Structure and dynamics of ordered water in a thick nanofilm on ionic surfaces*

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The structure and dynamics of water in a thick film on an ionic surface are studied by molecular dynamic simulations. We find that there is a dense monolayer of water molecules in the vicinity of the surface. Water molecules within this layer not only show an upright hydrogen-down orientation, but also an upright hydrogen-up orientation. Thus, water molecules in this layer can form hydrogen bonds with water molecules in the next layer. Therefore, the two-dimensional hydrogen bond network of the first layer is disrupted, mainly due to the O atoms in this layer, which are affected by the next layer and are unstable. Moreover, these water molecules exhibit delayed dynamic behavior with relatively long residence time compared with those bulk-like molecules in the other layers. Our study should be helpful to further understand the influence of water film thickness on the interfacial water at the solid–liquid interface.

Keywords: water nanofilm, solid surface, hydrogen bond, molecular dynamics simulation

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1. Introduction

The properties of fluids adsorbed on solid surfaces influence many natural processes, including spreading, wetting and dewetting, viscous dissipation, and lubrication on various kinds of solid surfaces.[1–6] Nanometer water films at the liquid–solid interface are of special importance, because the structure of a liquid within nanometers on a solid surface has a crucial influence on most of the interfacial properties.[7–16] Recently, it was found that water nanofilms may exhibit a two-dimensional ordered structure on particular solid substrates under ambient conditions, which is related to many important physical/chemical processes in various scientific areas.[8,17–27]

Our previous study directly observed an unexpected phenomenon that water cannot wet a water monolayer on an modeled ionic surface at room temperature using molecular dynamics simulations.[13] The water monolayer also formed a two-dimensional ordered structure, due to a special arrangement of the charge on the solid surface. These simulation results were verified by recent tapping mode AFM measurements: nanosized droplets on a self-assembled monolayer became fewer in number and larger in size with time.[28] Rotenberg *et al.* also found that a droplet of water beads up on the same surface (hydrophobic behavior), while individual water molecules adsorb strongly on a talc surface (hydrophilic behavior),[15] which is consistent with our observation that water does not wet a water monolayer. However, the thickness of water film may have great impact on the surface wetting behavior at the solid surface.[15,17]

In this article, we revisit the structure and dynamics of water on an ionic surface with water film of 3 nm in thickness, much thicker than the thin water film thickness of about 1.1 nm used in the previous work.[13] By analyzing the normalized atom density profiles, surface density profiles, angular distributions, normalized hydrogen bond density profile, and residence probabilities, we find that there is a dense monolayer of water molecules in the vicinity of the surface. Water molecules within this layer exhibit preferential orientations. These water molecules not only form hydrogen bonds with the neighbor water molecules in the same layer, but also with water molecules in the other layers. Moreover, these water molecules exhibit delayed dynamic behavior with relatively long residence time compared with those bulk-like molecules in the next layer. Particularly, the two-dimensional hydrogen bond network of the first layer observed in thin water film is disrupted in our study, and affected by the next layer. Our study should be helpful to achieve a better understanding of the influence of thickness upon the interfacial water at the solid–liquid interface.

2. Building of the structural model, and simulation method

Our model of ionic substrate is the same as the surface used in our previous study.[13] This substrate has a dimension of 4.428×4.26 nm^2 with a planar hexagonal struc-

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ture of neighboring bond length of 0.142 nm, as shown in Fig. 1(a). Positive and negative charges of the same magnitude 1.0e were assigned to the atoms located diagonally in neighboring hexagons. The modeled solid surface was overall neutral, and set at $z = 0$ nm for convenience. The atoms of the solid were modeled with Lennard–Jones parameters: $\varepsilon_{ss} = 0.4393$ kJ/mol, $\varepsilon_{ss} = 0.3343$ nm. The SPC/E[29] model was used for water, and the SETTLE algorithm[30] was used to keep the O–H distance at 1 Å and the H–O–H angle at 109.47°. A repulsive wall is placed at $z = 10$ nm, which was used to prevent vaporized water molecules from being trapped by the periodic image of the modeled solid surface.

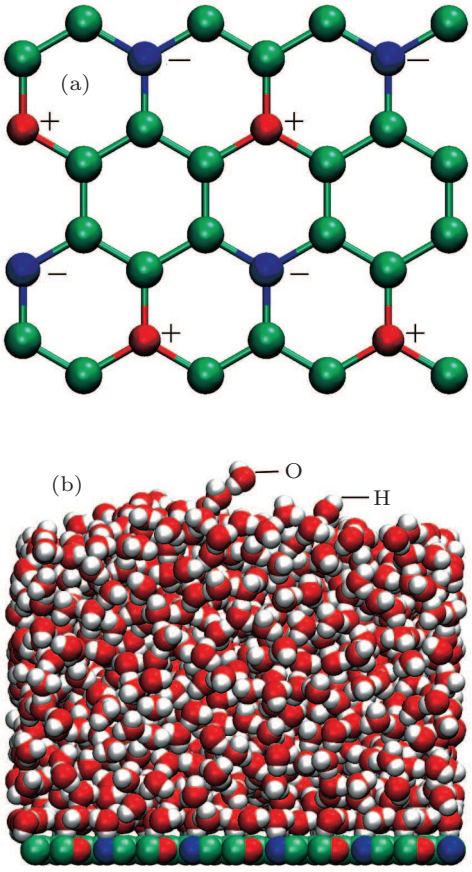


Fig. 1. (color online) (a) Geometry of the ionic surface. Only 2×1 unit cells are shown for clarity. Red, blue, and olive spheres represent the positive-charged, negative-charged, and neutral solid atoms, respectively. (b) Side view of the simulation system.

All simulations of our system (see Fig. 1(b)) were performed using Gromacs 4.5[31] with a time step of 1 fs in a canonical ensemble at a temperature of 300 K. Geometric combining rules were applied to calculate the Lennard–Jones interactions between different particles. The particle–mesh Ewald method[32] was used to treat long-range electrostatic interactions, and van der Waals interactions were treated with a cutoff distance of 1.0 nm. The temperature was controlled using a velocity rescaling thermostat.[33] Periodic boundary conditions were applied in the three directions. After equilibrating for 3 ns, the data were collected every 50 fs during the next 2-ns production run. For the simplicity of contrast, the system of only one water monolayer on the ionic modeled substrate was also simulated by using the same method described above.

3. Results and discussion

3.1. Normalized atom density profiles

The normalized density profiles for the O and H atoms of water molecules provide a basis for understanding how the structure of interfacial water is influenced by the presence of an ionic surface. As shown in Fig. 2, there are two distinct peaks for O atoms and three distinct peaks for H atoms. This clearly shows that the presence of the ionic surface affects the atom density of water at the solid–liquid interface. The locations of these peaks are listed in Table 1.

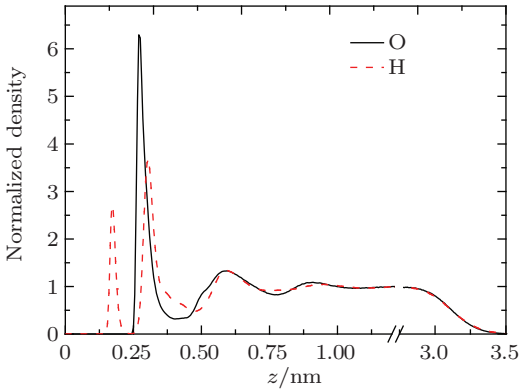


Fig. 2. (color online) Normalized atom density profiles for water O and H atoms, $\rho(z)/\rho_0$ (ρ_0 is the bulk atom density, 1.0 g/cm^3 for O and 2.0 g/cm^3 for H), along the z axis perpendicular to the ionic surface.

The first peak for O atoms at $z = 0.27$ nm is 0.1 nm above the corresponding H atoms at $z = 0.17$ nm. This suggests that water molecules in the first layer adopt a hydrogen-down orientation, and the hydroxyl groups are almost perpendicular to the surface since the bond length of O–H is 0.1 nm. The second peak for H atoms is 0.03 nm above the first peak for O atoms, suggesting that an average angle of about 17° is formed between hydroxyl groups and the surface, and (90° + 17°) is close to the H–O–H angle of 109.47°. From these results, we can conclude that the O atoms of the first peak and the H atoms of the first two peaks belong to the first layer of water molecules. Interestingly, a pronounced minimum in the atom density profiles for O atoms is observed at about 0.41 nm, indicating that a depletion layer appears near the surface. However, there are a considerable number of H atoms in this depletion layer, in contrast to the nearly complete absence of H atoms in the depletion layer on the top of the well-ordered bilayer structure in our previous study.[34]

Table 1. Locations of the atom density peaks for O and H atoms.

Atom type	First peak/nm	Second peak/nm	Third peak/nm
O	0.27	0.58	–
H	0.17	0.30	0.59

3.2. Surface density profiles

To further study the structural properties of water molecules within the first and second molecular layers, we calculated the x–y surface density distributions of water O atoms and H atoms on planes, whose locations correspond to the peaks in the atom density profiles (see Table 1). Atom density contour maps for the positive-charged, negative-charged, and neutral atoms of the substrate were also plotted as backgrounds. Thus, it is convenient to describe the local environment of adsorption sites, as shown in Fig. 3.

In the first water layer, the positive-charged H atoms below O atoms are all adsorbed on the sites of the negative-charged solid atoms (see Fig. 3(a)), mainly through electrostatic attraction. The planar locations of the adsorption sites of H atoms above O atoms preferentially locate in the region between the sites of the positive-charged and negative-charged atoms (see Fig. 3(b)). The O atoms have two types of planar locations of adsorption sites with almost equal probability (see Fig. 3(d)): one type is the same as H atoms below, and the other is the same as the sites of the positive-charged solid atoms, due to the electrostatic interaction.

In the second water layer, almost uniform distributions are observed for both H atoms (see Fig. 3(c)) and O atoms (see Fig. 3(e)). This proves the high translational freedom of water molecules in this layer.

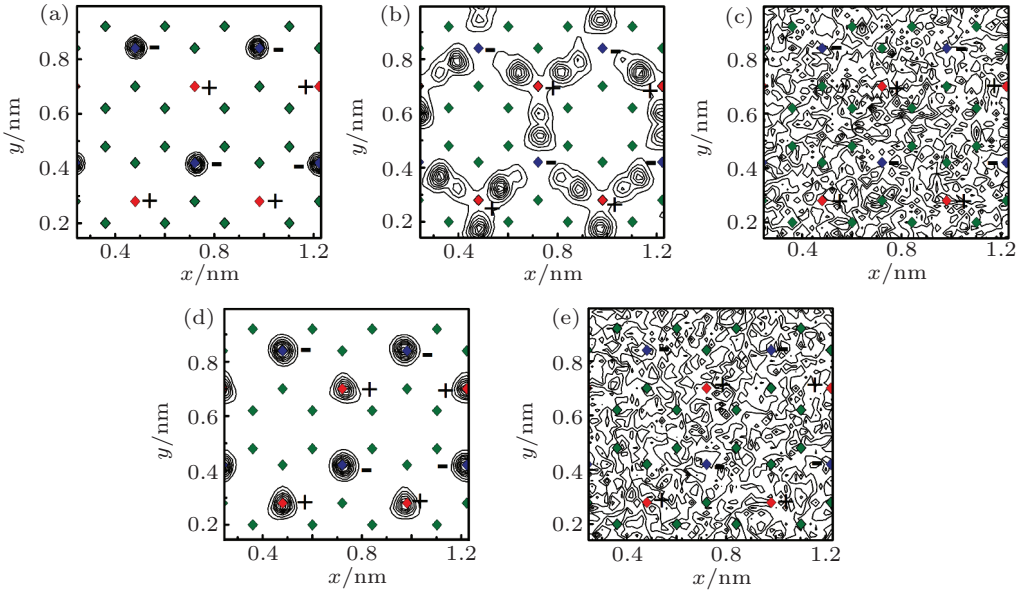


Fig. 3. (color online) The x–y surface density distributions. (a)–(c): the water H atoms within their first, second, and third peaks; (d),(e): the water O atoms within their first and second peaks. Only areas corresponding to 2×1 unit cells are shown. The red, blue, and olive diamonds represent the positive-charged, negative-charged, and neutral solid atoms of the ionic surface, respectively.

3.3. Angular probability density distribution

A more detailed picture of the orientation of water molecules is presented in Fig. 4, which describes the angular distributions of water molecules at four given distances from the surface. The angles are defined between the water OH vectors and the direction normal to the substrate. Based on deep analysis of Fig. 4, we can deduce the following conclusions:

(i) At $z = 0.27$ nm (see Fig. 4(a)), water molecules are predominately oriented with $\theta_{OH} \sim 160$–$180°$. This suggests that water molecules in the first layer show an upright hydrogen-down orientation. The angle between the other OH in the same water molecule and the direction normal to the substrate should be 180°–109.47°=70.53°, corresponding to the unobvious peak at $\theta_{OH} = 72°$. In this case, one H atom of each water molecule is adsorbed by a negative-charged atom of the surface. We note that these results are consistent with the orientation obtained in Figs. 2 and 3.

(ii) At $z = 0.37$ nm (see Fig. 4(b)), the water molecules are predominantly oriented with $\theta_{OH} \sim 0$–$20°$. This suggests that water molecules at this distance mainly show an upright hydrogen-up orientation. There is a peak at $\theta_{OH} = 107°$, close to the H–O–H angle of 109.47°. In this case, the water O atoms are adsorbed by the positive-charged atoms of the surface, but the orientations of the OH groups with a low probability are not as distinct as that exhibited in Fig. 4(a). This orientation cannot be observed in the system of the water monolayer, and explains why there are a considerable number of H atoms in this depletion layer.

(iii) At $z = 0.58$ nm (see Fig. 4(c)), there is a very broad peak at $\theta_{OH} = 85°$. Thus, the OH groups prefer to lie parallel to the surface, but are less oriented, and are slightly affected by the solid surface. This orientation is much more predominant in the system of the water monolayer, and thus water molecules in this monolayer form a two-dimensional ordered structure.

At $z = 1.2$ nm (see Fig. 4(d)), the orientation of water molecules disappears. Therefore, the solid surface has no influence on water molecules at this distance.

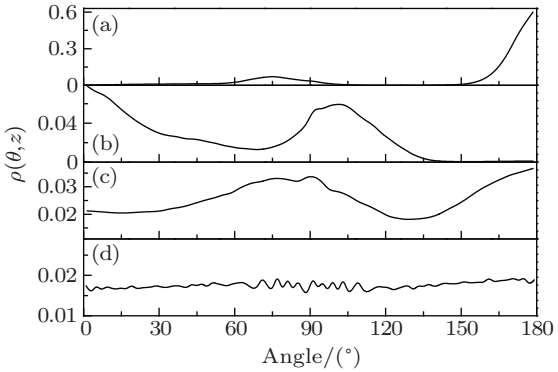


Fig. 4. Angular probability density distributions at (a) $z = 0.27$, (b) 0.37, (c) 0.58, and (d) 1.2 nm, respectively. The probability is normalized by the number of water molecules at any given distance and by a sinusoidal function to correct the angular distribution of a vector in space.

3.4. Hydrogen bonding

The normalized density profile of the hydrogen bonds formed between water molecules was computed as a function of distance from the surface. The geometrical criterion was used here to define the existence of a hydrogen bond such that the O···O distance is less than 0.35 nm, and simultaneously the angle H–O···O is less than 30°.[35] The position of one hydrogen bond is defined as the mid-distance between the hydrogen and oxygen of the two hydrogen bonded molecules. As shown in Fig. 5, the hydrogen bond density profile exhibits two distinct peaks at about 0.30 and 0.62 nm, respectively. Two-dimensional hydrogen bond network is not found in this study, but was observed in thin water film.

The location of the first peak in the hydrogen bond density profile is exactly the same with the location of the first atom density peak for O atoms, and is close to the location of the second atom density peak for H atoms (see Table 1). The density of the hydrogen bonds is 0 at $z < 0.25$ nm. Thus, we can conclude that H atoms for the first peak cannot participate in the formation of hydrogen bonds, which are attracted by the negative-charged atoms of the surface.

Comparing Fig. 5 with Fig. 2, we find that the water molecules within the first layer form hydrogen bonds mainly with the neighboring water molecules in the same monolayer. However, there are considerable hydrogen bonds in the depletion layer. Thus, we infer that water molecules in the first layer could also form hydrogen bonds with those in the subsequent layer. This clearly shows that the two-dimensional hydrogen bond network of the first water layer is disrupted by the next layer. Therefore, it is not surprising that we do not observe a two-dimensional hydrogen bond network.

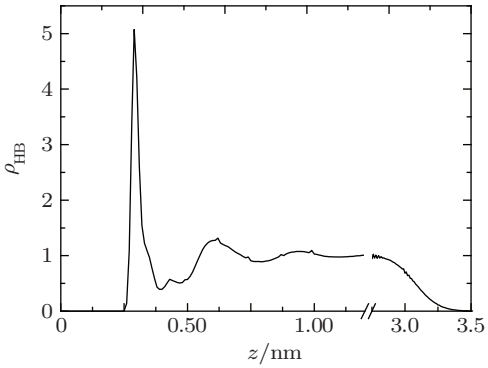


Fig. 5. Normalized density profile of the hydrogen bonds formed between water molecules themselves as a function of distance from the surface.

3.5. Residence probability

To study the dynamic behavior of interfacial water on the ionic surface, we calculated the residence probabilities within different structured layers. Residence probability is defined as the probability of finding one atom/molecule that continuously resides within a specific layer. The more slowly the probability decreases, the longer the atom/molecule resides in the slab considered. We provide the results on the residence probability $P(t)$ of water O atoms within their first two layers and the bulk (see Fig. 6(a)), and H atoms within their first three layers and the bulk (see Fig. 6(b)), respectively. In each case, a slab of thickness 1 Å was considered around the atom density peaks in Fig. 2 (see Table 1).

The results for O and H atoms show a similar qualitative behavior that the decay becomes faster as the distance from the surface increases. In Fig. 6(a), the time for $P(t)$ to decay to $1/e$ is about 42, 0.4, and 0.4 ps for water O atoms in the first two layers and the bulk, respectively. Note that the value of 42 ps for the first layer is about 100 times longer than the value of 0.4 ps for the bulk. In Fig. 6(b), the time for $P(t)$ to decay to $1/e$ is about 109, 1.2, 0.3, and 0.3 ps for water H atoms in the first three layers and the bulk, respectively. The value of 109 ps for the first layer is about 360 times longer than the value of 0.3 ps for the bulk. These results show that water molecules in the first layer exhibit delayed dynamics with relatively long residence times compared with bulk water. The residence time for H atoms in the first layer is much longer than that for O atoms, despite H atoms are much lighter than O atoms. Thus, the adsorption of H atoms is more stable than O atoms. Therefore, the upright hydrogen-down orientation (see Fig. 4(a)) has a higher probability than the upright hydrogen-up orientation (see Fig. 4(b)). Moreover, we deduce that the two-dimensional

hydrogen bond network is disrupted, mainly because the water O atoms in this layer are affected by the subsequent layer and become unstable. We also note that water molecules in the second layer exhibit bulk-like behavior.

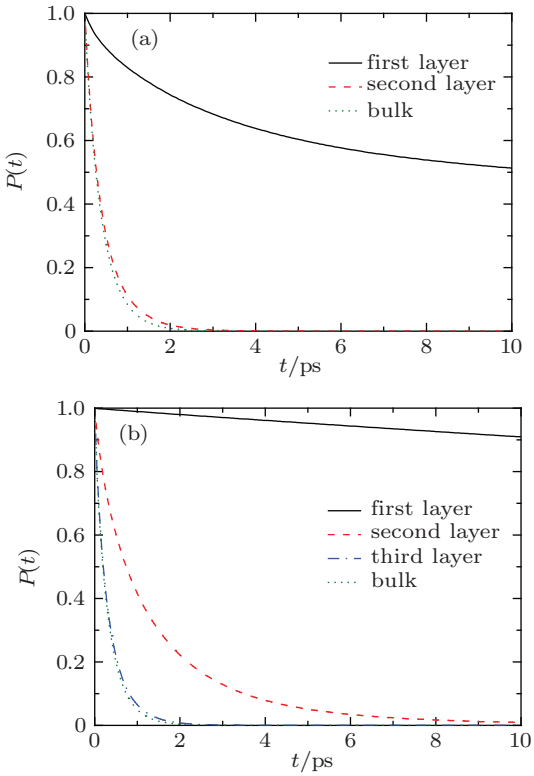


Fig. 6. (color online) (a) Residence probability for water O atoms in their first layer, second layer, and in bulk at $z = 1.2$ nm. (b) Residence probability for water H atoms in their first, second, third layers, and in bulk at $z = 1.2$ nm. The location of each layer is shown in Table 1.

4. Conclusions

In this work, we study the structure and dynamics of water in thick film on the ionic surface via molecular dynamic simulations. We find that there is one dense water monolayer formed at liquid–solid interface. Water molecules within this layer have a higher probability to adopt an upright hydrogen-down orientation with H atoms attracted by surface's negative-charged atoms, and also have a lower probability to show an upright hydrogen-up orientation with O atoms absorbed by surface's positive atoms. Water molecules in this layer form hydrogen bonds mainly with the neighboring water molecules in the same monolayer, but also can form hydrogen bonds with water molecules in the next layer as well, benefitting from a hydrogen-up orientation. These water molecules exhibit delayed dynamics with relatively long residence time compared with bulk water. The residence time for H atoms in the first layer is much longer than that for O atoms. Thus, the adsorption of H atoms is more stable than that of O atoms. Water molecules in the subsequent layer exhibit almost bulk-like behavior. However, the two-dimensional ordered structure of the first water layer observed in thin water film is disrupted, mainly due to the water O atoms in this layer, which are affected by the subsequent layer and become unstable.

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