The effects of confinement on the behavior of water molecules between parallel Au plates of (001) planes

Shin-Pon Ju

Department of Mechanical and Electro-Mechanical Engineering; Center for Nanoscience & Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan, Republic of China

Jee-Gong Chang

National Center for High-Performance Computing, No. 21, Nan-Ke 3rd Road, Hsin-Shi, Tainan, Taiwan, Republic of China

Jenn-Sen Lin

Department of Mechanical Engineering, National United University, Maio-Li 360, Taiwan, Republic of China

Yong-Sheng Lin

Department of Mechanical and Electro-Mechanical Engineering; Center for Nanoscience & Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan, Republic of China

(Received 10 December 2004; accepted 1 February 2005; published online 18 April 2005)

Molecular dynamics simulation is utilized to investigate the behavior of water molecules confined between two Au plates of (001) planes separated by gaps of 24.48, 16.32, 12.24, 11.22, and 10.20 Å. The simulation results indicate that the arrangements of the water molecules are dependent on the gap size. For the largest gap size, adsorption of the Au surface creates two permanent water layers in the vicinity of each Au plate. Furthermore, in this case, the gap size is sufficiently large to permit the formation of a central region within which the water molecules are randomly oriented in a similar manner to bulk water molecules. The results indicate that the orientation of the first water layer directly absorbed by the plate surface does not change as the gap size between the two Au plates is reduced. However, the orientations of the O–H bonds in the second water layer parallel to the surface rearrange to form hydrogen bonds between the water layers as the separation between the plates is decreased. Finally, an inspection of the variation of the self-diffusion coefficients with the gap size suggests that the difference between the dynamic properties of the water molecules in the z direction and the x–y plane decreases as the distance between the two Au plates increases.


I. INTRODUCTION

The behavior of confined water has attracted intensive research interest since confined water molecules play an important role in many fields.1–5 For example, in the biological systems of a restricted cell,1,2 confined water molecules can stabilize the biological macromolecules. In the field of nanobiology, confined water molecules can act as a lubricant between two solid surfaces. The viscosity of water and the frictional properties of the liquid-solid system are strongly influenced by the thickness of the confined water film.3–5 These particular material properties, whose characteristics are determined by the space occupied by the confined water, have been measured by various experimental methods, including x-ray scattering,1 quasielastic and inelastic neutron scattering,2 scanning force microscopy,7 and surface force balancing.4 The experimental results have revealed that the structure and dynamic properties of water molecules confined in a small space are different from those of their bulk water counterparts. Investigating molecular behavior using direct methods is difficult due to the very small characteristic scales involved. Consequently, numerical methods are generally adopted as a means of developing a deeper insight into the experimentally observed results. Molecular dynamics (MD) simulation is a powerful tool facilitating the investigation of molecular behavior at the atomic level. Using this technique, Gordillo and Martí performed a series of investigations to clarify the effects of nanotube confinement and temperature on the behavior of water molecules.6–8 Their results revealed that water molecules confined in carbon nanotubes experience a destruction of the hydrogen bonding network, which leads to a reduction in the average number of hydrogen bonds formed between the water molecules. This confinement effect was observed to exist even when the water molecules were in a supercritical condition. Furthermore, it was found that the hydrogen bonding network is also damaged by increasing temperature. As a result, the diffusion ability of the water molecules is enhanced as the temperature increases. Brovchenko et al. employed MD simulations to investigate the properties of water molecules in nanopores at an ambient temperature of 300 K and a pressure of 1 bar.9 Two values of the Lennard-Jones parameter ε were chosen,
i.e., $-1.93$ and $-4.62$ kcal/mol, to represent the weaker and stronger interactions, respectively, between water and the nanopores. The results demonstrated that a stronger water-pore interaction prompts the formation of two prominent water layers in the vicinity of the pore surface. Gallo et al. adopted a MD simulation approach to investigate the behavior of water molecules confined in a silica pore of 2 nm radius under various water density and temperature conditions. In a series of studies, the effects of water density and system temperature on the hydrogen bond network and water molecule arrangement in the silica pore were thoroughly investigated.\(^\text{10–12}\) The numerical results revealed that the local arrangement of the water molecules in silica pores is dependent on the density of water. Furthermore, it was shown that a strong interaction between the water molecules and the pore induces a distortion of the hydrogen network. In the high water density case, two distinct regimes are formed, i.e., near the pore surface and in the central region of the pore, respectively. The static and dynamic properties of the water molecules in these two regions are significantly different. Conversely, in the lower density case, only a surface absorbed layer exists and an anomalous diffusion is identified in the vicinity of the pore. Liu also employed MD simulations to inspect the behavior of water confined at low density in nanopores.\(^\text{13}\) Inhomogeneity was identified along the axial and radial directions. The axial diffusivity was found to be approximately four to ten times larger than the diffusivity along the radial direction. In addition to these investigations of water molecules confined in nanopores, the behavior of water molecules confined in nanoscale gaps has also been observed using MD simulation. Zangi and Mark found that the arrangement of water molecules is strongly dependent on the thickness of the gap between two parallel plates under ambient conditions.\(^\text{14,15}\) The numerical results indicated that for a constant number of water molecules confined within the nanoscale gap, continuously decreasing the separation distance between the two plates from 1.14 to 0.85 nm, 0.85 to 0.57 nm, and 0.57 to 0.41 results in the formation of three-layered, two-layered, and one-layered water structures, respectively. It is observed that the lateral diffusion coefficient drops in the one-layered and two-layered water structure regions because of the formation of a monolayer ice and a bilayer ice at some specific thicknesses of gaps.

From the discussions above, it is clear that MD simulation provides a powerful technique for investigating fundamental molecular behaviors at an atomic level. Accordingly, the present study utilizes MD simulations to investigate the behavior of water molecules confined in nanoscale gaps at a constant density of 0.973 g/cm\(^3\) and a constant temperature of 400 K. Specifically, this study investigates the arrangement of water molecules by considering the density concentration profiles of the oxygen and hydrogen atoms, the average number of H-bonds per water molecule \(n_{HB}\), and the orientation factor \(s(z)\). The self-diffusion coefficients of the water molecules along the \(z\) direction and the \(x\)-\(y\) plane are also examined in order to explore the dynamic properties of the confined water molecules along the directions parallel and normal to the two plates.

**II. SIMULATION MODEL**

Figure 1 presents a schematic diagram of the water molecules confined between two parallel Au (001) plates. Each plate is composed of a seven-layered structure with each layer comprising a total of 450 Au atoms. It is noted that the upper and lower Au layers are fixed in order to prevent the system from moving in a disorderly manner during the simulation. Furthermore, periodic boundary conditions are imposed in the \(x\) and \(y\) directions.

The present simulations consider various atomic interactions, i.e., interactions between the Au atoms, interactions between the water molecules, O–H bonding and H–O–H bending intramolecular interactions within individual water molecules, and interactions between the Au atoms and the water molecules. The atomic interactions between the Au atoms are modeled using the many-body, tight-binding potential method.\(^\text{16,17}\) Meanwhile, the intermolecular and intramolecular interactions of the \(H_2O\) molecules and the interactions between the \(H_2O\) molecules and the Au atoms are modeled using the flexible 3-centered (F3C) water model\(^\text{18}\) and the Spohr potential (as modified by Dou et al.) (Refs. 19–21), respectively.

This study focuses specifically on the influence of the gap size between two parallel plates on the behavior of the confined water molecules. Hence, the remaining simulation conditions, such as the water density (0.973 g/cm\(^3\)) and the system temperature (400 K), are assumed to be constant. The scaling method\(^\text{22,23}\) is used to scale the temperature of the water molecules and the Au atoms to an equilibrium temperature of 400 K during the simulation. The multiple time step method\(^\text{23,24}\) and the Verlet algorithm\(^\text{22,23,25}\) are employed to calculate the trajectories of the atoms. A small time step of 0.1 fs is used when simulating the fast motions associated with the bonding and bending of the water molecules. However, a larger time step of 1 fs is adopted when simulating all other motions.

**III. RESULTS AND DISCUSSION**

The statistical data presented in Figs. 2 and 3 are sampled from the system over a time period of 10 ps following the completion of a relaxation process of duration 30 ps.

Figure 2 presents the local reduced density distributions of the hydrogen and oxygen atoms, and the variation of the
O–H bond orientation factor \( s(z) \) along the vertical direction. The value of the bond orientation factor is given by

\[
s(z) = 1.5 \cos^2 \theta - 0.5,
\]

where \( \theta \) is the angle between the O–H bond and the direction normal to the plate (i.e., the \( z \) direction). The bracketed term expresses the average over the number of O–H bonds and time steps in the MD simulation. Values of \( s(z) = -0.5, 0.0, \) and 1.0 denote that the O–H bonds are oriented parallel to the plates, randomly, and normally to the plates, respectively.

To develop a clearer understanding of the local hydrogen bonding of the water molecules, Fig. 2 also shows the variation in the average number of H-bonds per water molecule \( n_{HB} \) with increasing distance from the bottom Au plate. In determining the value of \( n_{HB} \), the present study adopts the geometric criterion \(^6,7\) that a hydrogen bond will be formed if the distances between two oxygen atoms and the oxygen and hydrogen atoms of a pair of water molecules are less than the first minimum \(^18\) of the F3C O–O radial distribution function (3.4 Å) and the F3C O–H radial distribution (2.4 Å). \(^18\) In addition, this study specifies that the angle between the O–O and O–H directions must be less than 30°. In order to investigate the influence of the confined thickness on the water molecule arrangement, Figs. 2(a)–2(e) present the oxygen and hydrogen reduced density profiles, the bond orientation factor profile, \( s(z) \), and the \( n_{HB} \) profile for gap sizes of 24.48 Å, 16.32 Å, 12.24 Å, 11.22 Å, and 10.20 Å. In these figures, the left vertical axis indicates the reduced density \( \rho_{local}/\rho_{bulk} \) and \( n_{HB} \), while the right vertical axis indicates the value of the orientation factor \( s(z) \). The horizontal axis indicates the distance from the bottom of the lower plate. It should be noted that Figs. 2(a)–2(e) adopt different horizontal axis scales in order to show more clearly the variations of these curves for the different cases.

Figure 2(a) presents the results for the largest gap size of 24.48 Å. It is observed that three oxygen and hydrogen reduced density peaks are formed in the vicinities of both plates. The prominent nature of the first peak indicates that the water layer is adsorbed directly by the plate surface. The interaction between the plate and the water molecules becomes weaker as the interatomic distance increases, and hence the values of the second and third peaks are reduced. The first two peaks are clearly more pronounced than the third. This implies that two plane water layers are formed close to each Au surface. Moreover, the reduced densities of the oxygen and hydrogen atoms in the region between the two third peaks are close to 1, which implies that a bulk water arrangement exists in this region. Meanwhile, it is apparent that the variation of the orientation factor \( s(z) \) complements the variation of the oxygen density, i.e., the peaks and valleys of the \( s(z) \) profile correspond to the valleys and peaks of the oxygen density profile. The values of the first and second valleys of the \( s(z) \) profile are \( \approx -0.45 \) and \( -0.30 \), respectively. Accordingly, it can be surmised that most of the O–H bonds within the first and second water layers lie parallel to the plate surface and form a flat hydrogen network.
Moreover, the first and second peaks of the \( s(z) \) profile imply that the O–H bonds between the water layers rotate from the horizontal direction to form hydrogen bonds with the nearest water layer. The hydrogen atoms of these O–H bonds point toward the nearest water layer with the result that the hydrogen density is less than the oxygen density in the water layers, but is greater than the oxygen density in the region between the water layers. The high water molecule density in the first water layer increases the average number of hydrogen bonds \( n_{HB} \) to its maximum value in this layer. In other words, the water molecules within the first layer have the strongest hydrogen bonding. Since most O–H bonds in the first water layer are oriented parallel to the Au surface, the stronger hydrogen bonding is generated primarily by the plane hydrogen bonding network. From Fig. 2(a), it can be seen that the value of \( n_{HB} \) decreases between the first two water layers. There are very few water molecules in this region, and hence the water molecules which do exist have a reduced opportunity to form hydrogen bonds with other water molecules in this region. In other words, these particular water molecules lose the opportunity to form hydrogen bonds in the \( x-y \) plane, and hence the value of \( n_{HB} \) decreases rapidly. Since the water molecules in the randomly oriented region do not actually interact with the Au plates, the differences in the water molecule arrangements between the randomly oriented region and the water layer region are attributed most feasibly to the simple presence of the Au plates. Consequently, increasing the thickness of the nanoscale gap between the two plates simply leads to an increase in the thickness of the randomly oriented region and the water density in this region is much closer to the average density of 0.973 g/cm\(^3\). However, the density distribution of the water layers will not change because of the strong adsorption of Au plates.

In Fig. 2(b), the thickness between the two plates is reduced to 16.32 Å. The density, orientation factor, and hydrogen bond profiles of the first two water layers are similar to those observed in the previous case. However, for the reduced gap size considered in this figure, insufficient space exists to permit either the formation of a third peak or a randomly oriented region. Hence, a single water layer is formed in the central region. Consequently, five water layers are apparent in the figure rather than the six layers shown in the previous case. Each layer is connected with its nearest water layer by hydrogen bonding with the observation of the peaks of \( s(z) \) between water layers, which implies that most O–H bonds are almost normal to Au plates, so the hydrogen density is larger than oxygen density between water layers. The value of \( n_{HB} \) between the second water layer and the central layer increases because water molecules in this region have the opportunity to form hydrogen bonds with the upper and lower water layers in addition to other water molecules in the same region.

Figure 2(c) illustrates the profiles of the oxygen and hydrogen densities, together with those of \( s(z) \) and \( n_{HB} \) for a reduced gap size of 12.24 Å. The central water layer visible in the previous case (gap size 16.32 Å) is no longer apparent, and hence just four distinct oxygen layers are formed. Due to the stronger adsorption of the first water layer, the distribution of the oxygen and hydrogen atom densities in this particular layer are similar to those of the larger gap size cases. However, some O–H bonds in the second water layer close to the lower and upper Au plates, which originally lay flat in Figs. 2(a) and 2(b), rearrange in this reduced gap size case to form hydrogen bonds with the second oxygen layer close to the upper and lower Au plates, respectively. This results in a higher hydrogen density between the two second oxygen layers. Accordingly, compared to the cases shown in Figs. 2(a) and 2(b), a lower hydrogen density exists in the second layer in the present case. Since a reduction in the gap size between the two Au plates will significantly increase the repulsive energy of the water molecules, the only way to increase the attractive energy is to change the orientation of the O–H bonds in the second water layers to form hydrogen bonds between the two second oxygen layers.

Figure 2(d) shows the distributions of the oxygen and hydrogen densities, and those of \( s(z) \) and \( n_{HB} \) for the case of a 11.22 Å gap size. It can be seen that there is insufficient space between the two plates to form a second water layer, and hence only the first and central water layers are evident. An observation of the \( s(z) \) profile suggests that most water molecules in the central layer lie flat and that some hydrogen atoms form hydrogen bonds with the first water layers. As shown in Fig. 2(e), which shows the case where the gap size is further reduced to 10.2 Å, the hydrogen density decreases in the central layer, but increases in the region between the first water layer and the central layer. The O–H bond orientations of the water molecules in the central layer rearrange themselves in order to form more hydrogen bonds with the first water layer and to maintain a more stable structure as the thickness between the two plates decreases. Consequently, the value of \( n_{HB} \) in the central layer is smaller than in the central layer of Fig. 2(d) since fewer hydrogen atoms are in central layer.

Figure 3 presents the profiles of the self-diffusion coef-

![Graph showing self-diffusion coefficient in x-y plane and z direction](image)
TABLE I. Correlation between gap size and average number of hydrogen bonds per water molecule.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>10.2</th>
<th>11.22</th>
<th>12.24</th>
<th>16.32</th>
<th>20.4</th>
<th>24.48</th>
<th>32.64</th>
<th>36.72</th>
<th>40.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average hydrogen bonds per water molecule</td>
<td>3.17</td>
<td>3.27</td>
<td>3.28</td>
<td>3.18</td>
<td>3.14</td>
<td>3.11</td>
<td>3.07</td>
<td>3.07</td>
<td>3.06</td>
</tr>
</tbody>
</table>

ACKNOWLEDGMENT

The authors gratefully acknowledge the support provided to this research study by the National Science Council of the Republic of China under Grant No. NSC 93-2212-E-110-022.