Hydrogen-Bond Dynamics near a Micellar Surface: Origin of the Universal Slow Relaxation at Complex Aqueous Interfaces

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The dynamics of hydrogen bonds among water molecules themselves and with the polar head groups (PHG) at a micellar surface have been investigated by long molecular dynamics simulations. The lifetime of the hydrogen bond between a PHG and a water molecule is found to be much longer than that between any two water molecules, and is likely to be a general feature of hydrophilic surfaces of organized assemblies. Analyses of individual water trajectories suggest that water molecules can remain *bound to the micellar surface for more than 100 ps*. The activation energy for such a transition from the bound to a free state for the water molecules is estimated to be about 3.5 kcal/mol.

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The study of hydrogen bond (HB) dynamics has proven to be a very useful tool [1–3] to understand the origin of many fascinating dynamical properties of water which are due to its extended hydrogen bond network [4]. However, the same properties exhibit quite different behavior for water molecules at the surfaces of self-organized assemblies and biological macromolecules [5–9]. Recent time domain spectroscopic measurements have shown that their dynamics is considerably slower than their counterparts in bulk water, sometimes slower by *more than 2 orders of magnitude*. While the reorientation of water molecules and solvation of ions or dipoles in bulk water proceeds with an average time constant of less than a picosecond (ps), the same at protein surfaces gets extended to hundreds of picoseconds [7–10]. Such slow dynamics has been observed in proteins [7,9], microemulsions [8,11], micelles [8,12], lipid vesicles, and bilayers [13].

The slow dynamics of water molecules at heterogeneous surfaces seems to be universal and could be a collective effect originating from the surface and/or from the nature of the hydrogen bond network at the surface. The work of Cheng and Rossky [14] have already shown that water molecules at the surface of a protein can be structurally different from those in the bulk. A phenomenological theory developed recently proposes to explain the emergence of slow dynamics in terms of a dynamical equilibrium between bound and free water molecules at the surface [15]. Recent atomistic molecular dynamics simulations of an aqueous micellar assembly, the cesium pentadecafluorooctanoate (CsPFO), have shown that the orientational correlation function of the water molecules near the micelle show a dramatic slowing down in its long time decay [16]. Note that micelles are not only of great interest themselves, but they also mimic surfaces of many biological molecules. The presence of a compact hydrophobic core and a hydrophilic surface resembles proteins rather closely.

In this study, we explore the two most important microscopic aspects of water dynamics near the micellar surface—the hydrogen bond lifetime of the water-polar head groups (wPHG) hydrogen bond and also the *distance dependence* of the dynamics of the water-water hydrogen bond. The best way to study this dynamics is to investigate the hydrogen bond time correlation functions, $S_{\mathrm{HB}}(t)$ and $C_{\mathrm{HB}}(t)$ (defined below), introduced originally by Stillinger [17] and used by Luzar *et al.* [1] to study pure water and more recently by Chandra [2] to explore effects of ions in water on the lifetime of the hydrogen bond. The time correlation function $S_{\mathrm{HB}}^{\mathrm{wPHG}}(t)$ for the hydrogen bond between the polar head group and the water molecules on the surface is defined by

$$S_{\mathrm{HB}}^{\mathrm{wPHG}}(t) = \langle h_{\mathrm{wPHG}}(0) H_{\mathrm{wPHG}}(t) \rangle / \langle h_{\mathrm{wPHG}} \rangle, \tag{1}$$

where the population variable $h_{\mathrm{wPHG}}(t)$ is unity when a particular water molecule and a polar head group is hydrogen bonded at time t, according to an adopted definition, and zero, otherwise. On the other hand, $H_{\mathrm{wPHG}}(t) = 1$ if the tagged polar head group-water hydrogen bond remains *continuously* hydrogen bonded during the time duration t and zero otherwise. Thus, $S_{\mathrm{HB}}^{\mathrm{wPHG}}(t)$ describes the lifetime of a tagged pair. The angular brackets denote averaging over initial time values and over all water-PHG pairs. We employed a geometric definition of the wPHG hydrogen bond such that a water molecule was assumed to be hydrogen bonded to a surfactant if the distance between the oxygen of the water molecule and the carbon of the headgroup was less than 4.35 Å, and that the oxygen of the water molecule and the oxygen of the headgroup was less than 3.5 Å. These distance criteria were obtained from the first minimum in the respective pair correlation functions. For water-water hydrogen bonds, we have used the same criteria as used by Chandra [2], which were found to hold well for water-water hydrogen bonds near the interface also.

In order to understand the structural relaxation of a tagged hydrogen bond, one also defines the following time correlation function, $C_{\rm HB}^{\rm wPHG}(t)$,

$$C_{\rm HB}^{\rm wPHG}(t) = \langle h_{\rm wPHG}(0) h_{\rm wPHG}(t)\rangle / \langle h_{\rm wPHG}\rangle. \qquad (2)$$

Unlike $S_{\rm HB}^{\rm wPHG}(t)$, this correlation function is expected to exhibit a longtime tail [1,2].

The surfactant in this simulation is pentadecafluorooctanoate, with cesium being the counterion, commonly referred to as CsPFO. The CsPFO-H_2O system has been well studied experimentally [18]. The amphiphiles form disk-shaped micelles, stable over an extensive range of concentration and temperature. Details of our MD simulations have been discussed elsewhere [16,19]. The molecular dynamics simulation was carried out in the NVT ensemble for an aggregate of 62 CsPFO molecules in 10 562 water molecules. The potential for water molecules is the extended simple point charge (SPC/E) model [20], and the counterions carry a unit positive charge, which is compensated by a $+0.4e$ charge on the carbon of the octanoate headgroup and a $-0.7e$ charge on each of the oxygens of the headgroup [21]. The equations of motion were integrated with the reversible reference system propagator algorithm [22] using the PINY-MD program [23] with an outer time step of 4 fs. The analyses reported here were carried out from different sections of a subsequent 3.5 ns trajectory. The $S(t)$ and $C(t)$ functions were obtained with time resolutions of 12 fs and 1 ps, respectively. The results reported here are at a temperature of 300 K.

Figure. 1 shows the time dependence of the correlation function $S_{\rm HB}^{\rm wPHG}(t)$, with the inset showing the $S_{\rm HB}^{\rm ww}(t)$ (i.e., water-water) correlation function in bulk water, for comparison. Note the lengthening of the time scale in the H bonding with the PHG of the micelle. $S_{\rm HB}^{\rm wPHG}(t)$ can be fitted to a sum of three exponentials, with the longest time constant being equal to 9 ps which is to be compared with 0.97 ps in pure water. The amplitudes and time constants are given in Table I [25]. From these, one can obtain an average time constant of around 6.8 ps, which is 13 times larger than its value for the water-water hydrogen bond in pure water. It is difficult to pinpoint the reason for the slowdown of $S_{\rm HB}(t)$ at the surface. We found that the water molecules at the surface form bridge hydrogen bonds involving PHGs of the nearest neighbor surfactant molecules which could stabilize the wPHG hydrogen bond.

TABLE I. Parameters of multiexponential fits to the water-PHG hydrogen bond time correlation functions shown in Figs. 1 and 2.

Function	Time constant (ps)	Amplitude (%)
$S_{\rm HB}(t)$	0.3	5.9
	3.6	31.5
	9.1	62.6
$C_{\rm HB}(t)$	3.4	16
	29.0	63
	118.5	21

In Fig. 2, we show the hydrogen bond time correlation function $C_{\rm HB}^{\rm wPHG}(t)$. In the inset we show $C_{\rm HB}^{\rm ww}(t)$ for bulk water. Note again the lengthening of the long time decay. The values of the time constants and the respective amplitudes are given in Table I. In this case, the long time constant stretches to more than 100 ps. The reason for this unusual long decay time can be traced back to those trajectories which leave the micellar surface to go to the bulk but return after a long time to get bonded to the *same PHG* at the surface. This is in line with the explanation of the long time decay of the $C_{\rm HB}(t)$ function in bulk water [1,26]. In the present problem, the existence of such trajectories indicates the presence of correlations in the surface region. The $S(t)$ function is thus a more accurate

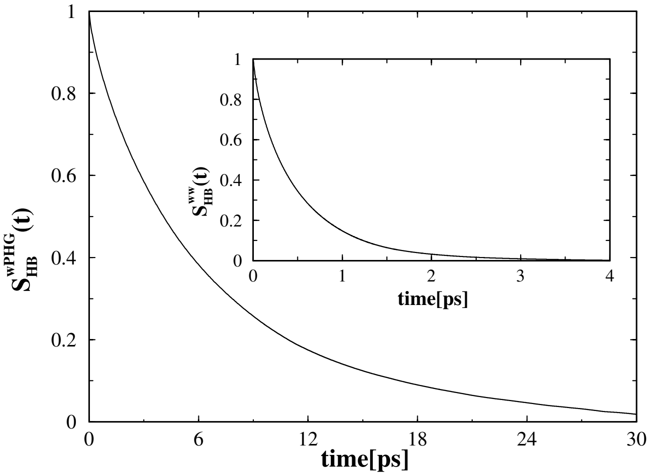

FIG. 1. $S_{\rm HB}^{\rm wPHG}(t)$ function for the hydrogen bond between the polar head group and water molecules. Inset shows the same between pairs of water molecules in pure water.

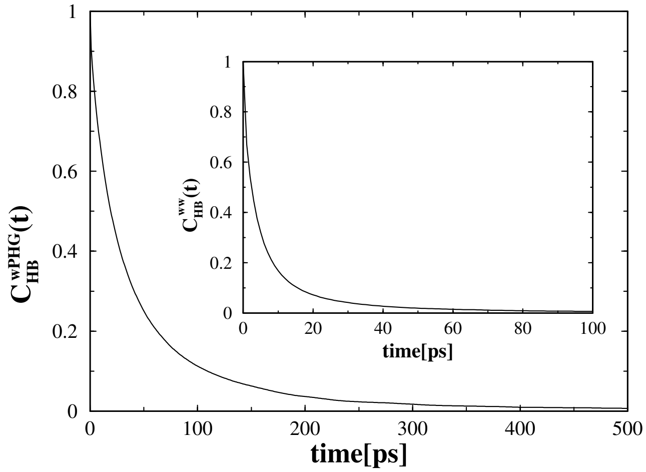

FIG. 2. $C_{\rm HB}^{\rm wPHG}(t)$ function for the hydrogen bond between the polar head group and water molecules. Inset shows the same between pairs of water molecules in the region far away from the micelle [24].

representation of the lifetime dynamics of the hydrogen bond than the $C(t)$ function, although the latter contains rich information on the correlated pair diffusion of the water molecules.

Analysis of the trajectories of the individual water molecules at the micellar surface reveals an amazing richness of events. In Fig. 3, we show representative trajectories over 800 ps, of four arbitrarily chosen water molecules that were hydrogen bonded to the surface at time zero. The plot shows the shortest distance, $D_{\text{W-PHG}}$, of each of the water molecules to the micellar surface as a function of time [27]. For example, the water molecule shown in the top left figure rattles near the surface for about 150 ps, diffuses into the bulk region, stays there for around 500 ps, and then revisits the micelle surface, presumably to form a new hydrogen bond with a PHG. It should also be noted that the micelle itself is quite fluxional over these time scales. Note also that while the $S_{\text{HB}}^{\text{wPHG}}(t)$ and $C_{\text{HB}}^{\text{wPHG}}(t)$ functions study the dynamics of a particular wPHG hydrogen bond (with average lifetimes of 6.9 and 43.7 ps, respectively), the apparently longer lifetime of bound water molecules shown in the trajectories in Fig. 3 arises from the fact that a water molecule can remain bound to the micellar surface even after its hydrogen bond with a particular PHG is broken.

Such dynamical processes involving water molecules affect the way they form hydrogen bonds between themselves. We have explored this aspect by studying the water-water hydrogen bond time correlation functions for water molecules that belong to different interfacial layers. In Fig. 4 we show the lifetime correlation functions, $C_{\text{HB}}^{\text{ww}}(t)$ and $S_{\text{HB}}^{\text{ww}}(t)$, between two water molecules that both exist at several regions away from the surface [27]. This function shows a sharp slowdown as the surface is approached closely. The time constant obtained from the S_{HB} function for the water molecules *within* 6 Å from the micellar surface is around 25%–30% larger than that for water molecules in the bulk region. The time constant for the same water molecules obtained from the C_{HB} function is about 45% slower than that for bulk water. Again, the S_{HB} function decays much faster than the C_{HB} one.

The simulation results can be combined with a theoretical model to obtain useful information on the micelle-water interaction. The model assumes a dynamical equilibrium between the "bound" and "free" states of water molecules at the micellar surface [15]. The dynamical variable $h(t)$ represents the instantaneous population of the bound state, and the correlation function, $C_{\text{HB}}^{\text{wPHG}}(t)$, gives, under the regression hypothesis (or linear response theory) [28], the decay of an initial ($t = 0$) bound state and its formation at a later time. Therefore, we can set, in the long time, $C_{\text{HB}}^{\text{wPHG}}(t) \sim e^{-t/\tau_{\text{BF}}}$, where τ_{BF} is the time constant for the bound to free transition. From Table I, we find the average time constant at 300 K to be 43.7 ps. We can obtain an activation energy E_A, for this transition using transition state theory to express the rate constant $(\frac{1}{\tau_{\text{BF}}})$, as

$$\frac{1}{\tau_{\text{BF}}} = \frac{k_{\text{B}}T}{h} e^{-E_A/k_B T}, \tag{3}$$

where k_{B} is the Boltzmann constant, T is the temperature, and h is the Planck constant. E_A is then found to be 3.34 kcal/mol. A similar analysis of $C_{\text{HB}}^{\text{wPHG}}(t)$ at 350 K (data not shown here) yields a time constant of 18.9 ps. Using an Arrhenius dependence of the time constant with temperature, we find that the activation energy is 3.50 kcal/mol, in close agreement with the result of the

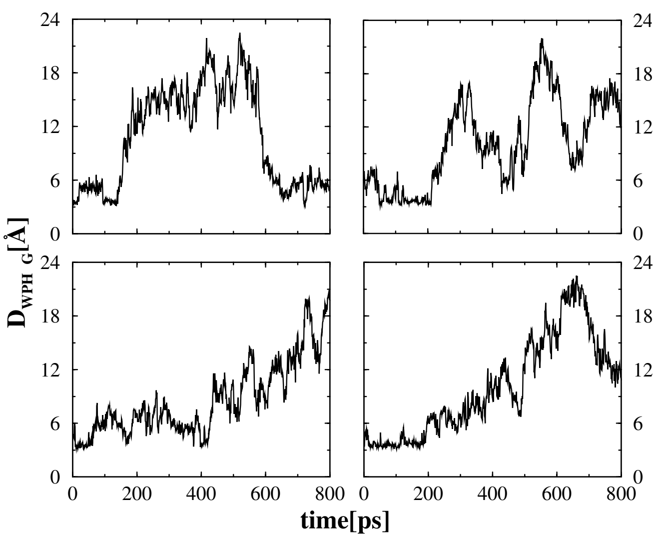

FIG. 3. Trajectory of four water molecules for a time period of 800 ps. The shortest distance of the water molecules to the micellar surface, $D_{\text{W-PHG}}$, is plotted against time.

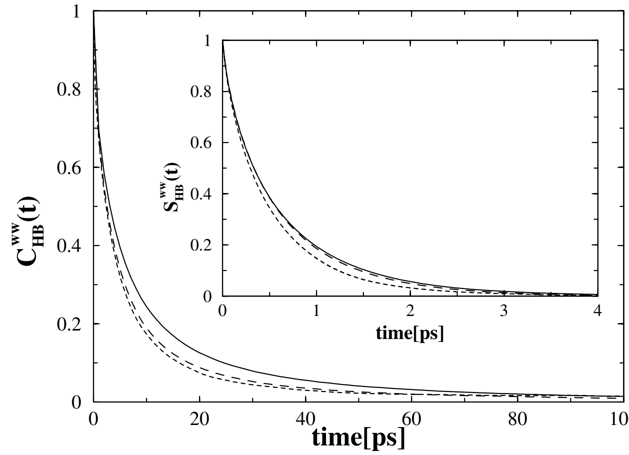

FIG. 4. The location dependence of the time correlation function, $C_{\text{HB}}^{\text{ww}}(t)$, for the hydrogen bond between pairs of water molecules located at different regions from the micellar surface [27]. Solid curve: within 6 Å; Long-dashed curve: between 6 and 9 Å ; Dashed curve: beyond 25 Å . Inset shows the similar location dependence of the $S_{\text{HB}}^{\text{ww}}(t)$ function for the hydrogen bond between pairs of water molecules.

transition state theory presented above, showing the robustness of the above analysis.

To conclude, we have carried out large scale atomistic molecular dynamics simulations of an aqueous micellar system, with emphasis on understanding the hydrogen bond breaking dynamics at the micellar surface. We find the rather surprising result that the hydrogen bond between the micellar polar head group and a water molecule has a much longer lifetime—almost 13 times larger than that in the bulk between two tagged water molecules. This longer lifetime could originate from the bridge bonds that the surface water molecules form with the PHGs and also from the coupling to the micelle which acts as a bath for HB excitations. Another interesting result is that the lifetime of hydrogen bonds between two tagged water molecules increases only by about 25%–30% as one approaches the micellar surface. Although this slowdown is not as dramatic as the slowdown in the orientational relaxation of the water molecules with large residence times near the interface, it is rather sharp. Analysis of the individual trajectories reveal that the quasibound water at the micellar surface (immobilized by double or more hydrogen bond bridges) may be partly responsible for the slow dynamics. The activation energy for the transition from a bound to a free state for the water molecules on the micellar surface, estimated from both the transition state theory and the temperature dependence of the hydrogen bond lifetime, is about 3.5 kcal/mol. The agreement between the rather simple model and the temperature dependent simulation data is remarkable. We believe that the results discussed here are generic to organized assemblies and biological macromolecules that possess a hydrophilic surface or hydrophilic pockets that are accessible to water.

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[24] The $C_{\mathrm{HB}}^{\mathrm{ww}}(t)$ function for pure water can show a spuriously long time tail which denotes the reformation of the hydrogen bond of a given pair. This effect should vanish in the thermodynamic limit, and the time correlation function will not possess a long time tail. The function in the inset for water molecules in the far region matches the correlation function obtained for a collection of 256 water molecules in bulk, exactly, up to 80 ps.
[25] Note that even in bulk water, the lifetime correlation function $S_{\mathrm{HB}}^{\mathrm{ww}}(t)$ is nonexponential, with three time constants, 0.07 ps (14%), 0.49 ps (70%), and 0.97 ps (16%). The average lifetime is 0.51 ps.
[26] $C_{\mathrm{HB}}^{\mathrm{ww}}(t)$ is also nonexponential in bulk water, with time constants 3.1 ps (61%) and 17.25 ps (39%). The average time constant is 7.2 ps.
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