Ordered water monolayer on ionic model substrates studied by molecular dynamics simulations postprint

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Abstract

The molecular behavior of interfacial water at solid/liquid interfaces is of fundamental significance in diverse technological and scientific contexts, and has therefore attracted extensive attention. On certain surfaces, water monolayers may exhibit ordered structural features, which can give rise to novel wetting phenomena. In this article, based on molecular dynamics simulations, we perform a detailed structural analysis of ordered water monolayers on ionic model surfaces with graphene-like hexagonal lattices under various charges and unit cell sizes. We analyze the water density profiles and potential of mean force, which underlie the distinctive hexagonal ordered water structures near the solid surface. The number of hydrogen bonds in the ordered water monolayer near the solid surface is systematically investigated.

Full Text

Preamble

Ordered Water Monolayer on Ionic Model Substrates Studied by Molecular Dynamics Simulations

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The molecular behaviors of interfacial water molecules at solid/liquid interfaces are of fundamental significance across diverse technical and scientific contexts, and have therefore drawn extensive attention. On certain surfaces, water monolayers may exhibit ordered features that result in novel wetting phenomena. In this article, based on molecular dynamics simulations, we present a detailed structural analysis of ordered water monolayers on ionic model surfaces with graphene-like hexagonal lattices under various charge states and unit cell sizes. We carefully examine water density profiles and potentials of mean force, which govern the formation of special hexagonal ordered water structures near solid surfaces. The hydrogen bond count within the ordered water monolayer near the solid surface is also investigated in detail.

Keywords: Ordered water monolayer, Hydrogen bond, Molecular dynamics simulations
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Introduction

The complex behaviors of interfacial water [1–9] are of great importance in research fields including protein stability and folding [10], molecular self-assembly [11], manipulation of biomolecules [12], and rearrangement of immunodeficiency virus [13], among others. These phenomena have attracted extensive attention [5–7, 14] because the molecular structure and dynamics of interfacial water molecules typically differ from bulk properties [15]. Interfacial water molecules play crucial roles in biophysical processes. For example, water effectively catalyzes the chiral interconversion of thalidomide [16], and dewetting transitions promote amyloid fibril formation [17].

Due to interactions between interfacial water and hydrophilic solid substrates, the diffusion of interfacial water [18] is slower and the lifetime of hydrogen bonds [19] is longer than in bulk water, as confirmed by experimental studies [20–22]. Recently, the ordered structure of interfacial water confined in one or two dimensions has been investigated extensively through both experimental and theoretical approaches.

In 2009, we reported a liquid water droplet on a water monolayer, termed “ordered water monolayer does not completely wet water,” on a model surface at room temperature [24]. Similar phenomena were subsequently observed in several experiments on sapphire c-plane electrolyte surfaces [25] and on self-assembled monolayer (SAM) surfaces with -COOH terminals [26, 27]. Additionally, theoretical simulations have found comparable phenomena on hydroxylated metal oxide surfaces of Al_2O_3 and SiO_2 [4], talc [28], and Pt(100) metal surfaces [29]. We also explored the effects of surface morphology [30] and the critical length of charge dipoles on the solid surface [31] on interfacial water structures and surface wetting behaviors.

In this article, based on molecular dynamics simulations, we investigate the structure and hydrogen bonding to provide detailed information about ordered water monolayers on ionic model surfaces with graphene-like hexagonal lattices under various charges and unit cell sizes. The article is organized as follows: Section III.A describes the ordered structure of the water monolayer near the surface. Section III.B examines water density and potential of mean force (PMF) [28]. Section III.C calculates the number of hydrogen bonds to demonstrate the stable formation of hydrogen bond networks within the ordered water monolayer. Finally, a brief conclusion is presented in the last section.

Simulation Details

We configured a hexagonal solid lattice with 1664 solid atoms, where the neighbor bond length l is described in Fig. 1 [Figure 1: see original paper], consistent with our previous studies [24, 32]. The initial systems for molecular dynamics simulations contained a water layer approximately 4.0 nm thick on the ionic model surface, where positive and negative charges were located diagonally in neighboring hexagons. Previous work demonstrated that such charge distributions significantly influence water molecule flux in nanotubes [12, 32]. All simulations were performed at $T = 300$ K (NVT ensemble) using Gromacs 4.5.4 [34] with a time step of 1.0 fs. The Lennard-Jones parameters for the solid atoms were $\varepsilon_{ss} = 0.105$ kcal/mol and $\sigma_{ss} = 33.343$ Å, and the SPC/E water model [35] was employed. The particle-mesh Ewald method [13] with a real-space cutoff of 1 nm was adopted for long-range electrostatic interactions, while a 10 Å cutoff was used for van der Waals interactions. Periodic boundary conditions were applied in all three directions. Each system was simulated for 4 ns, with the last 2 ns of data used for analysis.

Two series of simulations were performed to investigate ordered water monolayer formation on the hexagonal surface. In the first series, the charge q on solid atoms was varied from 0.6 e to 1.0 e at intervals of 0.1 e, with 5252 water molecules in simulation boxes of volume $6.395\ \text{nm} \times 6.816\ \text{nm} \times 20.110$ nm. The neighboring bond length of solid atoms was held constant at $l = 0.142$ nm. In the second series, the bond length l was set to 0.120 nm, 0.130 nm, 0.142 nm, 0.150 nm, and 0.160 nm, with $q = 0.8e$. The water layer thickness was maintained at approximately 4.0 nm, with water molecule counts of 3525, 4314, 5252, 5721, and 6564 in simulation boxes of 5.404 nm × 5.760 nm × 20.110 nm, $5.854\ \text{nm} \times 6.240\ \text{nm} \times 20.110$ nm, $6.395\ \text{nm} \times 6.816\ \text{nm} \times 20.110$ nm, $6.755\ \text{nm} \times 7.20$ nm × 20.110 nm, and 7.680 nm × 20.110 nm, respectively.

Results and Discussions

A. Structure Analysis of the Water Monolayer

To study the structure of water molecules in the monolayer on the solid surface, we introduced two angle parameters θ and ϕ as illustrated in Figs. 2(c) and 2(d) [Figure 2: see original paper]. The angle θ is defined as the angle between a water molecule' s dipole and the z axis, while ϕ is the angle formed between the projection of a water dipole onto the x-y plane and a crystallographic direction

[30]. The water monolayer is defined as water molecules in the first layer adjacent to the solid surface with an average thickness of 0.4 nm, consistent with our previous work [24] and with experimentally observable monolayers [36]. The second layer is defined as water molecules with an average thickness of 0.4 nm above the water monolayer.

As shown in Fig. 2(e) [Figure 2: see original paper], two peaks in the angle θ distribution confirm the existence of two distinct states, designated as state 1 and state 2 and depicted in Figs. 2(a) and 2(b). The left peaks at $\theta \approx 60^\circ$ represent state 1, where oxygen atoms are attracted by positively charged atoms, while the right peaks at $\theta \approx 120^\circ$ represent state 2, where O-H bonds point toward negatively charged atoms. Figure 2(f) shows the normalized probability distributions of angle ϕ with three peaks at $\phi \approx 0^\circ$, 120°, and 240°, demonstrating that water molecules in the monolayer can form a two-dimensional hexagonal configuration (Fig. 2(d)), consistent with our previous findings [24].

As q increases from 0.6 e to 1.0 e, all peaks in Figs. 2(e) and 2(f) become more pronounced, indicating that water molecules in the monolayer become increasingly ordered due to stronger binding by surface charges. However, the peaks vary significantly with bond length l. At $l = 0.142$ nm and $q = 0.8e$, the peaks are highest (Figs. 2(g) and 2(h)), corresponding to the most ordered water monolayer. As l deviates from 0.142 nm, the ordered hexagonal water monolayer gradually disappears. These results demonstrate that the ordered water structure depends strongly on both surface charge and appropriate unit cell size.

B. Water Density Distribution Profiles and PMF Curves

Figures 3(a) and 3(b) [Figure 3: see original paper] show water density as a function of z for different q and l values, where the reference $z = 0$ corresponds to the solid surface. All curves exhibit two peaks located at $z = 0.3$ nm and $z = 0.6$ nm. Due to strong charge binding at the surface, a pronounced density peak forms near the solid surface, creating the monolayer. Density increases with charge, reaching maximum values at $q = 0.9e$ and $1.0e$. With increasing cell size, density initially increases until $l = 0.142$ nm, beyond which it decreases, indicating formation and subsequent breakdown of the ordered structure.

Density relates to the potential of mean force (PMF), $F(z)$, through the expression $F(z) = -k_B T \ln(\rho(z)/\rho_w)$, where k_B is the Boltzmann constant and $\rho_w = 33$ nm^{-3} is the number density of bulk water. Here, $F(z)$ represents the free energy required to bring a water molecule from the bulk to a distance z from the solid surface. Figures 3(c) and 3(d) [Figure 3: see original paper] show PMF curves, with each curve displaying two valleys at $z = 0.3$ nm and $z = 0.6$ nm that account for surface adsorption. The minimum PMF at $z = 0.3$ nm is approximately -0.9 kcal/mol for $q \geq 0.8e$ and $l = 0.142$ nm. The PMF reveals the adsorption interaction strength of solid surfaces. Adsorption increases with charge, displaying a wide range of binding strengths that attract water molecules and form the ordered monolayer, which differs from bulk water behavior. Appropriate cell size is crucial for optimal adsorption interaction and monolayer formation. These PMF results indicate that water molecule distribution and ordered water monolayer formation are significantly affected by both charge and cell size.

C. Hydrogen Bonds in the Water Monolayer

The ordered water monolayer influences hydrogen bond formation among interfacial water molecules. We calculated the average number of hydrogen bonds per water molecule to neighboring water molecules within the same monolayer (“in the monolayer” H-bonds) and to water molecules in the second layer (“to the second layer” H-bonds), as shown in Fig. 4 [Figure 4: see original paper]. The geometric criterion for hydrogen bond existence between two water molecules requires an O-O distance less than 3.5 Å and simultaneously an H-O$\cdots$O angle less than 30° [37].

In Fig. 4(a) [Figure 4: see original paper], the number of hydrogen bonds within the monolayer increases while the number between the monolayer and second layer decreases as charge increases. Their sum remains at approximately 2.9 when $q \geq 0.8e$, approaching 3—the maximum number of hydrogen bonds any water molecule can form in the monolayer [24]. As calculated in Sec. III.B, the interaction energy between the monolayer and charged surface strengthens with increasing charge. Water molecules bound in the monolayer more readily form hydrogen bonds with neighboring molecules in the same layer. Competition exists between “in the monolayer” and “to the second layer” hydrogen bond formation; the increase in the former leads to a decrease in the latter due to weaker interactions between monolayer and second-layer water molecules.

In Fig. 4(b) [Figure 4: see original paper], when $l = 0.142$ nm and $q = 0.8e$, the average number of hydrogen bonds among water molecules in the monolayer is larger than for other configurations, while the number of hydrogen bonds between the monolayer and second layer is smallest. The total number of hydrogen bonds per water molecule in the monolayer is also approximately 3. Thus, large charge and appropriate unit cell size ($l = 0.142$ nm) cause water molecules in the monolayer to preferentially form hydrogen bonds within the water monolayer rather than with water molecules in the second layer. Clearly, unit cell size is also a key factor in hydrogen bond formation near the solid surface.

Conclusion

In summary, we have studied the structure, free energy properties, and hydrogen bonds of ordered water monolayers on ionic model surfaces with graphene-like hexagonal lattices under different charges and unit cell sizes using molecular dynamics simulations. The results indicate that both charge and unit cell size significantly affect water molecular behaviors in the monolayer, including molecular configurations and hydrogen bond networks. The charged surface exhibits strong adhesive interactions, as characterized by water density profiles and potentials of mean force. We have also carefully investigated the number of hydrogen bonds in the ordered water monolayer near the solid surface. These findings are expected to contribute to a deeper understanding of ordered water monolayers on surfaces.

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