is in particular attractive because it is relatively simple and straightforward, maintains the inherent characteristics of nanopores such as their mechanical strength and surface morphology, while affecting the nanofluidic behavior by influencing the configurations of polar liquid molecules in nanoenvironment. Note that although the employment of static charge groups (by introducing explicit electric charges near a nanopore) may trigger and speed up flow or infiltration of liquids, it cannot drive a continuous flow of water molecules through a nanopore.14,15

In the presence of an external electric field, because of its dipole and quadrupole moments, water molecules feature strong interactions with the electric field next to the charged or polar solutes, and they are attracted to the field exposed regions, which may affect the effective surface tension of water molecules on nanopore wall,16,17 also known as the electrocapillary effect. Garate simulated water-self-diffusion through single-walled carbon nanotubes (CNTs) using molecular dynamics (MD) simulations in the presence of an external electric field,18 and found that the permeation of water into the smaller nanotubes is enhanced by electric fields due to a decrease in the fluctuations of the number of water molecules inside the nanotubes, whereas the larger extent of rotational freedom of the water molecules in the larger nanotubes allows an improved dipole alignment with the electric fields, resulting in a reduced water self-diffusion flux. By imposing an external voltage to a NEAS consists of nanoporous silica in KCl solution, Lu et al. found that the interfacial tension decreases as the applied voltage increases, and the

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The nanotube is assumed to be rigid and previous studies\textsuperscript{20} have been rationalized for the SPC/E water model.\textsuperscript{17,35} The material for constructing CNTs is ensured to be hydrophobic\textsuperscript{28} close to that of bulk water, \( \rho_0 = 998.0 \, \text{kg/m}^3 \) at 300 K and 0.1 MPa by adjusting the total number of water molecules. A periodical boundary condition is imposed on the four lateral planes of the computational cell.

MD simulation is performed using LAMMPS (large-scale atomic/molecular massively parallel simulator), with the NVT ensemble at ambient temperature of 300 K.\textsuperscript{21,22} The nonbond interatomic van der Waals interaction is described by the 12–6 Lennard-Jones (1J) empirical forcefield, \( U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \), where \( \sigma \) denotes the distance between atoms, and \( \varepsilon \) and \( \sigma \) are the energy and length parameters, respectively. In the example CNT–water system described in Figure 1, due to the lack of available flexible water model for reproducing all behaviors of water deformation (e.g., oxygen–hydrogen bond, bond angle and bending frequency)\textsuperscript{33} when subjected to an electric field,\textsuperscript{24} the water is modeled by the most popular force fields of the extended simple point charge potential (SPC/E).\textsuperscript{25} The particle–particle–particle mesh (PPPM) technique with a root-mean-square accuracy of \( 10^{-4} \) is employed to handle the long-range Coulomb interactions between the sites associated with the oxygen atoms and the two hydrogen atoms. The carbon–oxygen LJ parameters are extracted from the experimental low-coverage isotherm data of oxygen adsorption on graphite.\textsuperscript{26,27} By using these molecular models and parameters, the graphene as the raw material for constructing CNTs is ensured to be hydrophobic\textsuperscript{28} in the absence of electric field; with the application of an external electric field, as will be shown below, the hydrophobicity will decrease; nevertheless, the system will not switch to hydrophilic.

When the solid and liquid phases are changed, e.g., with the employment of silica nanotube and electrolyte, relevant force field parameters can be found in refs.\textsuperscript{11,29,30}

Since the inner surface of nanotube is hydrophobic, after equilibrium the water molecules cannot enter into the nanotube spontaneously. By moving the piston upward in a quasi-static manner,\textsuperscript{31} the water phase is pressurized. At each time step, the effective applied pressure, \( P \), is evaluated by sampling a region with volume of \( V \) near the entrance of the nanotube, based on the intermolecular potential among water molecules via the Virial expression, \( P = N k_B T/V + \sum_{i} r_{ij} / 3 V^2 \), where \( N \) is the number of water molecules inside the sampling region, \( k_B \) is the Boltzmann constant, \( T \) is the system temperature, and the second term describes the contribution from the pair wise bond interaction among the \( N \) water molecules. \( V \) is taken to be sufficiently large to ensure a nearly isotropic density distribution of water. If the pressure is beyond a critical infiltration value, \( P_{\text{crit}} \) liquid starts to infiltrate and wet the nanopore. A uniform external electric field, \( E \), is applied along the axial direction of the nanochannel, whose magnitude varies between \( 10^{-2} \, \text{V/A} < |E| < 0.4 \, \text{V/A} \), which is on the same order of that for ion channels and membranes,\textsuperscript{33,34} and the results are compared with the reference system without electric field. Note that the applied electric field in this study does not include the field reduction due to water polarization, and this assumption has been rationalized for the SPC/E water model.\textsuperscript{17,35}

\section*{RESULTS AND DISCUSSION}

\subsection*{Infiltration Characteristics and Pore Size Dependence of Reference System.} We first explore the fundamental behavior of the reference system, by studying the infiltration of water molecules into a representative (16,16) CNT without an external electric field. Figure 2 shows the variation of the number of
infiltrated water molecules with the applied pressure. If the pressure is relatively low, only very few water molecules are incorporated in the meniscus near the entrance of the CNT, and when the pressure exceeds a critical value of about $P_{\text{in}} = 80$ MPa, the capillary resistance is overcome and water molecules burst into the CNT. Afterward, the pressure remains a constant, indicating that the inner surface of the CNT is quite smooth with little transport dissipation and the Laplace–Young equation can be applied at the nanoscale to correlate the infiltration pressure with solid–liquid interfacial tension.

By following the similar procedure, we investigate CNTs of different chirality (diameter), from which the pore size dependence of $P_{\text{in}}$ is given in Figure 3. The relative hydrophobicity decreases as the size of CNT gets larger with weaker solid–liquid interaction. It is important to note that the relationship between the critical infiltration pressure and pore diameter does not follow the $1/D$ dependence dictated by the classic Laplace-Young equation, which indicates the strong size dependence of other involved parameters, such as the surface tension and contact angle (see below). The size dependence is further coupled with the effect of applied electric field, explored next.

Effect of Electric Field on Infiltration Characteristics in CNT/Water System. With an applied electric field, the infiltration isotherm of the water-(16,16) CNT reference system is distinct. Figure 4 indicates that more water molecules can easily enter the CNT (at lower $P_{\text{in}}$) with the increase of electric field, as the system becomes effectively less hydrophobic. An interesting phenomenon can be found when the direction of the electric field is switched. In Figure 5a, when $|E| = 0.06$ V/Å, there is a small asymmetry for positive and negative electric intensities, where the $P_{\text{in}}$ of a small (10,10) CNT is slightly smaller (and the system is a bit less hydrophobic) upon a positive electric intensity than that with a negative electric intensity. Such a nanoconfinement-induced asymmetry is more obvious if the magnitude of the applied electric intensity is increased to $|E| = 0.1$ V/Å, Figure 5b. If the CNT gets larger, such as (18,18), then in case of a small magnitude of electric intensity (0.06 V/Å), the difference between the positive and negative electric intensity is negligible (Figure 6a); when $|E|$ is increased to 0.1 V/Å the asymmetry is apparent (Figure 6b) but the difference in infiltration behavior is still less prominent than that in the smaller (10,10) CNT.

Figure 7 plots the effect of electric field on $P_{\text{in}}$ for six different CNT radii. It is readily seen that the $P_{\text{in}}$ decreases with the increase of electric intensity. The asymmetry in positive and negative electric field is more obvious if the electric field is stronger, or when the CNT is smaller, and the system is slightly more nonwetting (with a higher $P_{\text{in}}$) in the presence of a negative electric field. These features are consistent with parallel experiment discussed below.

The underlying mechanism for electric field-dependent infiltration behavior is attributed to the inherent physical characteristics of solid–liquid interaction, such as the contact angle, surface tension, and density profile of confined liquid molecules, which are influenced by not only the electric field but also the size of the nanopore, elaborated in the next section.

Underlying Molecular Mechanism. At the equilibrium of infiltration process, with respect to the classic Laplace–Young
equation, \( P_{in} = -4\gamma \cos \theta / D \), where \( \gamma \) is the surface tension between water molecules inside CNT and vapor (vacuum in this study), \( \theta \) is the contact angle, and \( D \) is the effective (accessible) diameter of water molecules inside the nanopore. The applicability of the Laplace–Young equation at the nanoscale has been validated,\(^{36}\) as long as the relevant physical parameters (e.g., \( \gamma \) and \( \theta \)) incorporate size effects. In this section, we focus on the effect of electric field on \( \gamma \), \( \theta \), and \( D \) (as well as its coupling with the size effect), first qualitatively and then quantitatively.

First, in the absence of an external electric field (i.e., the reference system where \( \gamma = \gamma_0 \), \( \theta = \theta_0 \), and \( D = D_0 \)), the fact that a larger nanopore diameter results in a lower \( P_{in} \) is qualitatively consistent with Figure 3, except that as remarked earlier, \( P_{in} \) does not vary as \( 1/D \) in Figure 3. This indicates that at the nanoscale, both surface tension and contact angle are size-dependent. That is, the curvature of the nanochannel affects the configuration of confined liquid molecules, and hence both \( \theta_0 \) and \( \gamma_0 \) depend on \( D \). For the water–CNT system discussed herein, the overall effect is that the more constriction of water molecules in a smaller CNT subjects a stronger solid–liquid interaction, which leads to a lower \( \theta_0 \) and a higher \( \gamma_0 \).\(^{37}\)

When an external electric field is applied, according to the insight from classic electrochemistry theory, \( \gamma \cos \theta = \gamma_0 \cos \theta_0 - C\phi^2/2 \), where \( C \) is the interfacial capacity, and \( \phi \) is the applied potential difference.\(^{13}\) This equation indicates that regardless of the sign of the applied voltage, the effective interfacial tension \( \gamma \cos \theta \) always decreases with the magnitude of \( \phi \), and that would reduce the critical infiltration pressure, \( P_{in} \); these observations are qualitatively consistent with MD simulation results (Figure 7). Meanwhile, the classic theories cannot directly explain the size dependence of infiltration behavior (and its coupling with electric field dependence) and the asymmetry of positive and negative electric fields.

In order to quantify the molecular mechanism of water–carbon interaction in the nanoconfinement, two different model nanochannels, \((10,10)\) and \((18,18)\) CNTs, are chosen as representative cavities for accommodating water molecules. Figure 8 shows the density profile of water, \( \rho(r) \), along the radial direction of a \((10,10)\) CNT at the equilibrium after the water molecules have intruded the nanopore. The fluctuation of density profile is due to the hydrophobic nature of the considered nanotube, where most of the water molecules are confined in concentric rings/layers inside the tube; the similar characteristic of water distribution in CNTs has also been observed in other previous MD studies.\(^{2,12,38,39}\)
From Figure 8, under the applied electric field, the fluctuation amplitude of the density profile decreases; moreover, the difference of the density profile under the negative and positive electric fields indicates that the wetting properties are different. These features echo the above MD simulation results. Figure 9 shows the radial density profile of water molecules confined in the larger (18,18) CNT: it can be seen that the water structure contains more concentric layers with smaller amplitude (density) than that in the (10,10) CNT, and the smaller fluctuations in the density profile suggest a weaker solid—liquid interaction and thus less sensitivity to the external electric field (as well as the asymmetry of positive and negative electric fields). With further increase of CNT diameter, it is envisioned that the radial density profile distribution will become homogeneous and deduces to that of the classic fluid behavior.

Another important feature that can be obtained from the radial density profile is the position of the first solvation shell (FSS). In the absence of the external electric field, the distances from FSS to the nanotube wall (referred as the equilibrium distance here) are 2.280 and 2.305 Å for (10,10) and (18,18) CNTs, respectively. Both of them are close to the measured value of water drop on a graphene (2.5 Å), and the small difference is resulted from the curvature confinement effect. With the increase of the applied electric intensity, Figures 8 and 9 indicate that the position of FSS moves away from the nanotube axis, and reduces the equilibrium distance. This is consistent with the electrowetting characteristic of water on a graphene observed by Daub et al. For a given nanotube, a smaller equilibrium distance implies a larger effective diameter $D$, and according to the Laplace—Young equation, that is another factor contributing to the reduction of $P_{in}$ for the system under electric field.

Besides the effective pore size $D$, the surface tension $\gamma$ and contact angle $\theta$ affect the infiltration behavior in a more profound manner. We first deduce the quantitative information on $\theta$ through an independent analysis. Following the technique proposed by Werder et al., for water molecules confined in a given CNT, at the equilibrium state the spatial positions of the molecules at the meniscus front are averaged in a long computational time frame, and from that averaged meniscus profile, the contact angle is deduced, illustrated in Figure 10(a) for the example of (18,18) CNT subjecting to an electric intensity of 0.1 V/Å. In Figure 10(b) $\theta$ is presented as a function of electric strength, and the coupled pore size effect is also shown. For (10,10) and (18,18) CNTs, the contact angle $\theta_o$ is 106.6° and 112.4°, respectively, in the absence of electric field, consistent with the hydrophobic nature. With an applied electric field, the contact angle $\theta$ decreases, and such a reduction of hydrophobicity is also larger for positive electric strength than the negative one, consistent with the trend in $P_{in}$ (Figure 7). The anisotropy in water molecule response to the direction of an applied electric field indicates possible new electrochemistry mechanisms in a confining nanoenvironment.

Finally, based on the Laplace—Young equation, $P_{in} = -4\gamma \cos \theta/D$ and Figure 10(b), the electric field-dependent and size-dependent $\gamma$ can be calculated in Figure 10(c), where the variation and dependence of $D$ are taken into account. It can be seen that the surface tension of water in the (18,18) CNT is ~0.11 N/m without electric field, and it increases with the reduction of CNT diameter due to the effect of CNT curvature and density of confined water molecules. The result is consistent with that of MD results of 0.1269 N/m on the water—carbon system at 300 K. Like the contact angle, the surface tension also decreases with the external
electric intensity. The field-induced reduction of both \(\gamma\) and \(\theta\) contribute to the decrease of hydrophobicity (reduction of \(P_{in}\)) in the electrically controlled NEAS. The variation trend of surface tension and contact angle with respect to the applied electric field also agrees with the experiment for a water droplet resting on a graphene,\(^{43}\) yet we note that in the present study, the electric field effect is closely coupled with the pore size effect.

Extend to Other Nanopores and Liquid Phases. In previous sections based on a model CNT/water system, we have revealed some basic mechanisms of the effect of electric field on infiltration behaviors. Apparently, with different solid phase and liquid composition, the infiltration characteristics are distinct. For example, in the absence of electric field, the infiltration pressure may be favorably elevated through the introduction of electrolyte as well as using silica nanotube.\(^{30,47,48}\)

To demonstrate the influence of electric field on other systems, a silica nanotube (SNT) with pore size very close to that of (18,18) CNT and aqueous solution of sodium chloride (NaCl) (with molar concentration of 2.0 mol/L) are chosen as substitutes of the solid pore and liquid phase, respectively. Here the diameter of the (18,18) SNT (24.56 Å) is measured as the distance between two opposite oxygen atoms.

Following the same computational procedure above, Figure 11a plots the effect of the external electric field on \(P_{in}\). In comparison to the CNT/water system under the same electric intensity, with
the employment of SNT or aqueous solution of NaCl, the system becomes more hydrophobic with a higher $P_{in}$, with the electrolyte have a bigger impact. The corresponding contact angle, $\theta$, and surface tension, $\gamma$, are plotted in Figure 11, parts b and c, respectively: the results indicate that the increment of surface tension is mainly responsible for enhancing the hydrophobicity when the liquid/solid phases are changed. In case of the employment of electrolyte (in comparison with that of pure water), the additional work required to break the hydration shell for liquid infiltration makes $P_{in}$ higher, with an applied electric field, the cations and anions tend to move toward different directions and that is added to the electric strength-dependent infiltration barrier. In case where the SNT is used, the partially charged surface has a stronger interaction with the polar water molecule and that could lead to a stronger solid/liquid interfacial tension, which is also sensitive to the electric field. These findings could improve the energy absorption efficiency of NEAS.

**COMPARISON WITH EXPERIMENTAL DATA**

The simulation results are qualitatively compared with the data of a pressure induced infiltration experiment. The nanoporous material under investigation was a nanoporous silica crystal, which was surface treated to increase the degree of hydrophobicity of the inner surfaces of nanopores. The nanopores were confirmed to be open through a gas absorption analysis by using a Micromeritics Tristar-3000 Analyzer; the average pore diameter was about 14.6 nm. An aluminum foil was repeatedly folded to form aluminum layers, and treated silica disks of about 16.5 mg were inserted between the adjacent layers (Figure 12). The extra aluminum layers were connected together, forming an electrode and counter-electrode, respectively. The silica disks and the electrode were insulated by porous Teflon membranes, and thus a nanoporous layer stack is formed. This stack was placed at the bottom of a steel cylinder, inside which 10 g of 15% aqueous solution of potassium chloride (KCl) was sealed by another steel piston from the top. The inner surface of the cylinder was insulated from the liquid phase and aluminum layers by a Teflon layer. By using a direct current (dc) power source, an open-circuit voltage, $\phi$, was applied between the lower and a counter-electrode, which was separated from the silica-aluminum layer stack by a porous polystyrene membrane. The value of $\phi$ was in the range $-380$ to $+420$ V. By using an Instron machine, the piston was intruded into the cylinder at a constant rate of
0.5 mm/min (the loading rate was confirmed to be sufficiently slow so as not to introduce any rate effect). Since the nanopore inner surfaces were hydrophobic, only when the applied pressure was sufficiently high (beyond $P_{\text{eq}}$) a large number of water molecules could be forced into the nanopores.

The measured $P_{\text{eq}}$ as well as the deduced effective interfacial tension are given in Figure 12 as a function of the applied voltage, where the trend is qualitatively consistent with the computational results (Figures 7 and 10), suggesting that $P_{\text{eq}}$ decreases with increasing $|E|$, despite the difference between the experimental and simulation systems. In addition, the direction of the electric field has some effect on $P_{\text{eq}}$ and a lower $P_{\text{eq}}$ is observed in the presence of the positive electric field, which is also consistent with predictions in Figure 7. All these phenomena again suggest that the conventional electrochemistry theory should be enriched the nanoscale.

Note that the current agreement between simulation and experiment is rather qualitative, owing to several practical challenges that have not yet been overcome. First, the experimental system is much larger than the simulation cell, with the pore size larger and length longer. Second, the diameter of nanopores in the experimental systems is not quite uniform, and the pore structure is also quite complex. Third, the surface treatment used in experiment is difficult to incorporate into simulation. Last but not least, due to the size and time scale accessible to MD simulation, the electrical strength applied in simulation is much higher than that in experiment. A more quantitative coordination between simulation and experiment will be reported in future.

## CONCLUDING REMARKS

By taking advantage of the large specific surface area of nanoporous materials, a number of nanofluidic devices have been proposed whose functionality critically depends on the ability to control the effective solid—liquid interfacial tension. In this paper, we investigate the possibility of adjusting the liquid—solid interactions by using electric field, and explore the electric strength-dependent infiltration behaviors of water molecules into hydrophobic nanopores. Systematic MD simulations of CNT/water systems show that the critical infiltration pressure reduces with the increase of electric intensity or pore size. The factors contributing to the reduced hydrophobicity include the electrical induced variations of surface tension and contact angle, as well as radial density profile of confined liquid molecules. An interesting phenomenon of asymmetric response to positive and negative electric fields is discovered, which is associated with the asymmetry in radial density profile and contact angle. The coupling between the electric field effect and pore size effect is elucidated, as well as the effect of using electrolyte and polar nanopore. These unique nanoscale characteristics provide insights for the variation of the effective interfacial tension, which are qualitatively validated by using a parallel experiment, and similar trends of electric field dependencies are found.

The critical influence of the electrical field on the nanofluidic behavior is expected to facilitate the development of high efficiency nanodevices. For example, on the basis of electrically controlled switching of relative wetting/dewetting of nanopores, a nanoporous electric machine may be developed. Consider a nanoporous material that is soaked in a liquid, a constant pressure may be applied which is bounded by the infiltration pressure levels at different electric fields; thus, with the change of electric field, the relative hydrophobicity is varied and the liquid may spontaneously infiltrate the nanopores at a larger electric strength, which reduces the system volume and outputs mechanical work. The potential output of such a system may be estimated as the effective solid—liquid interfacial tension times the surface area of nanopore, which may reach the order of 100 J/g and thus orders of magnitude higher than conventional smart systems (e.g., piezoelectrics). The reduction of the infiltration threshold under electric field may also be used to fine-tune the energy absorption performance of the nanoporous solid/liquid composite. And the working mechanisms of these nanodevices will be underpinned by the unveiled principles of interactions between the nanoconfined liquid molecules and solid pore/channel, which may be further enriched in future by incorporating the effects of temperature, pore surface structures, and surface treatments, among others.

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(27) The van der Waals parameters between water and CNT will affect the threshold pressure. In the present study, we employ the most popular L-J parameters which have been proved to reproduce the experimental results in literature.
(31) During the loading process, the piston moves a small distance at each step and then is held fixed until the system reaches equilibrium.
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