I. INTRODUCTION

In recent surface force balance (SFB) experiments,1–3 purified water or hydration water in aqueous salt solutions has been found to be fluidic even under extreme confinement ($D < 1.0$ nm) between two mica surfaces. This subject can be traced back to the pioneering work on the surface forces between ionized mica surfaces immersed in dense electrolytes,4,5 and is of significant importance in relation to broad disciplines such as nanofluidics, transport phenomena in biological systems (ion channels, cell membranes, etc.), biolubrication, and clay swelling in geological science. A different experimental strategy, also using the surface force apparatus (SFA) with atomically smooth mica surfaces as confining walls, found very high shear response and extremely long relaxation time for $D < 0.6$ nm water film (corresponding to 1–2 monolayer (ML) of water).6

Our recent molecular dynamics (MD) simulations7 using a realistic molecular model for water-ion-mica complex8 showed that the fluidity of hydration water is sustained down to $D = 0.92$ nm (about three hydration layers), though the shear viscosity in this case is roughly two orders of magnitude higher than the bulk value, the same as that estimated in SFB experiments.2 In this paper we probe the origins of the fluidity for $D = 0.92$ nm and up and the high shear enhancement for $D ~ 0.6$ nm water films from the structure analysis of the confined hydration water. Recent molecular simulations show that the water film confined between two hydrophobic surfaces of 1–2 ML water is in a liquid phase at ambient conditions.9 Other studies showed that for explicit atomic walls, water films can readily form monolayer ice or bilayer ice depending on the plate separations.10,11 Thus, it would be of great interest to probe the hydration structure of water and the associated hydration shell of hydrated ions confined between two mica surfaces that are highly hydrophilic in nature. This study is also directly related to the understanding of ion transport and electro-osmotic phenomena in nanofluidic channels.12

II. SIMULATION METHODOLOGY

We select the real mica surfaces as the confining walls that were obtained from ab initio relaxations.13 The mica surface has a mineral structure of 2:1 layered dioctahedral (hydroxyl-) aluminosilicate with the muscovite formula of $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$.14,15 One mica layer consists of one octahedral aluminum sheet sandwiched by two tetrahedral siliccon sheets. Due to the substitution of Si by Al in tetrahedral sheet with a ratio of Al:Si = 1:3, the mica (001) surface has a relatively high negative charge density (2.1×10$^{14}$ e/cm$^2$) which is balanced by potassium ions (K$^+$. In MD simulations, we use the TIP4P (Ref. 15) rigid water model and the TIP4P water-ion-clay potentials developed by Boek et al.,5 which have been proven to be successful in predicting clay swelling. A detailed MD simulation approach has been given elsewhere.7 Since we are interested in high concentration salt solutions, under nanometer confinements most of the K$^+$ ions will remain on mica surfaces to balance the negative surface charges. Thus, any hydration effects are closely related to the hydration of K$^+$ ions.4,16 Similar to the pressure control in the Monte Carlo simulations for the clay swelling,8 we perform MD simulations in the isothermal-isobaric (NpT) ensemble at 298 K, in which a pressure $p$ of 1 bar is applied perpendicular to the mica surface. It should be noted that the pressure parallel to the mica surface may be quite different from the normal pressure due to the strong anisotropy of the confinement system. However, we do not calculate and control the lateral pressure since the structure and density of the confined fluid is not sensitive to the pressure.17 (see below). The thickness of the hydration film, $D$, is defined as the
equilibrium separation between the basal oxygen planes on the two mica surfaces.

III. RESULTS

A. The density distribution and water O–O radial distribution function

Figure 1 shows the density distributions of water oxygen and potassium ions for different hydration water films as a function of distance $z$ from the lower mica surface. For the hydration layers $D=2.44, 1.65$, and 0.92 nm, which correspond to 1152, 768, and 384 water molecules under confinement, the water density distributions have essentially the same features in the vicinity of the mica surfaces: there is a small adsorbed peak (A) followed by the first (B) and second (C) hydration peaks. For the largest hydration film [Fig. 1(a)], beyond 10 Å the water density approaches the bulk value. This density oscillation compares remarkably well with the x-ray reflectivity experimental results focusing on the water structure adjacent to one single surface, though the second hydration peak from the MD simulation is a little higher than the x-ray result. This agreement can be seen even for the $D=1.65$ nm hydration layer [Fig. 1(b)]. The small shift of the MD curves relative to the x-ray result may come either from the omission of long-range interactions from the clay substrate in the current model or from the different definition of the O basal plane in the experiment. For the $D=0.92$ nm water film [Fig. 1(c)] the water O density distribution presents three well-defined hydration peaks, with the minima substantially greater than zero.

Figure 2 displays the water oxygen-oxygen two-dimensional (2D) in-plane radial distribution functions $g(r)$ for different hydration layers. These lateral distribution functions correspond to the different density peaks shown in Fig. 1. In Fig. 2(a), the $g(r)$ at the adsorbed peak (A) coincides with the radial distribution of ditrigonal cavities of the mica surface, indicating that each adsorbed water molecule occupies one such ditrigonal cavity. For the hydration films of $D=0.92–2.44$ nm, the radial distribution functions at the first hydration peak (B) [Fig. 2(b)] begin to exhibit some disorder, which is characteristic of the liquid phase. The liquid structure becomes more evident from the $g(r)$ at the second hydration peak (C), but with much higher density [Fig. 2(c)]. For the water films of $D=1.65$ and 2.44 nm the $g(r)$ at the damped peak (E) is already quite close to the radial distribution function of bulk water.

To investigate the water structures under further confinement, we perform 16 MD runs with water contents varying from 372 to 192 water molecules. This is done in steps of 12 molecules. The last case corresponds to the water content of monolayer ice adsorbed on a single mica surface. We find that the three hydration peaks gradually collapse into two hydration peaks when the water contents decrease from 372 to 300 water molecules. For the two-layer films, there always exist nonzero density minima until the water content decreases to the last 192 water molecules, giving rise to a surface separation of $D=0.61$ nm. In this case, the bilayer liquid phase transforms into a bilayer ice with each layer consisting of one adsorbed layer and one hydration layer, as shown in...
the thickest hydration layer.

We estimate the effective volume occupied by the water molecules under confinement versus the hydration layer thickness. We find that the density of hydration water and the 2D diffusion constant of water molecules decrease much more significantly for the thicker water films and begins to decrease after the confined hydration water remains approximately at the same density. The drop in the 2D diffusion constant is much larger from the ordered structure shown in Fig. 4 than from the liquid phase to the bilayer ice. The mechanism of the transition from the liquid phase to the bilayer ice is still under investigation, but we note that for the water confined between hydrophobic walls, this transition is of first order.\(^{10}\)

**B. The density and diffusion of confined water**

Figure 3 shows the variations of the effective density of hydration water and the 2D diffusion constant of water molecules under confinement versus the hydration layer thickness. We estimate the effective volume occupied by the water molecules as \(V = (D - D_{\text{excl}})A\), where \(A\) is the lateral surface area and \(D_{\text{excl}}\) is the excluded distance due to the presence of the mica surface and potassium ions. We calculate \(D_{\text{excl}}\) from the thickest hydration layer (\(D = 2.44\) nm) and find \(D_{\text{excl}} = 0.122\) nm, which corresponds to the starting points of the density distributions of water oxygen in all cases in Fig. 1. Unexpectedly, as shown in Fig. 3, we find that the density of the confined hydration water remains approximately at the bulk value for the thicker water films and begins to decrease at \(D = 0.92\) nm. The drop of the diffusion constant is much more significant (about two orders of magnitude), as we have observed before.\(^{7}\)

Further increase in confinement leads to further decrease in density until the bilayer liquid phase is reached. The variation of density in the last stage sees a dramatic drop to the bilayer ice, whose density is much lower than that of ordinary ice \(I_h (\approx 0.9\) g/cm\(^3\)). This is due to the specific hydrogen-bonding network formed in hydration water, which is quite different from the tetrahedral hydrogen-bonding in ice \(I_h\) (see below). The similar trend of the variation of the diffusion constant of water is also shown in the inset of Fig. 3.

It has been suggested that confinement is equivalent to some pressure increase due to the long-range wall attractions to the solvent molecules,\(^{17}\) which promotes the melting of ice.\(^{1}\) Here, we see that an equivalent larger pressure of 150 bars (Ref. 17) applied to the hydration water films does not yield any significant changes either in the density or diffusion constant of water molecules (Fig. 3). The reason seems simple: water is largely an incompressible liquid in a broad range of pressures,\(^{20}\) which is quite different from the nonpolar organic liquids.\(^{17}\)

**C. The hydration shell structure and hydrogen bonding**

We now further consider the hydration shell structure of potassium ions and the hydrogen-bonding structure. In Fig. 1, all the distribution curves show that K\(^+\) peaks are located between the adsorbed and the first hydration peaks, suggesting that potassium ions are still attached to the mica clay surfaces and are only partially hydrated. This is consistent with Monte Carlo computer simulation results for the clay swelling of K-smectite, a mica-like clay structure.\(^{8}\) Figure 4 shows the equilibrium molecular configurations of the K\(^+\)-water hydration structure for \(D = 0.92\) and 0.61 nm films. The top views show that potassium ions, which were originally bound to Al-rich cavities \((\text{Si}_4\text{Al}_2)\) in the anhydrous state,\(^{15}\) are now moved to sites right above the substitution Al tetrahedra, also consistent with early observations.\(^{8}\) In Fig. 4(a), the top and side views clearly show that the hydration water is in a liquid phase for the \(D = 0.92\) nm film. Each ditrigonal cavity of the mica surface is occupied by approximately one adsorbed water (ad-water) molecule, followed by the subsequent hydration water (h-water) molecules. In the bilayer ice phase shown in Fig. 4(b), the unit cell in the top view contains six water molecules: the lower (marked by “1”) and upper (marked by “4”) ad-water molecules and four h-water molecules in two hydration layers (marked by “2” and “3,” respectively). The hydrogen-bonding network is different from the monolayer ice on a single mica surface;\(^{13}\) we find that ad-water 1 donates two hydrogen bonds to the basal oxygen atoms and forms another hydrogen bond with h-water 3; the h-water 2 contributes one hydrogen bond to the basal oxygen atom and forms two hydrogen bonds with ad-water 4 and hydration water 3. The equivalent rule for hydrogen-bonding formation applies to the ad-water 4 and h-water 3.

Figure 5 shows the ion-water oxygen partial radial distribution function \(g_{KC}(r)\) and the coordination number \(n_0\) around K\(^+\) for different hydration layers. It is interesting to...
see that for the liquid phase ($D=0.92–2.44$ nm), the $g_{KO}(r)$’s are very similar. The coordination numbers in the first hydration shell vary from 7.2 to 8.5, very close to that of K$^+$ in bulk water (7.6–10.3).\(^{21}\) This hydration shell structure, together with the significant diffusion of water molecules (Fig. 3) for the liquid films above $D=0.92$ nm,\(^{7}\) may explain the high lubricity of bound hydration layers observed in the SFB experiment.\(^2\) For the bilayer ice ($D=0.61$ nm), the average coordination number of water molecules in the first hydration shell is around 5 (see Fig. 5), much less than those in the liquid phase, and there is a sharp minimum at 3.4 Å. For all the hydration layers the positions of the first maxima in $g_{KO}(r)$ are located at 2.88 Å, the same as in the bulk liquid.\(^{21}\) This indicates that confinement does not alter the radius of the K$^+$ hydration shell. The nonzero minimum in $g_{KO}(r)$ implies that $n_0(r)$ has no plateau and a range of coordination numbers are possible.

**IV. DISCUSSION**

The comparison between the water oxygen density distributions from our further MD simulation and from the x-ray experimental result (Fig. 1) seems surprising, since in the experiment it was assumed that potassium ions were completely exchanged by H$_2$O$^+$ ions, i.e., the potassium ions were fully solvated\(^{18}\) in water, instead of being fully attached to the mica surfaces (undissolved in water). This water O density distribution with attached K$^+$ ions was also confirmed by a recent Monte Carlo computer simulation.\(^{22}\) In reality, a real mica surface obtained by cleaving and washing is somewhat intermediate between these two limiting cases,\(^{23}\) and the exact positions of the potassium ions that remain attached to the mica surfaces depend on the underlying distribution of Al substitutions that are largely random.\(^{14}\) We speculate that when considering these effects, the water O density distribution will not change dramatically. This is because the hydration structure near the mica surface is mainly determined by the hydrogen bonding between water molecules and between water and basal oxygen atoms.\(^{13}\) As shown in Fig. 3, the diffusion constant of bilayer ice ($D=0.61$ nm) is roughly four orders of magnitude lower than those of thick hydration films ($D=1.65–2.44$ nm) since the water molecules are severely constrained. We anticipate that the corresponding rotational correlation time of water molecules will be much longer in the $D=0.61$ nm hydration layer than in the $D=0.92$ nm layer;\(^7\) thus a higher viscosity and significant shear thinning over a wider range of shear rate will occur. This scenario may explain recent experimental findings for the shear response of the hydration water confined between two mica surfaces: when water is confined to 1–2 ML ($D<0.6$ nm), significant shear enhancement and very high shear viscosity at very low shear rate (in the regime of linear response)\(^6\) were observed. However, a slight increase in the thickness of the hydration layer to $0.8±0.3$ nm (approximately three water layers) will lead to a fluidic response, which is characteristic of the bulk liquid,\(^2\) and has been verified in our recent molecular dynamics simulations.\(^7\)

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In our recent paper,\textsuperscript{1} we mentioned in Ref. 6 some recent surface force apparatus (SFA) work done by S. Granick and Y. Zhu in the form of a private communication. This private communication should be written as “Recent SFA experiment using platinum-free mica surfaces [S. Granick and Y. Zhu (private communication)] shows shear enhancements for the hydration water films 1-2 water layers thick ($D < 0.6$ nm) similar to those in their original publication.” An inaccurate statement was published in our original Ref. 6.

We apologize for this confusion.