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Citation: J. Chem. Phys. 137, 184703 (2012); doi: 10.1063/1.4763984
View online: http://dx.doi.org/10.1063/1.4763984
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v137/i18
Published by the American Institute of Physics.

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Simulations of structural and dynamic anisotropy in nano-confined water between parallel graphite plates

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(Received 9 June 2012; accepted 11 October 2012; published online 9 November 2012)

We use molecular dynamics simulations to study the structure, dynamics, and transport properties of nano-confined water between parallel graphite plates with separation distances (H) from 7 to 20 Å at different water densities with an emphasis on anisotropies generated by confinement. The behavior of the confined water phase is compared to non-confined bulk water under similar pressure and temperature conditions. Our simulations show anisotropic structure and dynamics of the confined water phase in directions parallel and perpendicular to the graphite plate. The magnitude of these anisotropies depends on the slit width H. Confined water shows “solid-like” structure and slow dynamics for the water layers near the plates. The mean square displacements (MSDs) and velocity autocorrelation functions (VACFs) for directions parallel and perpendicular to the graphite plates are calculated. By increasing the confinement distance from H = 7 Å to H = 20 Å, the MSD increases and the behavior of the VACF indicates that the confined water changes from solid-like to liquid-like dynamics. If the initial density of the water phase is set up using geometric criteria (i.e., distance between the graphite plates), large pressures (in the order of ~10 kbar), and large pressure anisotropies are established within the water. By decreasing the density of the water between the confined plates to about 0.9 g cm⁻³, bubble formation and restructuring of the water layers are observed.

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I. INTRODUCTION

Water is found in gas, liquid, and solid phases under ambient conditions in the biosphere and despite its simple chemical composition and structure has many unique physical properties. Many specific roles of water in biological processes have been studied, but some of its behaviors are still not completely understood.¹ The behavior of water in confined environments can have interesting implications in chemistry, biology, and electrochemistry² and is the subject of much study. The specific interactions of water with hydrophobic species in micro- and nano-environments (such as water channels in living organisms) are important in understanding biological functionality in these cases.³,⁴

The structures, properties, and behaviors of confined water in nanoscale spaces are very different from those of the bulk water phase and have been studied in hydrophobic and hydrophilic media with experimental surface force apparatus,⁵ differential scanning calorimetry,⁶ neutron diffraction,⁷ and nuclear magnetic resonance⁸ techniques. The phase behaviors of confined fluids are altered and excluded-volume effects become more apparent.⁹ Iiyama et al.¹⁰,¹¹ determined the structure of water molecules in a hydrophobic nanopore with X-ray diffraction experiments. The electronic radial distribution function (RDF) indicated that the numbers of nearest-neighbor molecules of the confined water are less than that of bulk liquid water and the long-range ordered structures of these water phases are different. X-ray diffraction spectra of confined water in nanopores show sharp peaks while there are no sharp peaks in spectra of bulk water. The results indicate directly the formation of ice-like structure of water adsorbed in the hydrophobic nanopores. X-ray diffraction results also show that the structure of water at 303 K confined in a hydrophobic environment with pore widths of 7.5 Å is more ordered than in water in larger 11.3 Å pores, without a phase transition detected in the water structure as a function of the pore size.¹¹

Interpreting the results of experiments in terms of the microscopic structure and dynamics of confined fluids is sometimes difficult and atomistic simulations are performed to describe changes in hydrogen bonding, molecular orientation preferences, transitional and rotational dynamics of confined fluids.

There have been many recent molecular dynamics (MD) and Monte Carlo simulation studies of water confined to slit-shaped nanopores¹²–²⁴ and nanotubes.²⁵–²⁹ These simulations have been performed for slit widths in the range of 6–400 Å, water densities (geometric and effective, see below) in the range of 0.6–1.33 g cm⁻³, and temperatures in the range of 50–300 K. Recently, computational studies investigated the effect of confinement on surface polarity³⁰ and infrared spectra of water,³¹–³⁴ the effects of pressure and temperature on confined water,³⁵,³⁶ comparison of effects of pressure and confinement on water,³⁷ electrodynamics of confined water,³⁸ the behavior of confined water between mica walls,³⁹ and the effect of confinement on melting temperature of water.⁴⁰

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In simulations of the confined liquid phase, the structure and dynamics of the water phase become anisotropic and depend on the slit width $H$. The structure and hydrogen bonding of the liquid layers adjacent to the confining surface are different from those further away from the surface. The diffusivity of the molecules also depends on the slit width and is significantly different in the lateral and transverse directions with respect to the slit walls.

An important and non-trivial issue in performing simulations of water confined between plates is the density of water used in the simulations. If the two confining plates are separated by a distance $L_z$, the geometric density is defined with reference to the geometric volume between the plates, $V_{gt} = L_x L_y L_z$. In practice, due to steric repulsion effects, molecules are confined within a distance of $L_z'$ and have access to an effective volume $V_{eff} = L_x L_y L_z'$. These distances are shown in Figure 1. The effective volume depends on the temperature and pressure of the confined water phase and is not a constant value. We distinguish between these two volumes and their corresponding density values below.

Simulations can be initially set up such that water is placed in the entire geometric volume between the plates and the geometric density of water is $\sim 1$ g cm$^{-3}$. Upon equilibration, the steric repulsions between the wall atoms and water drive the water molecules away from the surface and the effective water density becomes significantly higher than the geometric value. Since the graphite plates are kept rigid and fixed in most simulations, this increase in density leads to very high densities and pressures on the confined water. In some cases, the resulting pressures are high enough to transfer bulk water into solid regions of the water phase diagram. To understand the behavior of confined water, it is important to distinguish between the effects of the very high pressure on the behavior of the water (due to the setup of the simulations) from the effects of confinement between the slit nanopore. Distinguishing between the confinement and pressure effects becomes important when studying confined water at atmospheric pressure (the study of which can be important in biological systems) and confined water under high pressure conditions in geophysical or technological applications. In reality, graphite plates are flexible and can only withstand a limited range of hydrostatic pressure from the confined water before distorting or breaking. It is therefore important to pay careful attention to the pressure of the fluid inside the slit to guarantee that the simulation conditions are an accurate representation of the real confined water system.

The structure of a confined water phase is non-homogeneous in directions parallel and perpendicular to the graphite plates. This leads to anisotropy of the lateral and transverse components of the pressure tensor in the confined water phase. The dynamics of the water molecules in the different directions are also not isotropic and so the mean-square displacement (MSD) or velocity autocorrelation function (VACF) can be different with respect to different directions in the confined water phase. A systematic study of confinement effects, in particular with respect to the anisotropies caused by confinement, is a goal of this work. Depending on the simulation setup for confined systems, the density of confined water may vary considerably from that of ambient conditions and we will study the effects of the density on water properties. The range of water densities studied in previous simulations show that some confinement studies are performed under extreme pressures and involve water compressed to densities up to 1.3 g cm$^{-3}$. At the other extreme of low geometric densities, there is the possibility of bubble formation in the fluid phase, which also causes complications in interpreting the results of the simulations of the confined system.

In this work, we use MD simulation to study a suite of structural, dynamic, and transport properties of confined water between hydrophobic graphite plates arranged as a slit nanopore. We built four systems with inter-wall distances of 7, 10, 15, and 20 Å. We first study water in each slit with geometric densities $\sim 1$ g cm$^{-3}$. For each case, we determine an approximate effective density of the water after equilibration of the simulation. We then consider different initial geometric densities for each slit width. In many previous simulation studies, simulations with only a single slit width, and or a range of slit widths between 6 and 14 Å have been studied. Our goal is to compare the properties of confined water in the four slits under identical simulation conditions. Analyses on the $z$-density profile, RDF, MSD, VACF, and self-diffusion coefficients are performed with attention paid to anisotropies in these quantities in different spatial directions. The computational methodology used in this work is described in Sec. II. In Sec. III, the results of the MD simulations are discussed. The paper ends with a summary and conclusions in Sec. IV.

II. COMPUTATIONAL METHODS

We used the extended simple point charge (SPC/E) model of water. The Lennard-Jones 12-6 potential parameters used to represent the van der Waals interactions between water oxygen atoms and the carbon atoms of the confining graphite layers are given in Table I. In previous simulation studies, wall-water interactions were represented by the Lennard-Jones 9-3 potential$^{13,42-44}$ or modified Lennard-Jones potentials. Other studies$^{13,16,20}$ used the Lennard-Jones 9-3 potential with the $z$-coordinate which is the perpendicular distance of the water oxygen to the structureless wall. Previous work showed that the equation of state in

![FIG. 1. A schematic representation of the confined water between the graphite slab model used in this work.](image-url)
confined fluids is in better agreement with experiment when the Lennard-Jones 12-6 potential with the r-coordinate representing the distance of a water oxygen to the particular carbon atom making up the wall is used.55–58 Potential parameters for interactions between heteroatomic pairs are calculated using the Lorentz-Berthelot mixing rules, \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \) and \( \varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \). Our force field is similar to that chosen in previous work that states the smallest pore width for confinement of water molecules in each simulation are given in Table II.

We used crystallographic information to construct the graphite wall in the simulation cell, see Figure 1. The unit cell is replicated in \( xy \)-plane creating graphite sheets with dimension 44.8 \( \times \) 45 Å\(^2\). Each side of the graphite slit consists of two graphite sheets with natural interspacing layer distance of 3.35 Å. The pairs of graphite sheets were incorporated into the simulation unit cell with different inter-wall distances \( H = 7, 10, 15, \) and 20 Å. These distances are chosen according to previous work that states the smallest pore width for confined water is \( H\sigma = 2 \), and after \( H\sigma \sim 12 \), confined water behaves similar to bulk water.52,53 The isolated nanopore geometry is modeled by leaving a 28 Å vacuum gap between the two graphite walls along the \( z \)-direction (see Figure 1) in all simulations.54

The constant volume, constant temperature (NVT) simulations were performed with the Nosé-Hoover algorithm with the DL_POLY program version 2.18.57 The equations of motion were integrated using the Verlet leapfrog algorithm and a time step of 1 fs. The relaxation time used for thermostat is 0.2 ps. Electrostatic interactions are calculated with the Ewald summation technique.59 The cutoff for long-range potentials is chosen as 11 Å.

We calculated the bulk SPC/E water density at 1 bar and 300 K to be 0.994 g cm\(^{-3}\) which is in good agreement with previous reported values. In the nanopore simulations, water molecules are arranged within the confinement area between the two graphite layers with distances of 7, 10, 15, and 20 Å to give geometric density of 0.998 g cm\(^{-3}\). Initial configurations are generated by randomly placing water molecules between graphite layers within the \( L_z \) range. The numbers of loaded water molecules in each simulation are given in Table II.

Each system is first equilibrated with a set of two consecutive NVT ensemble simulations, each with a total of 900 ps simulation time with 200 ps equilibration. Structural and dynamical properties are analyzed by performing NVE simulations starting from the equilibrated NVT simulations. The MSDs are calculated by averaging over a set of four consecutive 1 ns NVE runs, each with a production time of 800 ps. The VACFs are calculated by averaging four short NVE runs each with 15 ps production time. The initial configuration for the VACF runs is the last configuration of long run used for calculating the MSDs. Self-diffusion coefficients for water models such as TIP4P and SPC/E have been calculated and compared with experimental results and are used to compare with the results of our simulations.

After equilibration, due to an exclusion distance around the graphite surface for the water molecules from the Lennard-Jones potential, the water molecules do not occupy the entire width \( H \), between the slits, but rather a width of approximately \( L_z' = H - \sigma_{C,OW} \). We use the relation of Kumar et al.16

\[
L_z' = L_z - \left[ \frac{\sigma_{O-C} + \sigma_{O-O}}{2} \right]
\]

to calculate the effective density for the simulations. In our simulations, \( L_z' = L_z - 3.2245 \). For geometric densities \( \sim 0.998 \text{ g cm}^{-3} \), the effective density and pressure on the encapsulated water molecules is thus be substantially larger than bulk water values under ambient pressures. For the \( H = 7 \) Å simulation, the highest possible geometric density is 0.81 g cm\(^{-3}\). For geometric densities higher than this value, the simulations would not converge.

We also performed simulations with different effective water densities for all \( H \) distances. The numbers of loaded water molecules in these simulations and the resulting range
of effective densities after equilibration are also tabulated in Table II.

The relations between the MSD and self-diffusion coefficient for molecules in homogeneous unconfined (bulk) systems are standard and given in the supplementary material. For water confined in the z-direction, the self-diffusion coefficient is calculated by assuming the system is two dimensional with \( d = 2 \) in Eq. (S2). In the present work, we calculate the “lateral” self-diffusion coefficient \( D_{\parallel} \) for motion parallel to the confined direction using the Einstein relation,

\[
D_{\parallel} = \frac{1}{4} \lim_{t \to \infty} \frac{d}{dt} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle, \tag{2}
\]

where \( \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \) is the ensemble average of the MSD parallel to the wall (xy-plane) over sufficiently large time interval.

The relations of the velocity-autocorrelation function and the Green–Kubo integral\(^{62–64} \) for the self-diffusion coefficient of homogeneous systems are given in the supplementary material. In the confined fluid, the lateral VACF, denoted as \( \text{VACF}_{\parallel} \), is used to compute the lateral self-diffusion coefficient,

\[
D_{\parallel} = \frac{k_B T}{m} \int_{0}^{\infty} \text{VACF}_{\parallel}(t) dt. \tag{3}
\]

### III. RESULTS AND DISCUSSION

#### A. Transverse density profile, radial distribution functions, and structure of confined water

The structure of water in confined systems is not isotropic. The z-density profiles of confined water oxygen and hydrogen atoms between the parallel graphite walls from NVE simulations at 300 K are shown in Fig. 2. The z-density profile peaks are symmetric with respect to the center of the slit and the density is the highest near the graphite walls. The distances between the first large peaks of z-density profiles and graphite wall (\( z_s \)) are given in Table III. The relative location of oxygen and hydrogen z-density profiles of water molecules in each confined system in Fig. 2 shows that on average (particularly for small slit separations of 7 and 10 Å), hydrogen atoms of the outer layer of water molecules are located closer to the graphite layers than the corresponding water oxygen atoms. The results of Fig. 2 are consistent with previous calculations on similar systems.\(^{18, 19, 65, 66} \) Additional small peaks in the hydrogen atom z-density plots (shown with asterisks in Fig. 2) indicate hydrogen atoms pointing away from the slit walls. In \( H = 7 \) Å simulations, the outer and inner hydrogen peaks of the first water layer are of similar height. In the \( H = 10–20 \) Å simulation z-density profiles, the higher hydrogen peaks near the graphite surface suggest that water molecules in contact with the carbon surface have dipole moments oriented parallel to the surface. The layered structures of the water phases are shown in snapshots of the simulations for different \( H \) values given in Fig. S1 of the supplementary material.\(^{61} \) Further discussions on the structure of water for the different slit widths are also given in the supplementary material. The effective densities for the different simulations are given in Table II.

To determine the lateral structure of the water molecules (in the xy-plane parallel to the graphite plates) for the \( H = 7 \) Å simulation, we averaged water coordinates over an 800 ps trajectory. As shown in Fig. 3(a), the average lateral positions of the water molecules in the two layers are distributed with approximately one water molecule beneath the center of each hexagonal carbon ring in the graphite layer. Figure 3(b) shows the top view of the hexagonal structures in the water layer which mirror the graphite ring centers. The water molecules forming the hexagonal structures are non-planar and staggered in the z-direction, see Fig. 3(c). Previous \textit{ab initio} MP2 studies on water clusters near graphite sheets or fused-benzene models reported that hexamer water ring structures (which are one of the least stable configurations in the gas phase) have the largest binding energy on the graphite surface.\(^{67} \) Han \textit{et al.}\(^{23} \) related the structure of water near the surface to the formation of hexagonal ice. However, their work reports the formation of hexagonal ice at temperatures less than 280 K. The hexagonal structures of the confined water observed may reflect the structure of graphite walls or the high pressure of the confined water for the \( H = 7 \) Å simulation.

The hexagonal arrangement for the water layer adjacent to graphite is only found in confined water in the \( H = 7 \) Å sim-

---

**TABLE III.** The distance from the graphite wall to the maximum peak of the z-density profiles of Fig. 2, \( z_s \).

<table>
<thead>
<tr>
<th>( H (\text{Å}) )</th>
<th>( z_s ) for oxygen atoms (Å)</th>
<th>( z_s ) for hydrogen atoms (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2.82</td>
<td>2.60</td>
</tr>
<tr>
<td>10</td>
<td>2.93</td>
<td>2.78</td>
</tr>
<tr>
<td>15</td>
<td>3.10</td>
<td>3.09</td>
</tr>
<tr>
<td>20</td>
<td>3.20</td>
<td>3.05</td>
</tr>
</tbody>
</table>

---

FIG. 2. The z-density profile of hydrogen (solid lines) and oxygen (dashed lines) of water along confinement direction for different confinement distances at 300 K. The asterisks show additional small peaks indicating the positions of hydrogen atoms in inner layers of water molecules.
ulation and other systems with $H = 10$, 15, and 20 Å did not show this hexagonal arrangement in the outer water layers.

The radial distribution function of oxygen-oxygen ($g_{\text{O-O}}(r)$) and oxygen-hydrogen ($g_{\text{O-H}}(r)$) atom pairs of water over the entire confined systems are shown in Figs. S2(a) and S2(b) of the supplementary material. The RDFs of bulk SPC/E water at 300 K are also given in Figs. S2(c) and S2(d) for comparison. In agreement with previous simulations, both confined and bulk systems have the first peak of $g_{\text{O-O}}(r)$ at $\sim 2.7$ Å and the nearest neighbor water intermolecular distances are therefore not changed upon confinement. A similar observation holds for the first peak of $g_{\text{O-H}}(r)$ which is located at $\sim 1.67$ Å. Further discussions on the RDFs and normalized RDFs of these systems are presented in the supplementary material (Fig. S3).

Due to the layered structure of the confined water phase, a single RDF is not completely representative of the water structure. To better characterize the structure of the water layers in the confined systems, two-dimensional lateral RDF functions in the $xy$-plane for the different water layers, $g_{xy}(r)$, are shown in Fig. 4. In Fig. 4(a), we show the $g_{xy}(r)$ for the water layer adjacent to the graphite plate for the $H = 7$–15 Å cases. We observe that for the $H = 7$ Å case, the water layer near the graphite surface has a RDF characteristic of the solid phase with well-defined long-range order, whereas in the other two cases, the lateral RDFs are more liquid-like. In Figs. 4(b) and 4(c), we show the lateral RDFs for the outer and middle layers of the $H = 10$ and 15 Å simulations. In the $H = 10$ Å, there is substantial inhomogeneity in the structure of the outer layers and middle layer, whereas in the $H = 15$ Å simulations, the lateral structures of the layers are more homogeneous.

The pressure tensor components for the equilibrated NVT simulations for the different pore widths and geometric density $\sim 1$ g cm$^{-3}$ are given in Table II. The pressure tensors are anisotropic with the lateral components $P_{xx}$ and $P_{yy}(P_{||})$ approximately equal and significantly smaller than the transverse component $P_{zz}(P_{\perp})$. Due to the nature of the simulation setup, the magnitudes of the components of the pressure tensors for the confined water systems with geometric densities $\sim 1$ g cm$^{-3}$ are in the kbar range, see Sec. III C for further discussion.

From separate simulations (see supplementary material Fig. S3), we see that the effects of pressures in the range of 1 bar–7.7 kbar on the RDF of bulk water show that the variations in the second and third peaks of the RDFs are less than that of changes in the RDF as a result of different confinement.$^{68,69}$ These results point to the conclusion that increased pressure in the confined systems is not responsible for structural changes observed in the different confinements.

**B. Dynamics, mean square displacements, and velocity auto-correlation functions**

The trajectory of selected individual water molecules in the layers adjacent to the walls for 30 ps (with a snapshot registered every 5 fs), as shown in Fig. S4 of the supplementary material, we found that in the $H = 7$ and 10 Å cases, the center of mass of the water molecules adjacent to the graphite walls have limited mobility. For simulations with $H = 15$ and 20 Å, the center of mass of the water molecules are mobile, although their diffusion is not necessarily the same as the bulk water molecules. By tracking water molecules in different layers in the four confined systems, we found that water molecules located in layers adjacent to the slit walls have lesser tendency to mix with other water molecules. The solid-like mobility of
the water molecules near the wall for $H = 10$ and 7 Å is low and water molecules of the outer layers are considered as immobile.

The layered structure and different mobility of water molecules in different layers show that an average MSD over all water molecules in the system may not give a good local representation of the dynamic behavior of the water molecules in the confined system. The calculated mean square displacements for oxygen atoms of confined water molecules at 300 K over three dimensions, parallel to the graphite walls ($\text{MSD}_x$, $\text{MSD}_y$, $\text{MSD}_z$), and perpendicular to the walls ($\text{MSD}_\perp = \text{MSD}_z$) are shown in Fig. 5(a). The MSDs of the confined water systems with slit separations of 15 Å or more show liquid-like behavior over long times and for smaller slit separations, the mobility decreases and confined water changes to solid-like dynamics. For reference, we give the MSD of bulk SPC/E water at 300 K obtained from separate simulations. For all confined systems, the transverse MSD in the $z$-direction is much smaller than that of the lateral $x$- and $y$-directions (which are effectively equal). The MSDs for the bulk water simulation are larger than those of the confined systems. To better compare results, the different MSD components of each nanopore are shown in a single plot in Fig. 5(b). The effect of confinement on molecular motion in $z$-direction is clearly seen in $\text{MSD}_\perp$ graph of Fig. 5(a) which shows that this component is significantly smaller than the MSDs in the lateral directions.

In addition to the smaller geometrical distance available for motion in the $z$-direction, the $P_{zz}$ components of the average tensor pressure given in Table II are significantly larger than the lateral $xy$-components. A combination of geometric confinement and higher pressure can lead to the smaller $\text{MSD}_\perp$ in the $z$-direction. Similar inhomogeneities in the radial and lateral diffusion of water molecules have also been observed in a cylindrical nanopore environment. In contrast to our results, Leng and Cummings observe mobility of hydration layers between mica surfaces for 1 bar pressure.39

In the discussion of Fig. 4, we observed that the lateral RDF depends on the $z$-coordinate in the slit. The mobility of water molecules for different transverse cross sections of the slit will also not be the same. Although we calculate the MSD values averaged over all $z$-coordinates, these MSDs can be $z$-dependent.

Self-diffusion coefficients of water from MSD plots based on Einstein relation for four confined systems with geometric density near 1 g cm$^{-3}$ at 300 K with SPC/E bulk water at 50 (supercooled), 265, and 300 K for comparison are given in Table IV. The self-diffusion coefficient for bulk SPC/E water at 300 K is calculated to be $2.73 \times 10^{-9}$ m$^2$ s$^{-1}$ which is in good agreement with previous work.41, 71–73 The diffusion coefficients in the $z$-direction are between 4 and 10 times smaller than those in the lateral direction. The melting point of SPC/E water is 210 K.

Previous studies showed that at 240 K, for a system with $H = 11.0$ Å, TIP4P water molecules confined close to the wall move faster than the water molecules in the middle layer.16 Although TIP4P water is liquid at this temperature, due to the low kinetic energy content of the water molecules at 240 K, these results are difficult to compare with our work. The self-diffusion coefficient of hypothetical supercooled water at 50 K is of the same order of magnitude as confined water with $H = 7$ Å (see Table IV). The ratios of $D_z$ to $D_x$ and $D_z$ to the overall $D$ for different confinements are also shown in Fig. S5.

The VACF for the oxygen atom of water molecules, parallel to the graphite walls ($\text{VACF}_||$) and perpendicular to the walls ($\text{VACF}_\perp = \text{VACF}_z$) for confinements from $H = 7$ to

FIG. 5. (a) The computed MSD components for different confinements and bulk water at 300 K; (b) the different components of the MSD for each confinement.
TABLE IV. The self-diffusion coefficient \( (D) \) in \( 10^{-9} \, \text{m}^2 \, \text{s}^{-1} \) for confined water at 300 K calculated from the MSD and VACF plots.

<table>
<thead>
<tr>
<th>( H (\text{Å}) )</th>
<th>( D ) MSD</th>
<th>( D ) VACF</th>
<th>( D_H ) MSD</th>
<th>( D_H ) VACF</th>
<th>( D_z = D_x ) MSD</th>
<th>( D_z = D_x ) VACF</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.50</td>
<td>1.30</td>
<td>2.11</td>
<td>1.459</td>
<td>0.81</td>
<td>0.84</td>
</tr>
<tr>
<td>15</td>
<td>0.67</td>
<td>0.71</td>
<td>0.95</td>
<td>0.945</td>
<td>0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>10</td>
<td>0.024</td>
<td>0.068</td>
<td>0.031</td>
<td>0.095</td>
<td>0.0095</td>
<td>0.0018</td>
</tr>
<tr>
<td>7</td>
<td>( 9.4 \times 10^{-5} )</td>
<td>( 11 \times 10^{-5} )</td>
<td>( 10 \times 10^{-5} )</td>
<td>( 10 \times 10^{-5} )</td>
<td>( 0 \times 10^{-5} )</td>
<td>( 0 \times 10^{-5} )</td>
</tr>
<tr>
<td>Bulk water (300 K)</td>
<td>2.73</td>
<td>2.75</td>
<td>2.70</td>
<td>2.614</td>
<td>2.77</td>
<td>3.03</td>
</tr>
<tr>
<td>Bulk water (265 K)</td>
<td>1.09</td>
<td>1.07</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Bulk water (50 K)</td>
<td>( 2.7 \times 10^{-5} )</td>
<td>( 2.6 \times 10^{-5} )</td>
<td>( 2.9 \times 10^{-5} )</td>
<td>( 2.9 \times 10^{-5} )</td>
<td>( 0 \times 10^{-5} )</td>
<td>( 0 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

20 Å are shown in Fig. 6. The behaviors of components of the VACFs for different \( H \) values are shown in Fig. 7 where SPC/E bulk water at 300 K is used as a reference. The VACFs in confined water systems decay faster than bulk water and the rate of decay increases with the increase of confinement from \( H = 20 \) to 7 Å (Fig. 7). The time scales of the decay of the VACFs in all confined systems studied are quite similar and the first zero in the VACFs \((x\text{-axis intercept})\), which is a measure of the mean collision time (back-scattering time) appears after \( \sim 0.03-0.06 \) ps. The mean collision time is the shortest for the system with \( H = 7 \) Å. For bulk water, the first zero of VACFs appears near 0.16 ps, which is consistently larger than the corresponding times in confined systems. After the first zero, the VACFs show a negative region corresponding to cage effects. This region extends to \( \sim 0.2 \) ps for the confined system with \( H = 7 \) Å and \( \sim 0.55 \) ps for bulk water. The second zero in the \( x \)-axis in the VACFs is a measure of the velocity randomization times. The value of graphite inter-wall distances determines the detailed oscillation behavior of the water dynamics between these two zero times (see Fig. 6). The greater number of collisions involving the water molecules in the system with the \( H = 7 \) Å randomizes their velocities sooner. This is a reflection of the increased solid-like behavior of the confined water systems.

Evaluation of diffusion coefficients of confined waters from the integration of VACFs using the Green–Kubo methods is not straightforward due to the oscillations in the VACFs at large times (Fig. 7). The self-diffusion coefficients calculated in this manner are given in Table IV. The diffusion coefficients for bulk water and confinements with \( H = 20 \) and 15 Å using the slope of MSD and the integration of VACFs are close in magnitude. With increase in confinement, especially in \( H = 7 \) Å, the result from Green–Kubo relations are not reliable and VACFs have more oscillations and finding an appropriate upper time limit for evaluation of the integral becomes difficult.

C. Density effects and bubble formation

We studied how changes in the effective density affect the structure and dynamic properties of confined water. The \( z \)-density profiles of oxygen and hydrogen atoms for different numbers of water molecules in the slit in the simulation with \( H = 7 \) Å are shown in Fig. 8. When the water molecules confined between the graphite layers are decreased from 380 to 285, reducing the geometrical density from 0.8 to 0.6 \( \text{g cm}^{-3} \), the two water layers merge into a single layer. The snapshots

![FIG. 6. The calculated VACFs curves for confinements with \( H = 20, 15, 10, \) and 7 Å at 300 K.](image1)

![FIG. 7. The change in the VACF components in different confinements. The VACF of bulk SPC/E water at 300 K is given as reference.](image2)
of the structure of the water phases for these densities are

given in Fig. S6 of the supplementary material. The exact

numbers of water molecules in these simulations are tabulated

in Table S1 of the supplementary material.

We studied different effective densities (given in Table II)

for slit separations $H = 7-20$ Å. For all densities, the pressure

in these confined systems is non-isotropic, with component

of the pressure tensor in $z$-direction being considerably larger

than that of the two lateral components. We decreased the

densities to obtain equilibrated effective water densities be-

tween the plates of $\sim 1$ g cm$^{-3}$ which is the water density near

$\sim 1$ bar.

With decreasing geometric density, the components of

the pressure tensor become negative and bubbles form in the

simulation systems. The formation of bubbles is clear in $xy$-

plane projection for the $H = 20$ Å shown in Fig. 9(a). In

the $H = 7$ Å simulations, the ordered structure of the wa-

ter molecules in the $xy$-plane is retained as the geometrical
density is reduced, but “bubbles” are still formed in the water

distribution as shown in Figure 9(b). This suggests that the or-
dering of the water molecules in small nano-confined systems

is the result of confinement and not a reflection of the high

pressures in these systems. With decrease in density in the

confined system to a geometric density of 0.423 g cm$^{-3}$,

the ordered water arrangement is still observed in the $H = 7$ Å

simulations, even despite the negative pressure in the $z$-
direction. In this ordered structure, each water molecule

formed four hydrogen bonds, as shown in Fig. 9(b) with the

green dashed lines.

Snapshots of simulations with $H = 15$ Å and different

effective densities are shown in Fig. 10. The formation of

bubbles between the graphite plates is seen in the low effec-
tive water density simulations. A general observation from

Table II is that when the effective density decreases to about

0.9 g cm$^{-3}$, bubbles form in the aqueous system between the

slits. The lateral and transverse components of the pressure
tensor are negative in this density region. The bubble forma-
tion transforms the remaining water phases to local effective
densities that are close to the bulk density of 1 g cm$^{-3}$ which

strengthens the hydrogen bonding within the existing water

phase. Bubble formation occurs at the expense of a decrease

in the entropy of the system. A further thermodynamic char-
acterization of the bubble formation process and an analysis

of the changes in hydrogen bonding structure and lifetimes

FIG. 8. The effect of the number of water molecules between the slits on the
$z$-density profile of oxygen and hydrogen for the $H = 7$ Å simulation.

FIG. 9. (a) Top view of simulation cell which shows bubble formation in
$H = 20$ Å with geometric density of 0.68 g cm$^{-3}$; (b) formation of ordered
structure in $H = 7$ Å with geometric density of 0.423 g cm$^{-3}$.

FIG. 10. Snapshots looking down along the $z$-axis of the water phases for
$H = 15$ Å at 300 K simulations with different numbers of water molecules
between the plates (as specified on the panels).
which occur as a result of the decrease in effective density between the slit plates will remain for a future publication.

Pressure in confined systems with \( H = 20 \text{ Å} \) or less is anisotropic and the confined liquid is subject to strong capillary forces (negative tension) in different directions. As water is almost incompressible, in Table II for \( H = 20 \text{ Å} \) we see that decreasing the geometrical density from 0.890 to 0.875 g cm\(^{-3}\) (the number of water molecules in the simulation from 1200 to 1180), causes the lateral pressure to change from 0.06 to −0.11 kbar, while the pressure component in the \( z \)-direction changes from 0.42 to 0.21 kbar. The oxygen-oxygen RDFs for these systems with various densities, plotted in Fig. S8, shows there are no great changes in the shapes of the RDFs with decreasing geometrical density and local structure in water phases is conserved.

Generally, in confined systems, the pressure is higher than that in the bulk water systems with the same effective density. Results in Table II show in confined systems with \( H = 10, 15 \), and \( 20 \text{ Å} \) and small changes in the geometrical density can lead to very different pressures.\(^4\)\(^5\)\(^7\) The confinement distance is a thermodynamic variable in these cases and can affect the predicted pressure values.

IV. CONCLUSIONS

We used MD simulations to characterize structure, dynamics, and transport properties of nano-confined SPC/E water molecules between the hydrophobic parallel graphite plates in various separation distances from 7 to 20 Å with different geometrical water densities at 300 K. Identical molecular dynamics conditions are used in all cases with care given to proper equilibration and convergence of the dynamic properties. Water molecules in confined regions behave differently from bulk water molecules and are different with respect to the \( z \)-density profile, mean square displacement, velocity autocorrelation function, diffusion coefficient, and particle trajectory visualization. Our simulations show the structure and dynamics of the confined water phase become anisotropic and depend on the slit width \( H \).

The \( z \)-density profiles show that hydrogen atoms in confined water molecules are located closer to the graphite layers than the corresponding oxygen atoms. The layer of water molecules adjacent to the surface are distributed approximately one water molecule per six-carbon ring on the graphite layer with a regular hexagonal structure seen only in case with \( H = 7 \text{ Å} \). This feature of the confined water depends on the confinement distance within graphite walls and is not related to the high pressure phase transition of water to hexagonal ice. Trajectories of water molecules in various layers, indicated water molecules located in the outer layers near the graphite walls have less mobility and tendency to mix with other water molecules located in other layers. These layers have more solid–like behavior. Calculated RDFs also indicate that the nearest neighbor water intermolecular distances are not changed upon confinement. The effect of geometric and effective water density on the RDFs is also investigated. There is no clear ordering of water layers in the center of the slit nanopore in system with \( H = 20 \text{ Å} \) and some bulk-like properties begin to appear in this case.

The MSD and VACF results show that with increasing confinement from \( H = 20 \) to 7 Å the confined water molecules behave solid-like which is consistent with the previously described RDF results. The diffusivity of the water molecules depends on the slit width and is significantly different in the lateral and transverse directions with respect to the slit walls. For all confined systems, the transverse MSD in the \( z \)-direction is much smaller than that in the lateral \( x \)- and \( y \)-directions.

Pressure in bulk water is a function of temperature and density but in confined water pressure depend on temperature, density, and the inter-wall separation between graphite plates. The pressure tensors in the studied confined systems are anisotropic with the lateral \( xy \)-components \( (P_{xx}, P_{yy}, \text{ or } P_{zz}) \) approximately equal and significantly smaller than the transverse component \( P_{zz} \). The VACFs in confined water systems decay faster than bulk water and the rate of decay increases with increasing of confinement. The mean collision times and velocity randomization times are the largest in the bulk system and decrease with smaller slit size. Self-diffusion coefficients are calculated using the Einstein relation and the Green–Kubo integral.

In Sec. III C, we investigated the effect decreasing the amount of water between the confined graphite plates. When the effective density of the water between the plates is decreased to about 0.9 g cm\(^{-3}\), negative pressures appear and bubbles are formed in the water phase. This bubble formation can have important repercussions on the application of the behavior of liquids in nano-slits and nano-tubes in biological, technological, and geophysical contexts.

ACKNOWLEDGMENTS

The computational support of the Physical Chemistry Department of the Isfahan University of Technology is gratefully acknowledged. H.M. thanks Mrs. S. Azhari of the Department of Chemistry, Isfahan University of Technology, for guidance and acknowledges Dr. T. Youngs of the Atomistic Simulation Centre of Queen’s University Belfast for assistance with some FORTRAN codes. We thank Mr. Y. Afshar for assistance with the lateral RDF code.
