Phase, Structure, and Dynamics of the Hydration Layer Probed by Atomic Force Microscopy

Liyi Bai, Zhengqing Zhang, and Joonkyung Jang

Department of Nanoenergy Engineering, Pusan National University, Busan 46241, Republic of Korea

ABSTRACT: Using the molecular dynamics method we simulate the hydration layer probed by an atomic force microscope (AFM) tip. We investigate how the AFM tip affects the phase, structure, and dynamics of the intrinsic hydration layer formed on a hydrophobic carbon plate. Without the AFM tip the molecular packing and orientation of the hydration layer are ordered up to the second molecular layer. With approaching the tip, the hydration layer is perturbed and eventually evaporates. The force–distance curve in AFM lacks an oscillation typically found for the hydration layer formed on a hydrophilic surface. The molecular diffusions parallel and perpendicular to the plate are, respectively, enhanced and restricted by the tip. The molecular reorientation is significantly slowed down by the tip and plate, which disrupt the hydrogen-bond network present in the bulk water.

INTRODUCTION

In an aqueous solution or under ambient condition a structurally ordered layer of water ubiquitously grows on a solid surface. Such a hydration layer significantly affects the wetting of a surface and the freezing process involving a heterogeneous nucleation. Interestingly, a hydration layer develops not only on a hydrophilic but also on a hydrophobic surface.

Atomic force microscopy (AFM) is widely used to probe the molecular structure of a hydration layer. With frequency-modulated AFM one can measure the force on the tip with tens of pN resolution, and the tip–surface distance can be resolved as small as 1 Å. As an AFM tip approaches a surface within 1 nm, the force on the tip typically oscillates with varying the distance between the tip and the surface. If the period of oscillation in the force–distance curve matches the molecular diameter of water, the oscillation is ascribed to the transition between the molecular layers. Unfortunately, no exact relationship exists between the force measured by AFM and the structure of the hydration layer. A theory which relates the force–distance curve to the molecular density profile has been developed, but the scope of theory is limited to a hard-sphere liquid probed by a single molecular probe.

Probing the hydration layer on a hydrophobic surface by means of AFM is further complicated by the possible phase transition of water: if confined between two close hydrophobic objects, liquid water evaporates to a vapor. This drying transition gives rise to a hydrophobic force which is stronger and longer ranged than the van der Waals force between the tip and the surface. The previous studies on the drying transition focused on, for simplicity of analysis, the case where two parallel plates are immersed in liquid water. Less is known about the hydrophobic force relevant to the AFM experiment where a sharp nanoscale tip interacts with a surface.

AFM primarily probes the molecular packing along the direction normal to a surface (e.g., force vs distance from the surface). However, since water is an associative liquid forming the hydrogen-bond network, its structure shows a preferential orientation at an interface. Therefore, a full description of the structure of the hydration layer requires the molecular orientation as well. Also of interest are the dynamic properties such as the molecular diffusion and reorientation dynamics. These dynamic properties of the hydration layer are related to the transport of water in the microfluidics for example. In principle, the molecular orientation and dynamics of water can be explored by using spectroscopies such as sum-frequency generation spectroscopy, X-ray and neutron scattering, and two-dimensional infrared spectroscopy. These advanced spectroscopic experiments are more challenging to execute and difficult to interpret than their bulk phase counterparts because the bulk phase water, dominating in number, easily wipes out the signals from the interfacial water.

Given the experimental hurdles in probing the phase, structure, and dynamics of a hydration layer as probed in AFM, a molecular simulation emerges as a viable option. Herein, using all-atom molecular dynamics (MD) simulation, we study the hydration layer formed between an AFM tip and the plate, both of which are made of hydrophobic carbon. In the context of an AFM experiment performed in liquid water, we investigate the drying transition and the hydrophobic force measured by an AFM tip. We derive the scaling behavior of the hydrophobic force with varying the size of tip. We investigate how the molecular packing and orientation of the hydration layer are influenced by the presence of the tip. The molecular

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diffusion and reorientation dynamics in the hydration layer are investigated and compared with those in the bulk water.

**MOLECULAR DYNAMICS SIMULATION METHODS**

We emulated an AFM experiment by placing a hemispherical tip above a plate in liquid water (Figure 1). Both the tip and the plate were made of carbon and carved out from the face-centered cubic (FCC) lattice with a lattice spacing of 3.567 Å. This fictitious FCC lattice was used to create atomically smooth surfaces of the tip and plate. The radius of the tip, \( R \), was varied as 9, 11, 15, and 17 Å by fixing the lateral dimension of the plate to 34 Å \( \times 34 \) Å. We varied the vertical distance between the bottom of the tip and plate \( D \) from 2 to 10 Å with an interval of 1 Å. The number of water molecules was around 8000, varying with \( D \).

We employed the extended simple point charge (SPC/E) \(^{30} \) model of water which has proven to capture the experimental features such as the surface tension, compressibility, and vapor–liquid equation of state under ambient conditions. \(^{31,32} \)

In this model each water molecule had partial charges of \(-0.8476\) and \(+0.4238\) on oxygen and hydrogen atoms, respectively. The long-ranged Coulomb interaction was taken into account by using the Ewald sum method. \(^{33} \) Oxygen atoms additionally interacted with each other through the Lennard–Jones (LJ) potential, \(^{21} \)

\[
U^{ij}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right],
\]

where \( \epsilon_{ij} \) and \( \sigma_{ij} \) are the energy and length parameters set to 3.166 Å and 0.6502 kJ mol\(^{-1}\), respectively. \(^{34} \) The pair interaction between oxygen and carbon atoms was described by the LJ potential with \( \sigma_{ij} \) and \( \epsilon_{ij} \) of 3.190 Å and 0.4389 kJ mol\(^{-1}\), respectively. \(^{35} \) The contact angle of water on the present plate was reported to be 107.74°, \(^{35} \) confirming the present plate and tip were hydrophobic.

We equilibrated each simulation system by running a 200 ps long MD simulation in the canonical ensemble (NVT) at 300 K. We then ran a 2 ns long isothermal–isobaric (NPT) simulation at 300 K and 1 atm by applying the Nose–Hoover thermostat and barostat. \(^{36,37} \) Water molecules were held rigid by using the SHAKE algorithm. \(^{21} \) The cutoff distance of the LJ interaction was 10 Å. The equation of motion was propagated using the velocity Verlet algorithm \(^{38} \) with a time step of 2 fs. All of the simulation methods were implemented using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD package. \(^{39} \)

**RESULTS AND DISCUSSION**

**Phase Behavior and Force–Distance Curve for the Hydration Layer.** Figure 1 illustrates the drying transition of water confined between the tip and the plate for tips with various radii \( R \). With closely approaching the tip toward the plate \( (D < 7 \text{ Å}) \), the water confined between the tip and the plate evaporated, giving a cavity near the bottom of the tip. On average, the cavities were concave menisci in shape. The \( D \) value below which the drying transition occurred increased as \( R \) increased, meaning the drying transition became longer ranged with increasing \( R \). Regardless of the presence of the drying transition, water molecules were depleted in the regions close to the tip and plate, giving thin layers deplete with water.

We checked the local density of water \( \rho \) by counting the molecules below the tip (those inside the box drawn in the inset of Figure 2a (top)). Figure 2a shows \( \rho \) vs \( D \) for tips with various \( R \). Regardless of \( R \), \( \rho \) was smaller than the bulk density of 1.00 g cm\(^{-3}\) because of the water-deplete layers near the tip.
and plate (see above). As $D$ decreased from 10 Å, $\rho$ dropped down to a vapor density $< 0.5$ g cm$^{-3}$. We defined the distance at which the drying transition occurs $D_c$ as the $D$ value where $\rho = 0.5$ g cm$^{-3}$. $D_c$ (marked with an asterisk) was numerically obtained from the linear interpolation of the data. Figure 2b clearly shows that $D_c$ increased with increasing $R$, signifying the drying transition occurred at a longer distance with increasing size of the tip. Similarly, the previous MD simulation showed that for the water confined between two ellipsoids $D_c$ linearly grows with increasing size of the ellipsoid.$^{40}$ Another MD simulation reported that the drying transition of water confined between hydrophobic plates with a lateral size of 32 Å × 32 Å occurs at $D_c \approx 7.9$ Å.$^{41}$ This value is close to that obtained from the present fit with $R = 32$ Å ($D_c = 8.3$ Å). A standard AFM experiment employs $R$ of 2–20 nm. The present scaling fit, for example, gives $D_c = 5.6$ nm for an AFM with $R = 20$ nm. The prior experiment utilizing a tip with a radius of 75 μm$^3$ reported that water evaporated at $D_c = 3.5$ μm. Our fit extrapolated as $D_c = 19.5$ μm for $R = 75$ μm. This overestimation of $D_c$ compared to the experimental value might arise from the fact that the present tip is atomically smooth. The experimental tip, by contrast, can have small bumps (roughness) on it. One of these bumps presumably serves as an effective tip with a radius smaller than the original tip radius. The resulting $D_c$ should therefore be smaller than that from the tip without any bumps.

We calculated the force exerted on the AFM tip, $F_z$. The force was projected along the direction normal (z axis) to the plate. Figure 3a shows $F_z$ vs $D$ by varying $D$ from 2 to 10 Å for the tips with $R$ of 9, 11, 15, and 17 Å. A positive (negative) $F_z$ corresponded to a repulsive (attractive) force between the tip and the plate. All of the force-distance curves had the same qualitative behavior: $F_z$ vanished for $D > 10$ Å and became repulsive for $D < 3$ Å. In between the force was attractive with its minimum located near 3–4 Å. Due to the drying transition, the tip experienced a largely attractive hydrophobic force from the plate. Consequently, the force did not oscillate with changing $D$, unlike the force measured for the hydration layer on a hydrophilic surface.$^{4,43}$ Figure 3a also shows that with increasing $R$ the force became longer ranged (decaying to zero at a longer distance) and more attractive. The attractive part of the force was well fitted to an exponential function of $D$: $F_z = Ae^{-D/D_0}$, where $D_0$ is the characteristic decay length of the force. The exponential fits were drawn as the dotted lines in Figure 3a. As shown in Figure 3b, $D_0$ increased from 1.3 to 1.9 Å with increasing $R$ from 9 to 17 Å. The linear fitting gave $D_0 = 0.07543R + 0.609$ (Å), which extrapolated as $D_0 = 1.6$ nm for $R = 20$ nm, for example. This value of $D_0$ agrees with several AFM experiments,$^{44-48}$ which reported that the decay length of the force ranges from 0.12 to 2 nm. Also, a decay length of 3.8 Å was predicted for the force between two plates immersed in water by using the Lum, Chandler, and Weeks theory.$^{49,50}$

The minimum of $F_z$ vs $D$ represents the maximal attraction on the tip from the plate, called the pull-off force.$^{51}$ The scaling of the pull-off force with changing $R$ is shown in Figure 3c. The pull-off force increased with increasing $R$, agreeing with the previous work of Gelb et al.$^{52}$ who simulated the force on a nanoscale tip in a nonpolar liquid. Using the linear fit to the pull-off force we could estimate the pull-off force for an AFM with a tip much larger than the present one. For example, the linear scaling fit gave a pull-off force of 26.8 mN for $R = 20$ mm. The experimental pull-off force measured for $R \approx 20$ mm in pure water was $\sim 4–8$ mN,$^{53}$ several times smaller than that of the present fit. Presumably, the present atomically smooth tip and plate enhanced the range of drying transition and pull-off force compared to those of a typical AFM experiment which employed a corrugated tip and surface. Such a corrugation (bump) on top of the AFM tip should function as an effective tip which is smaller than the original tip. As the effective tip is reduced with the presence of corrugation, the resulting pull-off force should decrease as seen in Figure 3c.

**Molecular Structure of Hydration Layer.** The packing of water molecules in the hydration layer was investigated by examining the local density of water $\rho$ vs the height from the plate $z$, $\rho(z)$. Here, $\rho$ was redefined as the density of water below the bottom of the tip, so that $z$ varied from 0 to $D$ (the
region inside the box drawn in the inset of Figure 4a). We redefined the local region here in order to examine how the intrinsic hydration layer was affected by the tip. Shown in Figure 4a are the \( \rho(z) \) with \( D = 10 \) Å obtained for tips with different \( R \). For comparison, we plotted the density profile obtained without the tip. For all cases, \( D \) is fixed to 10 Å. (b) Local density profile \( \rho(z) \) for various \( D \). \( D \) is varied as 10, 9, 8, 7, 6, 5, and 4 Å for the tip with \( R = 11 \) Å. Note \( \rho(z) \) is defined for \( z \leq D \). Lines serve as a visual guide only.

Figure 4. (a) Density profile of the hydration layer. Local density \( \rho \) is plotted vs the height from the plate \( z \) by counting water molecules below the bottom of the tip \( (z \leq D, \text{those inside the box drawn in the inset}) \). Density profile is shown for tips with \( R \) of 9, 11, 15, and 17 Å. For comparison, we plot the density profile obtained without the tip. For all cases, \( D \) is fixed to 10 Å. (b) Local density profile \( \rho(z) \) for various \( D \). \( D \) is varied as 10, 9, 8, 7, 6, 5, and 4 Å for the tip with \( R = 11 \) Å. Note \( \rho(z) \) is defined for \( z \leq D \). Lines serve as a visual guide only.

and 7.6 Å, respectively. The widths of the first and second peaks were approximately 3 Å, signifying the first and second molecular layers were ordered and compactly packed on the plate. The third peak in \( \rho(z) \) was not well defined however: its width was much smaller than those found for the first and second peaks. In the absence of the tip especially, the third peak completely vanished and \( \rho(z) \) leveled off to the bulk water density for \( z > 7 \) Å. Therefore, the third molecular layer, induced by the tip, was not as well developed as the first and second layers due to the plate. The sharp curvature of the tip could not give an ordered molecular packing along the direction normal to the plate.

Figure 4b illustrates how \( \rho(z) \) was affected by reducing \( D \) from 10 to 4 Å (for the tip with \( R = 11 \) Å). As \( D \) decreased from 10 to 9 Å, the third minor peak of \( \rho(z) \) disappeared and the second peak broadened. This signifies that the second and third molecular layers merged due to an increased confinement by approaching the tip toward the plate. With further reducing \( D \) to 8 Å the second peak shrank in width back to its original value, indicating that the third layer vanished and the well-defined second layer re-emerged. Up to this point the first peak was nearly unchanged in its position, height, and width. With decreasing \( D \) from 8 to 7 Å the second peak significantly shifted to a lower value in position and height and reduced in width, signaling that the second layer faded away. The first
peak also reduced in height slightly. As \( D \) reduced from 7 to 6 Å the first peak drastically reduced in height and the second peak vanished due to the drying transition. With further decreasing \( D \), the density peak shortened further in height but not as drastically as in the change found for the drying transition (\( D \) from 7 to 6 Å). The drying transition (\( D < 7 \) Å) completely destroyed the intrinsic hydration layer, which was ordered up to the second molecular layer. Even without the drying transition the second molecular layer was significantly perturbed by approaching the tip (\( D = 7 \) Å), but the first layer remained intact. Likewise, in the AFM imaging of a calcite–water interface, Fukuma et al. experimentally found the first hydration layer is unchanged during the imaging.10

We examined the molecular orientation of the hydration layer by checking for each water molecule the angle between its OH bond and the surface normal of the plate \( \theta \) (see the inset of Figure 5d). In Figure 5 the probability distribution of \( \theta \) is plotted vs the height from the plate \( z \). Several distinct peaks existed in the distribution. When the tip was relatively far away from the plate, \( D = 10 \) Å (Figure 5a), three peaks were found in the first layer (\( z = 2–5 \) Å) at \( \theta \approx 20^\circ, 100^\circ, \) and \( 154^\circ \). The peak at \( 20^\circ \) arose from the OH groups pointing away from the plate and toward the bulk water above the hydration layer. This orientation was called the bulk (b) orientation25 in the previous study (this and other orientations were drawn in the bottom right of Figure 5). The third narrow peak at \( \theta \approx 154^\circ \) represents the OH groups pointing toward the plate, called the dangling (d) orientation.25 In the second layer (\( z = 5–8 \) Å) a broad peak was found around \( \theta \approx 80^\circ \) corresponding to another t orientation where the OH group is nearly parallel but slightly away from the plate. This orientation was called the anticlathrate t orientation where the OH bond is slightly pointing away from the plate (as for the left molecule in the bottom right panel). The other peak near \( \theta = 154^\circ \) corresponded to the d orientation. Table 1 lists the percentages of the four preferential orientations discussed above. With reducing \( D \) from 10 to 9 Å, all of the peaks in the distribution above remained intact (Figure 5b). With further decreasing \( D \) to 8 Å, the distribution of the second layer was squeezed slightly. In the first layer the peak with the d orientation was broadened.

**Figure 5.** Probability distribution of the orientation of the OH groups of the hydration. Distribution is color mapped as a function of \( \theta \) and \( z \). By fixing \( R \) to 11 Å, the distance of the tip from the plate \( D \) is varied as 10, 9, 8, and 7 Å. Representative molecules with the four preferential orientation are drawn in the inset of panel d. Tangential orientations in the anticlathrate and clathrate arrangements are drawn in the left and right molecule of the inset, respectively.

<table>
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<th>Table 1. Percentages of the Preferential Orientations of the OH Groups of Water in the Hydration Layer*</th>
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<td>( D ) (Å)</td>
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*The percentages are listed by varying the tip-plate distance \( D \) from 10 to 7 Å. The percentage of each orientation is calculated by summing the probability distribution of \( \theta \) over the corresponding range shown in parentheses. The anticlathrate and clathrate configurations of the t orientation are illustrated in Figure 5a, 5b, and 5c.
and the t orientation became more dominant. With decreasing 
$D$ to 7 Å, the two peaks in the second layer merged into a 
single broad peak ranging from 30° to 180°. The three peaks in 
the first layer also merged into one with the prominent 
maximum at the t orientation. The molecular orientation for 
$D < 7$ Å was not shown because the hydration layer evaporated 
due to the drying transition. Overall, the molecular orientation 
with the confinement was dominated by the (clathrate and 
anticlathrate) t orientation which amounted to up to 54% for 
$D = 7$ Å (Table 1). The percentages of b and d orientations 
were less than 3% and 7%, respectively. With decreasing $D$, the 
t orientation (clathrate and anticlathrate) became more 
dominant and the d and b orientations reduced in percentage. 
The dominance of the t orientation was consistent with the 
previous study on the hydration layer formed on a hydro- 
phobic silica surface.$^{25}$ In contrast, the OHs of the hydration 
layer on a hydrophilic surface were reported to take the 
d orientation mostly.$^{54,55}$

Experimentally probing the orientation of water primarily 
used a spectroscopic method to detect the shift in the 
vibrational frequency of OH stretching. For example, the 
Raman peak at a frequency of $\sim 3661 \pm 2$ cm$^{-1}$ was assigned to the 
dangling OH groups pointing toward the nonpolar groups 
of a solute dissolved in water.$^{56}$ Also, the vibrational sum-
frequency generation (vSFG) measurement$^{57}$ of the interfacial 
water on a hydrophobic solid showed a pronounced peak at 
3680 cm$^{-1}$, which is assigned to the dangling OH groups 
pointing toward the surface. vSFG was also used to detect the 
dangling OH groups of water near a polar surface by 
controlling the pH of water.$^{28,58}$ These experiments however 
cannot provide the detailed knowledge on the molecular orientation (specific values of $\theta$) as presented in Figure 5.

**Dynamic Properties of Hydration Layer.** We calculated the diffusivity of the hydration layer along the direction parallel or normal to the surface of the plate. The time-dependent diffusivity along the axis $\alpha (= x, y, z)$, $D_\alpha(t)$, was defined as

$$D_\alpha(t) = \int_0^t C_{v_\alpha v_\alpha}(\tau) \, d\tau$$

where $C_{v_\alpha v_\alpha}(\tau) = \langle v_\alpha(t)v_\alpha(0) \rangle$ is the time correlation function (TCF) of the molecular velocity along the $\alpha$th axis. In calculating $D_\alpha(t)$ however only water molecules below the bottom of the tip were included (those inside the box drawn in the inset of Figure 4a). Consequently, the long-time limit of $D_\alpha(t)$ could not be defined because water molecules eventually escaped from the region below the tip. Nevertheless, $D_\alpha(t)$ converged within a few picoseconds, and the converged value could estimate the diffusivity of the hydration layer.

We show in Figure 6a the normalized $C_{v_\alpha v_\alpha}(t)$ for the molecular velocity parallel to the plate ($v_\alpha = v_x, v_y$) with varying $D$ along with that of the bulk water for comparison. $C_{v_\alpha v_\alpha}(t)$ quickly decreased to a dip near 0.03 ps and then further to the negative minimum located at $\sim 0.3$ ps. The TCF quickly declined because each molecule quickly lost memory of its initial velocity due to the collisions with surrounding molecules, which is characteristic of a dense liquid environ-
ment. The negative minimum (anticorrelation) arose from the back scattering of a molecule from the collision with 
surrounding molecules. Compared with the bulk diffusion, the TCFs of the hydration layer had relatively shallow dips and

![Figure 6](https://example.com/figure6.png)
minima, signifying that the molecules moving parallel to the plate experienced less collisions than those in the bulk water. Consequently, as shown in Figure 6b, the corresponding diffusivity $D_\parallel(t)$ (with $D = 10$, 8, or 7 Å) was larger than that of the bulk water, $2.6 \times 10^{-5}$ cm$^2$/s (which was close to the experimental value, $2.4 \times 10^{-5}$ cm$^2$/s and that reported in another simulation$^{59}$). $D_\parallel(t)$ increased from zero to its maximum within 0.2 ps and then plateaued to a constant. With reducing $D$ from 10 to 7 Å, $D_\parallel(t)$ further increased. Therefore, the molecular diffusion parallel to the plate became faster with the increased hydrophobic confinement.

A contrasting behavior was found for $C_\parallel(t)$ and $D_\parallel(t)$ along the direction normal to the plate ($\alpha = z$). The TCF shown in Figure 6c had a less prominent (or no) dip at 0.09 ps and the negative minimum near 0.3 ps, which was deeper than that of the bulk water. The molecules in the hydration were therefore more restricted in moving along the direction normal to the plate. This restriction increased by reducing $D$ from 10 to 7 Å, giving a deeper negative minimum in $C_\parallel(t)$. Consequently, the corresponding diffusivity $D_\perp(t)$ was smaller than that of the bulk water. Also, $D_\perp$ was smaller than $D_\parallel$ signifying the diffusion perpendicular to the plate was slower than that parallel to the plate. Similarly, in the prior MD simulation of water confined in a carbon nanotube$^{59}$ Marti et al. found that water diffuses faster along the direction parallel to the tube wall than along the direction perpendicular to the wall.

We studied the rotational dynamics of the water molecules of the hydration layer. Figure 7a shows the TCF, $C_{\omega\omega}(t) = \langle \vec{\omega}(t) \cdot \vec{\omega}(0) \rangle$, where $\vec{\omega}(t)$ is the angular velocity of a water molecule at time $t$. $C_{\omega\omega}(t)$ had multiple oscillations and relaxed to zero within 0.2 ps. The decay of $C_{\omega\omega}(t)$ was much faster than that found for $C_\parallel(t)$ above (Figure 6). Irrespective of the degree of confinement, $C_{\omega\omega}(t)$ illustrated a strong anticorrelation at 0.025 ps, indicating the fast molecular libration arising from the hydrogen-bond network in a dense liquid water. With the tip and plate present, the negative minimum near 0.025 ps and the second maximum near 0.05 ps slightly increased and decreased from those of the bulk water, respectively. Therefore, the rotation became slightly more inertial (free) in the presence of the tip and plate because the hydrogen-bond network of the bulk water was disrupted by the tip and plate. The TCFs with different $D$ values were virtually identical.

The rotational density of states (rDOS) was defined as $rDOS(\nu) = \int_0^\infty du C_{\omega\omega}(t)\cos(\nu t)$. Shown in Figure 7b are the rDOSs of the bulk and confined water with $D = 7$–10 Å. The maximum of rDOS was found at $557$ and $546$ cm$^{-1}$, respectively, for the bulk and confined water. On average, the rDOS of the hydration layer was slightly red shifted by reducing $D$. The average frequencies of rDOSs were $582.4$, $567.6$, $567.6$, and $563.1$ for the bulk water and the hydration layers with $D = 10, 8$, and $7$ Å, respectively. Kumar et al.$^{60}$ reported that the rDOS of water confined in a carbon nanotube red shifted from that of the bulk water: with reducing the tube diameter from 10.9 to 8.2 Å the peak position of rDOS red shifted from $\sim 450$ to $\sim 150$ cm$^{-1}$. By contrast, the present rDOS was only slightly different from the bulk counterpart. Presumably, the present tip did not strongly restrict water as a carbon nanotube due to the open geometry of the present confinement. The previous MD simulation also reported that the rDOS red shifts from the bulk one for water confined between two fully oxidized graphene membranes.$^{61}$

Above we have seen that the molecular angular velocity relaxed within 0.2 ps, and this short-time dynamics was governed by the molecular libration which was not much different from that of the bulk water. We additionally investigated the long-time rotational dynamics governed by the large-amplitude reorientation of a molecule. To do so we calculated the second-order reorientational TCF, $C_2(t) = \langle P_2(\cos \theta(t)) \rangle$, where $P_2$ is the second-order Legendre polynomial and $\theta(t)$ is the time-dependent $\theta$ value (see above). We calculated $C_2(t)$ as this is relevant to various experiments including the polarization anisotropy and nuclear magnetic relaxation.$^{62,63}$

$C_2(t)$ for the hydration layers with $D = 10,8$, and 7 Å for the bulk water (plotted on the log scale) are plotted in Figure 8a. The short-time portion of $C_2(t)$ is drawn in the inset. Clearly, $C_2(t)$ relaxed with two different time scales: $C_2(t)$ initially decayed with a subpicoseconds time scale and then slowly with a picoseconds time scale. The fast and slow relaxations, respectively, arose from the libration of the OH groups and from the reorientation involving the jumps between the preferential orientations found above (b, t, and d orientations). $C_2(t)$ could be well fit by the biexponential function $C_2(t) = A e^{-t/\tau_1} + (1 - A)e^{-t/\tau_2}$, where $\tau_1$ and $\tau_2$ are the characteristic time scales for the slow and fast relaxations, respectively. The fitting parameters are listed in Table 2. The $\tau_1$ value for the bulk water was 2.5 ps, agreeing with the time scales of 1.7–2.6 ps obtained from various experiments.$^{64–67}$ When confined between the tip and the plate, $C_2(t)$ decayed much slower than that of the bulk water. This rotational
The reorientation correlation time $\tau_{\text{reor}}$ defined as $\tau_{\text{reor}} = \int_0^\infty C_2(t)dt$. As listed in Figure 8a, $\tau_{\text{reor}}$ was 4.42 ps for the bulk water and 5.67, 7.14, and 9.52 ps for the hydration layers with $D = 10$, 8, and 7 Å, respectively. In order to understand this trend, note that the reorientation in the long time could be regarded as the jumps between the preferential orientations $b$, $t$, and $d$. Each jump in the molecular orientation required breaking an old H bond and subsequently forming a new H bond. Owing to the presence of the tip and plate the approach of a new H-bond partner was more hindered compared to that in the bulk water. This excluded volume created by the tip and plate slowed down the jumps between the orientations. With decreasing $D$ this excluded volume effect became even more important and therefore the relaxation of $C_2(t)$ became slower.

### CONCLUSION

AFM is widely used to probe the hydration layer formed on an extended surface, but we do not understand exactly how an AFM image is related to the underlying structure of the hydration layer. Also, it is unclear to what extent an AFM tip perturbs the intrinsic structure of the hydration layer. For the hydration layer formed on a hydrophobic surface AFM is further complicated by the drying transition of the hydration layer. With this perspective we investigated the phase, structure, and dynamics of the hydration layer formed on a hydrophobic plate as probed by AFM. As the AFM tip closely approached the plate, the hydration layer spontaneously evaporated. Owing to this drying transition, the AFM tip experienced a largely attractive hydrophobic force. We investigated the scaling behavior of the hydrophobic force by varying the size of the tip. The molecular packing was ordered up to the second molecular layer on the plate. The molecular diffusions along the directions parallel and normal to the plate were, respectively, enhanced and restricted by the tip and plate. The molecular orientation in the hydration layer was dominated by the OH groups nearly parallel to the plate surface. The hydrogen-bond network of the hydration layer was perturbed by the hydrophobic tip and plate. Consequently, the molecular reorientation was slowed down and the rotational density of states of the interfacial water were red shifted from those of the bulk water.

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: jkjang@pusan.ac.kr. Phone: +82-51-510-3983.*

**ORCID**

Zhengqing Zhang: 0000-0003-2403-1461

Joonkyung Jang: 0000-0001-9028-0605

**Notes**

The authors declare no competing financial interest.

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