Electric-Field Induced Restructuring of Water at a Platinum-Water Interface: A Molecular Dynamics Computer Simulation

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We performed four molecular dynamics simulations of water lamina embedded between two Pt(100) walls. The Pt surfaces were uncharged in the first simulation. In the other three simulations the charge densities (σ) had the values of 8.85, 26.55, and 35.4 $\mu C/cm^2$ on the left wall and values opposite in sign on the right wall. When $\sigma = 0$ or 8.85 $\mu C/cm^2$, the adsorbed water layer had all its oxygens in the atop position and every surface site was covered by a water molecule. When $\sigma = 26.55$ $\mu C/cm^2$, the adsorbed water layer split into a bilayer. At $\sigma = 35.4$ $\mu C/cm^2$ water between the two Pt(100) surfaces freezes into a crystal structure with domains of a distorted cubic ice.

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A detailed molecular level description of structure and dynamics of water next to metallic surfaces is of fundamental importance for electrochemistry, catalysis, and corrosion studies. The information on the structure of a water monolayer at an interface with a metal can be obtained using different experimental techniques [1,2]. In the case of a bulk water/metal interface, some information on the structural properties of water at the interface is available. Thus, very recently Toney *et al.* [3] used *in situ* x-ray scattering to measure the water density profile perpendicular to a Ag(111) surface. From the experimental data Toney *et al.* [3] concluded that the layer of water next to the metal has a far greater density than that of bulk water. This implies that the hydrogen-bonding network is disrupted in the water layer next to the metal. Such a conclusion contradicts the results from computer simulations on water next to the metal surface [4–8]. Nevertheless, one should realize that the metal surface in the experiment of Toney *et al.* [3] was charged, while many of the simulations were performed with uncharged surfaces. Even when the simulations were performed with charged metal surfaces [8], the surface charge densities were below the charge density reported in the experiment of Toney *et al.* ($\sim$25 $\mu C/cm^2$). It is therefore important to determine how the variation in the surface charge density influences the structure of water next to the surface. To find out about this influence we performed four molecular dynamics computer simulations of water enclosed between two Pt(100) surfaces separated by a distance of 40 Å. The surface charge densities (σ) in these simulations were taken to be 0, 8.85, 26.55, and 35.4 $\mu C/cm^2$ on the left surface and correspondingly opposite values on the right surface. The external electric fields produced by these charges had the corresponding values of 0, 1, 3, and 4 V/Å.

Our system in the simulations consisted of 512 SPC/E [9] water molecules confined within two Pt(100) surfaces. The potential of interaction between the Pt surface and the water molecules used in the simulations is the one developed in our laboratory and described in Refs. [5] and [6]. The unit cell in the present simulations is a parallelepiped with the square base of dimensions $L_x = L_y = 19.6$ Å. The distance between the surfaces was chosen to achieve, in the simulation with the uncharged surfaces, a density of water close to 1 g/cm^3 in the middle of the box. Periodic boundary conditions were imposed in the (x, y) plane. Molecular dynamics was performed using the Verlet algorithm and the SHAKE routine. A time step of 2.5 fs was adopted. Velocities were scaled occasionally to maintain the temperature around 300 K. Long range forces were taken into account using the scheme developed by Aloisi *et al.* [10]. We observed that the equilibration runs took more time when a larger surface charge density was used. Thus, with uncharged surfaces we were satisfied with a total run of 100 ps. When the surface charge density had a value of 8.85 $\mu C/cm^2$, the run was extended to 250 ps. For larger charge densities the total length of the run was extended to 500 ps. The data were collected for the last 50 ps of the first run and the last 100 ps for the next three runs.

The oxygen and hydrogen density profiles obtained from our runs are displayed in Figs. 1(a)–1(d). The density profiles from the run with no surface charge are displayed in Fig. 1(a) and are similar to the ones from Refs. [4] and [5]. When the surface is charged with a surface charge density of 8.85 $\mu C/cm^2$, very small changes are observed in the oxygen density profile, while the change in the hydrogen density profile is more pronounced [see Fig. 1(b)]. The observed changes in the density profiles indicate that a reorientation of water molecules under the influence of the external field has occurred. The oxygen and hydrogen density profiles from our simulations with $\sigma = 8.85$ $\mu C/cm^2$ look very similar to the ones obtained in the simulations of Nagy and Heinzinger [8]. As we can see from Fig. 1(c), the oxygen and hydrogen density profiles undergo a substantial change when the surface charge density is increased to the value of $\sigma = 26.55$ $\mu C/cm^2$, which is close to the surface charge

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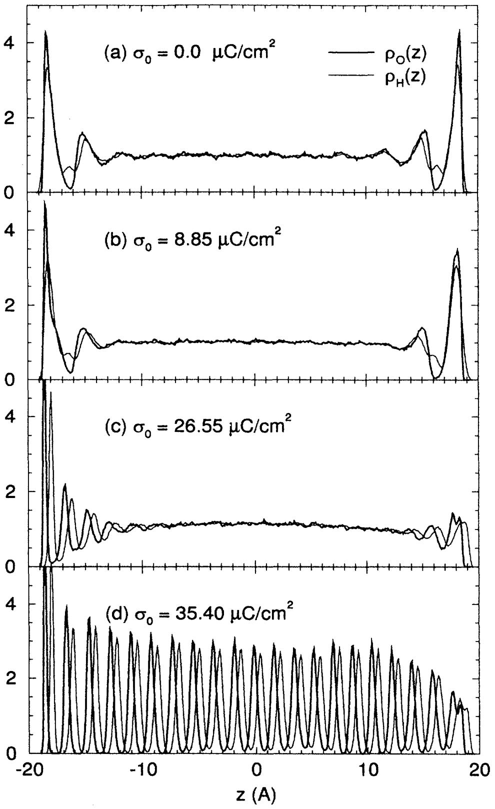

FIG. 1. Normalized density profiles of oxygen and hydrogen atoms for the systems with (a) no surface charge density on the Pt surface, (b) surface charge density of 8.85 μC/cm^2, (c) 26.55 μC/cm^2, and (d) 35.40 μC/cm^2. The positively charged surface is on the left, the negatively charged surface is on the right.

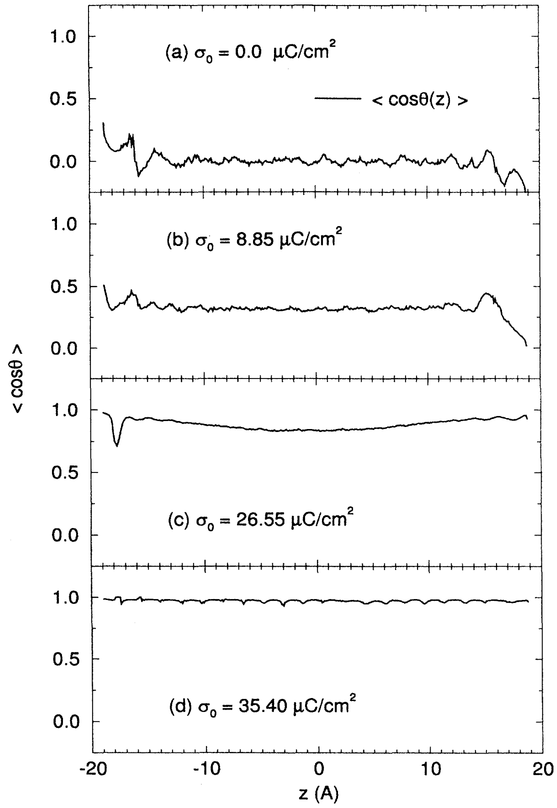

FIG. 2. Average degree of polarization (cosine of the angle between the dipole and the positive direction of the z axis) of the water molecules as a function of z. The panels correspond to the same systems as in Fig. 1.

density in the experiment of Toney *et al.* [3]. Particularly, we observe that at the positively charged surface more structure of water is developed, where four distinct layers of water can be now seen. (Note that to compare the structure of water next to the surface obtained from our simulations and from the experiment of Toney *et al.* [3] one has to look at the structure of water next to the negative plate charged to a density of –8.85 μC/cm^2, and at water next to the positive plate charged to a density of 26.55 μC/cm^2, since the charge densities in the experiment were estimated to be ~ -10 and 25 μC/cm^2.)

To see how the orientational properties of water molecules change with the increase of surface charge density we display in Figs. 2(a)–2(d) the profile of the average cosine of the angle between the dipole moment of the water molecule and the z axis (axis perpendicular to the surface). Although water dipoles display an orientational preference when water molecules are situated next to the uncharged surface (more details of this preference and its implications are given in Refs. [5–7]), this preference disappears in the middle of the lamina. In the case of charged surfaces the water dipoles in the middle of the lamina also display an orientational preference due to the dipole alignment with the external electric field. Such an alignment becomes rather pronounced (~80%) when the surface charge density reaches the value of 26.55 μC/cm^2. Figures 1(c) and 2(c) clearly show that substantial structural changes occur in the water lamina when it is enclosed between charged surfaces and when the surface charge density is close to the experimental one.

To better understand the changes in the structure of water next to the surface we considered the stroboscopic pictures [Figs. 3(a)–3(d)] of water oxygens in the layer next to the uncharged or positively charged surfaces. The pictures are obtained by plotting a dot every 1 ps, representing the (x,y) position of an oxygen atom that belongs to the water molecule from the first layer. For the uncharged surface we observed [Fig. 3(a)] that all oxygens belonging to the first layer are situated in the atop positions. The same is observed when the surface charge density is 8.85 μC/cm^2 [Fig. 3(b)]. From Fig. 3(b) we also observe that the motion of water in the adsorbed layer has more diffusional character compared to the motion of the same layer when the surface was uncharged. This indicates that some structural changes may happen when the surface charge density is increased. And indeed,

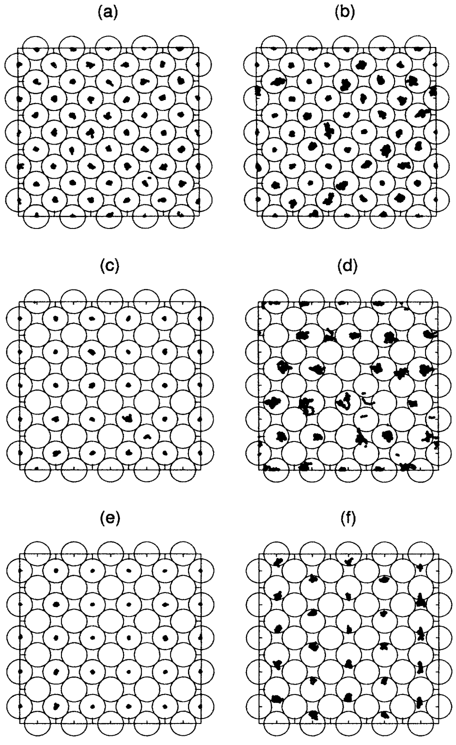

Fig. 3. Projections of positions of oxygen atoms on the (x, y) plane (plane parallel to the Pt surface) for (a) the layer of water adsorbed on the uncharged Pt(100) surface, (b) the layer of water adsorbed on the Pt(100) surface with the surface charge density of 8.85 $\mu\mathrm{C/cm}^2$, (c) the first layer of water next to the Pt(100) surface charged to a surface charge density of 26.55 $\mu\mathrm{C/cm}^2$, (d) the second layer of water next to the Pt(100) surface charged to a surface charge density of 26.55 $\mu\mathrm{C/cm}^2$, (e) the first layer of water next to the Pt(100) surface charged to a surface charge density of 35.40 $\mu\mathrm{C/cm}^2$, and (f) the second layer of water next to the Pt(100) surface charged to a surface charge density of 35.40 $\mu\mathrm{C/cm}^2$.

when the surface charge density reaches the value of 26.55 $\mu\mathrm{C/cm}^2$ only half of the Pt atoms were covered by oxygens in the atop positions [Fig. 3(c)].

To understand what happened to the rest of the atop water molecules, consider the stroboscopic picture displayed in Fig. 3(d). It shows that the second half of the water molecules that occupied the atop positions at lower surface charge densities moved to a second layer. Thus, at some surface charge density, the adsorbed water layer splits into a bilayer. This bilayer is not the one that was proposed to explain the structure of water in high-vacuum experiments [2] and not the one we postulated to exist next to an uncharged Pt surface [6,7]. When the Pt surface is uncharged, the water bilayer is a bilayer in the orientational sense only, with the orientational structure of water at the interface somewhat characteristic of the hexagonal ice-I [6,7]. The bilayer therefore contains a first orientational sublayer with dipoles in "flip up" position, while a second sublayer has both flip up and "flop down" dipoles. From Fig. 2(c) we see that the dipoles of the water molecules in the second layer are oriented along the electric field and therefore are all flip up. The oxygen positions in the second layer from our third simulation also show a movement from the atop sites to the interstitial sites, which oxygens have to occupy to create a bilayer with a structure similar to a cubic ice-I structure. In Fig. 1(c) we also noted that the distance between the adsorbed layer and the second layer is ~ 1.7 Å. All these observations indicate that in our third simulation a restructuring of water towards a cubic ice-I form takes place at the charged interface.

The charge density of 26.55 $\mu\mathrm{C/cm}^2$ seems to be producing a field that is not strong enough to result in a crystallization of water in the whole volume of the lamina. Therefore, one would like to ask what will happen if we increase the value of the external field acting on water? Will the crystallization occur in the whole volume (in spite of the high temperature and high density of water)? After all, it was recently shown by simulations that the application of an electric field to the bulk supercooled water at density ~ 0.94 g/cm^3 produced cubic ice [11]. To answer the above-posed questions we performed a simulation where we increased the surface charge density to 35.4 $\mu\mathrm{C/cm}^2$. The results from this simulation are displayed in Figs. 1(d), 2(d), 3(e), 3(f), 4(a), and 4(b). Figure 1(d) shows that indeed the layering of water characteristic for solid state has occurred. Figure 2(d) shows that the dipoles of water molecules in the lamina are aligned completely with the external electric field. Figures 3(e) and 3(f) show that the bilayer of water next to the positively charged plate is rather rigid. Figure 4 shows that the whole water lamina is not crystallized into perfect cubic ice-I, although domains of a strained cubic ice-I structure are clearly visible in the pictures. [For comparison, we present a snapshot of a perfect cubic ice in Fig. 4(c).]

In summary, based on the results of our simulations of water next to a charged Pt surface we conclude that no dramatic increase of the water density and a destruction

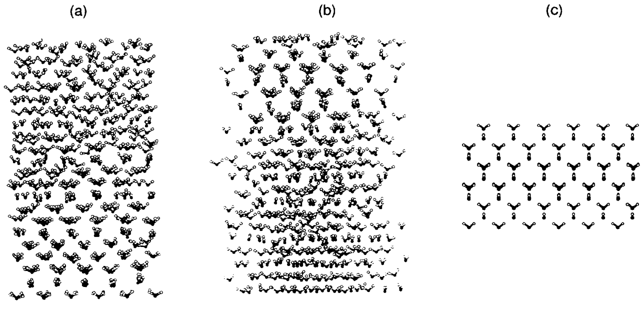

FIG. 4. (a) A snapshot from a simulation where water is placed between two Pt(100) surfaces which are charged to a surface charge density of 35.40 $\mu\mathrm{C/cm}^2$. (b) The same snapshot but from a different angle. (c) A snapshot representing the structure of an ideal cubic ice-I.

of the hydrogen-bonded network similar to the one proposed by Toney *et al.* is observed in our simulations. On the contrary, the hydrogen-bonded network not only survives when the field is turned on, but is responsible for the structural changes observed in the simulations. When the homogeneous electric field is turned on, water, in order to adapt to a new environment, restructures itself and eventually crystallizes into domains of strained cubic ice. This way the hydrogen-bonded network can remain intact and the orientational polarization of water can be aligned along the field. The imperfect structure of ice is due to the presence of a specific Pt surface (which is incommensurate to the cubic ice structure), which is the wrong density for ice and high temperature.

It is appropriate to mention here that the experimental measurements of Toney *et al.* were performed in a 0.1 M solution of NaF. According to Toney *et al.* the ions do not significantly adsorb on the metal and the interfacial ion concentration is small; nevertheless, the external field in experiments is screened by the ions. This fact makes it difficult to perform a direct comparison between the experiment and our present simulations. Ions may also contribute to the x-ray scattering amplitude, thus complicating the picture even more.

An indication that an electric field may produce a layering of water between microscopically separated plates was given previously in the Monte Carlo simulation of Aloisi *et al.* [10]. The occurrence of a phase transition in water between two charged plates due to the buildup of the electric field was also demonstrated in the molecular dynamics simulation of Watanabe, Brodsky, and Reinhardt [12]. But in the latter simulation the metallic plates were very close to each other, so that all the water between the plates was interfacial water and was therefore in the liquid crystal state even in the absence of the field. The phase transition occurring under the influence of the external field was therefore a transition from one form of a liquid crystal state to another. A layering transition in a waterlike liquid situated next to a charged surface was also predicted by Torrie, Kusalik, and Patey [13], who solved reference hypernetted chain equations for a model of hard spheres with embedded dipoles and quadrupoles situated next to a curved charged surface. But while Torrie, Kusalik, and Patey observed that the orientational structure of their liquid is not changed under the influence of the field, our simulations indicate that there is a dramatic change in the orientational ordering of water when the external field is increased.

Our results indicate that under the influence of the external electric field the transition of liquid water to crystalline water occurs at some value of surface charge density which is between 26.55 and 35.4 $\mu\mathrm{C/cm}^2$. The precise value may depend on the model of water used, treatment of long range forces, and other details of the calculations. Our present simulations were done using a rigid water model. The way in which the flexibility of the water molecule can influence the qualitative results is unknown. The influence of the long range forces on the quantitative outcome is rather large. Thus in our preliminary calculations without long range correction we obtained the critical charge value to be somewhere close to 17.7 $\mu\mathrm{C/cm}^2$. Nevertheless, our present results along with the results obtained from previous computer simulations [10,12,14], from theory [13], and, most importantly, from the experiments [15–17] strongly suggest that the external electric field can trigger a phase transition occurring in water next to charged surfaces. The existence of such a transition may have important consequences in many areas of research.

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