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Dynamics of bound and free water in an aqueous micellar solution: Analysis of the lifetime and vibrational frequencies of hydrogen bonds at a complex interface

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In order to understand the nature and dynamics of interfacial water molecules on the surface of complex systems, large scale, fully atomistic molecular dynamics simulations of an aqueous micelle of cesium perfluorooctanoate (CsPFO) surfactant molecules have been carried out. The lifetime and the intermolecular vibrational frequencies of the hydrogen bonds that the water molecules form with the hydrophilic, polar head groups (PHG) of the surfactants are calculated. Our earlier classification [S. Balasubramanian *et al.*, Curr. Sci. **84**, 428 (2003); e-print cond-mat/0212097] of the interfacial water molecules, based on structural and energetic considerations, into bound and free types is further validated by their dynamics. Lifetime correlation functions of the water-surfactant hydrogen bonds show the long-lived nature of the bound water species. Surprisingly, the water molecules that are singly hydrogen bonded to the surfactants have a longer lifetime than those that form two such hydrogen bonds. The free water molecules that do not form any such hydrogen bonds behave similarly to bulk water in their reorientational dynamics. A few water molecules that form two such hydrogen bonds are orientationally locked in for durations of the order of a few hundreds of picoseconds; that is, much longer than their *average* lifetime. The intermolecular vibrational frequencies of these interfacial water molecules have been studied from the power spectra of their velocity autocorrelation function. We find a significant blue shift in the librational band of the interfacial water molecules, apart from a similar shift in the near neighbor bending modes, relative to water molecules in bulk. These blue shifts suggest an increase in rigidity in the structure around interfacial water molecules. This is in good agreement with recent incoherent, inelastic neutron scattering data on macromolecular solutions [S. Ruffle *et al.*, J. Am. Chem. Soc. **124**, 565 (2002)]. The results of the present simulations appear to be rather general and should be relevant to the understanding of the dynamics of water near any hydrophilic surface.

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I. INTRODUCTION

Water molecules that are present on the surface of soft, complex systems have been the focus of attention for a long time [1–8]. Not only are the intrinsic structure and dynamics of such water molecules themselves interesting, but their ability to influence the structure, dynamics, and function (in the case of biologically relevant complex systems) has made the study of interfacial water a subject of paramount interest to a wide spectrum of researchers from different areas [9,10]. Micellar solutions are also used as reaction media, and interfacial water in such microdisperse systems plays an important role in determining the reaction kinetics [11]. A variety of experimental, computational, and theoretical tools has been employed to study its properties. Dielectric relaxation experiments have shown the presence of a distinct relaxation peak that could be related to the dynamics of water bound to the surface of a macromolecule [12,13]. Evidence for the existence of bound water and its slow dynamics has also been provided by local probes, such as NMR [14] and solvation dynamics experiments [15–18].

Computer simulations have enormously aided our understanding of these complex systems [19–26,7]. Employing the state of the art molecular dynamics simulations, we have recently established the presence of a slow component, running into hundreds of picoseconds, both in the orientational relaxation of the interfacial water molecules and also in the solvation dynamics of ions that are present near the water-micelle interface [22,23,25], consistent with time resolved fluorescence experiments [16]. A gainful analysis of the solvation time correlation function into its partial components provided us insight into the microscopic origin of this slow dynamics. We found that the major contribution to the slow solvation of ions arose from their interactions with the polar head groups of the surfactants [22]. The observation of the slow component in the decay of the dipolar reorientational time correlation function of the interfacial water molecules [23,24] led us to investigate into the cause of the dramatic slowing down of orientational relaxation. Careful analysis of the results demonstrated that it is caused by the long-lived hydrogen bonds that the water molecules form with the hydrophilic and polar head groups that constitute the micellar surface [26]. Specifically, we calculated the lifetimes of such hydrogen bonds through appropriate time correlation functions (TCF) and found that they are nearly 5 to 10 times longer lived than the hydrogen bonds that water molecules form between themselves. We showed that this longer lifetime profoundly influences the intrinsic dynamics of water molecules at the interface, in terms of their ability to rotate, to translate, and their capability to solvate free ions.

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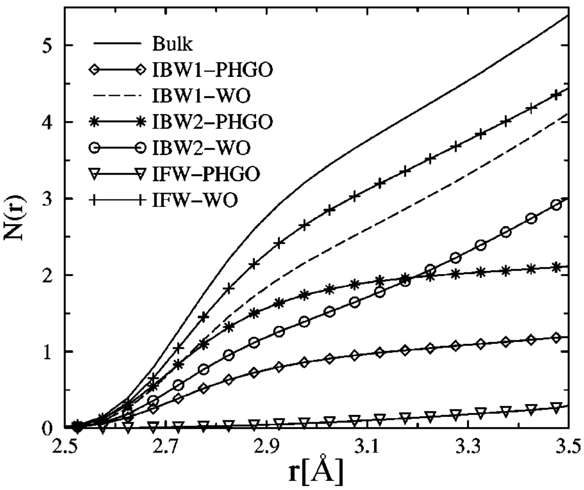

FIG. 1. Running coordination numbers of oxygen atoms around oxygen atoms of interfacial water molecules, compared to data for bulk water. PHGO refers to the oxygen atom of the polar head groups and WO that in a water molecule. IFW, IBW1, and IBW2 denote interfacial water molecules with zero, one, and two coordinations to polar head groups, respectively.

Furthermore, in a recent communication, we have presented, microscopic evidence for the presence of three kinds of water molecules in the interfacial layer [27,28]. This classification was based on the number of hydrogen bonds that an interfacial water molecule makes with the polar head groups of the surfactants. We found that about 80% of the water molecules in the interface are singly coordinated to the surfactants, and that the rest of the interfacial water molecules are evenly divided into categories that either form two hydrogen bonds with two *different surfactant molecules* or those that do not form hydrogen bonds with the macromolecule at all. The former class of water molecules that form one or two hydrogen bonds with the surfactants can thus be called *bound* and the latter as *free*. We introduced a nomenclature to identify such species as IBW2—for water molecules that form two hydrogen bonds with two different surfactants, IBW1—for water molecules that form only one such hydrogen bond, and IFW—for water molecules that do not form such water-PHG (w-PHG) hydrogen bonds. The ratio of IBW2:IBW1:IFW was found to be distributed as 1.1:8:0.9. Because of the enhanced strength of the w-PHG bond, IBW2 has a lower potential energy than IBW1. Yet, it is not found in abundance as it is disfavored entropically due to its requirement of a constrained environment, due to the rarity of events in which two surfactants need to be present around it at the proper orientation, and geometry. Thus, we had shown that the bound and free classification has both energetic and structural basis. The water molecules at the interface retain their *nearly* tetrahedral coordination, similar to bulk water, and their coordination shell gets completed by the formation of hydrogen bonds with other water molecules in the vicinity. This can be observed from the running coordination numbers of oxygen atoms around various types of interfacial water molecules shown in Fig. 1. The figure clearly shows that the first coordination shell of interfacial waters contains both, the oxygen atom of polar head groups (in the case of IBW1 and IBW2) as well as other water molecules. The distribution of the angle subtended by pairs of oxygen atoms in the first coordination shell around an interfacial water molecule exhibits a dominant peak at the tetrahedral angle of 109.5° and a smaller, but non-negligible peak at 65°, that indicates the presence of first shell neighbors in the interstitial site around an interfacial water molecule.

It should be pointed out at this stage that this classification of bound and free applies to *interfacial* water and therefore, does not refer to bulk water. Indeed, the existence of such free (or quasifree, if we need to distinguish from bulk water) species *at the interface* could have far reaching consequence in the understanding of both macromolecular activity, such as molecular recognition and water dynamics.

In light of our earlier observations on the slow dynamics of interfacial water [22], it would be interesting to examine if the bound-free paradigm [29,15] can have a much more robust dynamical basis as well. This is required because the hydrogen bond lifetime analysis provides a slow down by a factor of 10 at the maximum. Thus, although the slow down of this lifetime is probably the fundamental process, it does not fully explain the reason for the dramatic slow down, to the extent of more than 2 orders of magnitude that we observed in simulations and others observed in experiments. In this paper, we explore this aspect of the interfacial water molecules. Details of their structure and energetics have been reported earlier [27,28]. Here we focus on their dynamics. We find that the *long-time slow decay observed in the dipolar reorientational TCF of the interfacial water molecules can be directly attributed to the doubly bonded bound water species*. We also discuss results on the lifetimes of these species and we find surprisingly that the singly bonded water species is the longest lived among the three species of interfacial water molecules.

An additional important aspect of this paper is an analysis of the intermolecular vibrational frequencies of the interfacial water. With the recent advent of nonlinear spectroscopic methods that use lasers in the midinfrared region, the dynamics of hydrogen bonds between water molecules has been studied experimentally. In such a technique, one studies the change in the intramolecular O-H stretching frequency for water molecules in different environments. Such studies have shed considerable light on the dynamics of the hydration layer around alkali and halide ions in aqueous salt solutions [30,31]. We foresee such experiments to be performed for the bound water molecules described here. Unfortunately, we cannot study the change in the intramolecular O-H frequency of the bound water molecules, since our water model has a rigid geometry. However, we provide details on the vibrational spectrum of the bound water molecules by studying the Fourier transform of the velocity autocorrelation function of water molecules. We find that both the librational and bending frequencies undergo a significant *blue shift*, signalling the enhanced rigidity in the structure of the surface water. This blue shift in libration frequency is in good agreement with recent incoherent, inelastic neutron scattering data on macromolecular solutions [32]. These results are expected to be rather general and should be relevant to the understanding of dynamics of water near any hydrophilic surface.

The organization of the rest of the paper is as follows. In the following section, we present the details of the systems and of MD simulations. Section III present results on hydrogen bond lifetime. Section IV contains results of our analysis of the frequencies of intermolecular vibrations. Section V concludes with discussion of the results.

II. DETAILS OF SIMULATION

The surfactant in our simulations is cesium perfluorooctanoate (CsPFO), which has a carboxylate head group and a fluorinated tail. It forms oblate ellipsoidal micelles in water [33,34]. We have studied one micelle, an aggregate of 62 of these surfactants in a simulation box of 10 562 water molecules. An atomistic molecular dynamics simulation of this system at 300 K was performed, whose details have been reported earlier [22,25,26]. Here we provide essential information on the methods used for analysis of the data pertaining to dynamics of the bound water molecules. The simulations were performed in the *NVT* ensemble with an integration time step of 4 fs, using the RESPA algorithm [35] and the PINY_MD package [36]. The model for water is the SPC/E [37] and the interaction potential used has been described earlier [22,23]. Coordinates of all the atoms were recorded every 12 fs and the correlation functions presented here were calculated from such a trajectory. In order to calculate the atomic velocity TCFs, we generated a 15-ps long trajectory, where the coordinates and velocities of all the atoms in the simulation were recorded every time step, so as to accurately obtain the initial fast decay of the velocity TCFs. The hydrogen bond lifetime correlation functions were obtained from a trajectory of length 50 ps, with a time resolution of 12 fs. The long-time behavior of some of these functions were obtained from another trajectory of length 3.3 ns, with a time resolution of 1 ps.

An important determinant of the dynamics of water molecules is the reorientation of its dipole vector that can be probed with NMR measurements. We have calculated the dipole-dipole TCF, defined as

$$C_{\mu}(t)=\frac{\langle \vec{\mu}_i(t+\tau)\cdot\vec{\mu}_i(\tau)\rangle}{\langle \vec{\mu}_i(\tau)\cdot\vec{\mu}_i(\tau)\rangle}, \tag{1}$$

where $\vec{\mu}_i(t)$ is the dipole moment vector of ith water molecule at time t and the angular brackets denote averaging over water molecules as well as over initial configurations τ.

Further, we have calculated the lifetime of the hydrogen bonds that the bound water molecules form with the polar head groups of the surfactant. These have been characterized in terms of two time correlation functions $S_{\mathrm{HB}}(t)$ and $C_{\mathrm{HB}}(t)$. These TCFs can be defined using the functions $h(t)$ and $H(t)$, which signify the presence or absence of the hydrogen bond at any time t, and are given as [38–44,26]

$$h(t)=1 \quad \text{if a pair of atoms are bonded at time } t,$$

$$=0 \quad \text{otherwise,}$$

$$H(t)=1 \quad \text{if a pair of atoms are continuously bonded between time 0 and time } t,$$

$$=0 \quad \text{otherwise.}$$

Using these definitions, the bond lifetime correlation functions are defined as

$$S_{\mathrm{HB}}(t)=\frac{\langle h(\tau)H(t+\tau)\rangle}{\langle h\rangle},$$

$$C_{\mathrm{HB}}(t)=\frac{\langle h(\tau)h(t+\tau)\rangle}{\langle h\rangle}, \tag{2}$$

where $S_{\mathrm{HB}}(t)$ probes the continuous existence of a hydrogen bond, while $C_{\mathrm{HB}}(t)$ allows for the reformation of a bond that is broken at some intermediate time. The former is thus a strict definition of the hydrogen bond lifetime, while the latter is more permissive. The true lifetime of a hydrogen bond lies somewhere in between the two time constants obtained from these functions.

In defining the presence of a hydrogen bond, we employ two distance conditions and one energy criterion, as advocated earlier [43]. These criteria and their legitimacy with regard to the hydrogen bond formed between water and the polar head group have been discussed earlier [27,28]. Here we just state the definition. We assume a water molecule to be hydrogen bonded to a polar head group, if (a) the distance between the oxygen of the water molecule and the carbon of the headgroup is within 4.35 Å, (b) the distance between the oxygen atom of the water molecule and any of the oxygens of the polar head group is within 3.5 Å, and (c) the pair interaction energy between the water molecule and the head group is less than −6.25 kcal/mole.

We have also calculated the lifetime correlation function of the interfacial water species, denoted as $S_W(t)$ and $C_W(t)$. Their defnitions are similar to $S_{\mathrm{HB}}(t)$ and $C_{\mathrm{HB}}(t)$, above. However, they are dependent on functions, $h(t)$ and $H(t)$ that are unity when a particular water molecule is of a certain type, and are zero, if it is not. Thus, these need to be distinguished from the $S_{\mathrm{HB}}(t)$ and $C_{\mathrm{HB}}(t)$ functions, which are descriptions of the lifetime of the hydrogen bond. In making this distinction, we allow for the existence of a water molecule in any of the three states—IFW, IBW1, or IBW2, despite the ephemeral loss of a hydrogen bond with a particular PHG.

In order to study the vibrational spectrum of the intermolecular hydrogen bonds, especially those of the bound water at the interface, we have carried out the Fourier transform of the velocity autocorrelation function of water molecules defined as $C_{\mathrm{vv}}(t)$,

$$C_{\mathrm{vv}}(t)=\frac{\langle \vec{v}_i(t+\tau)\cdot\vec{v}_i(\tau)\rangle}{\langle \vec{v}_i(\tau)\cdot\vec{v}_i(\tau)\rangle}, \tag{3}$$

where $\vec{v}_i(t)$ is the velocity vector of atom i in a water molecule at time t and the angular brackets denote averaging over all atoms of such type in the system and over initial

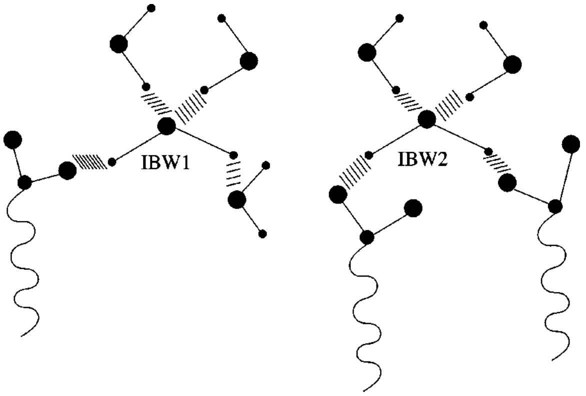

FIG. 2. Schematic representation of IBW1 and IBW2 types of interfacial water molecules. Water molecules at the interface that are not hydrogen bonded to any surfactant, but are instead coordinated fully to other water molecules in the vicinity, are denoted as IFW.

times τ. The Fourier transform of the velocity correlation function provide a direct measure of the vibrational density of states as a function of the frequency.

III. RESULTS: LIFETIME OF THE HYDROGEN BOND AND OF INTERFACIAL SPECIES

We have provided a schematic illustration in Fig. 2 of the two bound interfacial water species that describes their bonding pattern with the head groups. The free water molecules are present in the interfacial region, however, they are not oriented properly to form a hydrogen bond with the PHG. As discussed earlier [27,28], the concentration of IFW:IBW1:IBW2 is 9:80:11.

A. Lifetime of the water-surfactant hydrogen bond

We had shown earlier that the hydrogen bond formed between the water molecules at the interface and the polar head groups of the surfactant has a much larger lifetime than the hydrogen bonds that water molecules form between themselves [26]. In Fig. 3, we show similar lifetime correlation functions for the individual species in the interfacial region. Consistent with our earlier observations [26], the $S_{\mathrm{HB}}(t)$ functions for both the bound species are much slower than the corresponding function for the water-water hydrogen bond in pure water. The function for IBW1 water is slower than that for the doubly hydrogen bonded IBW2 water species. The latter is in a constrained bonding arrangement [27,28], and thus the average lifetime of any one of its hydrogen bond is shorter than that formed by the IBW1 water species. In our earlier work [26], the condition on the pair energy of the water molecule with the PHGs to determine the presence of a hydrogen bond was not included. The current results, which include such an energy criterion, confirm our findings on the long lifetime of the bound water-PHG hydrogen bond [26]. In addition, we are also able to clearly distinguish the contributions from the two types of interfacial bound water.

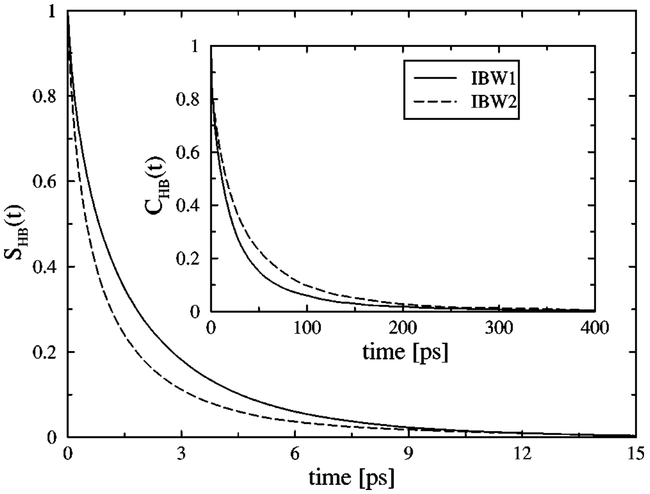

FIG. 3. Hydrogen bond lifetime correlation function $S_{\mathrm{HB}}(t)$ for IBW1 (continuous line) and for IBW2 (dashed line) types of water molecules. The inset shows the decay of $C_{\mathrm{HB}}(t)$ for the same.

The $C_{\mathrm{HB}}(t)$ function, presented in the inset of Fig. 3, shows a similar trend as the $S_{\mathrm{HB}}(t)$ function. As noted earlier, this function allows for the reformation of the hydrogen bond, and thus would take into account, recrossing of the barrier as well as long-time diffusive behavior. Again, we find a characteristic slow decay in its relaxation. The relatively longer lived $C_{\mathrm{HB}}(t)$ function for the IBW2 species could come from the break and reformation of the bond over short distances or angles. The IBW2 species will have a higher propensity to reform hydrogen bonds than the IBW1 species, since the latter is only singly hydrogen bonded to the PHGs. Note that in this formalism, we only track the existence of a particular bond of the interfacial water species, and hence the behavior of the functions for IBW1 and IBW2 may not be very different.

B. Lifetime of the interfacial water species

A bound water species could remain bound (to another PHG), even if the hydrogen bond it had originally formed with a particular PHG is broken. Hence, it is important to obtain information on the lifetime of the species, apart from the lifetime of the w-PHG bond discussed in Fig. 3. We present these data on the lifetime correlation function of the species in Fig. 4. As discussed in the preceding section, these functions are essentially similar to the $S_{\mathrm{HB}}(t)$ functions defined above, but instead are defined for the identity of the species involved. We observe that the IFW species is short lived and that the IBW1 species is the longest lived. In our earlier work, we had concluded that the IBW1 species is the thermodynamically stable species [27,28]. The current calculations indicate that this species is also dynamically more stable than the IBW2 or the IFW species. The IBW2 species, although preferred on energetic grounds due to the contribution from two strong w-PHG hydrogen bonds, is disfavored entropically. It requires the simultaneous presence of two

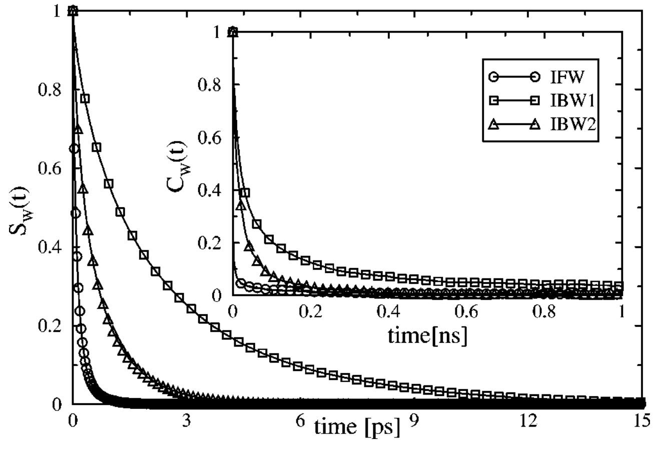

FIG. 4. Species lifetime correlation function $S_W(t)$ for different interfacial water molecules. The inset shows the $C_W(t)$ function for the same. Numerical data points are shown infrequently for clarity.

surfactant head groups in the proper geometry, which is rare. We present the $C_W(t)$ functions in the inset of Fig. 4. Again, the function for IBW1 is much slower than that IBW2 or that of IFW. The slow component presumably arises out of a few water molecules (say, of IBW1 type) that lose their identity and reform a w-PHG hydrogen bond either with the same PHG or with another PHG. These molecules probably have long residence times within the first few hydration layers around the micelle.

Within the interfacial region, there is a constant exchange of water molecules between the three states, IBW2, IBW1, and IFW. The microscopic reactions between IBW2 and IBW1 on one hand and IBW1 and IFW on the other, are reversible and are described by four distinct rate constants, as described below,

$$\mathrm{IBW2} \underset{k_{12}}{\overset{k_{21}}{\rightleftarrows}} \mathrm{IBW1} \underset{k_{F1}}{\overset{k_{1F}}{\rightleftarrows}} \mathrm{IFW}. \quad (4)$$

Determining these rates in such a complex system that is also *open* to bulk water, is a challenge to us and to other simulators, although the basic formalism exists [45]. Here, we concentrate on generic features that one can derive based on the concentrations of these species. The reactions delineated here are the elementary events, and hence the condition of detailed balance must be obeyed for each of these reactions. The ratio of IBW1 to IBW2 is ≈ 8. Hence the rate of production of the IBW1 species from the IBW2 species (k_{21}) must be a factor of 8 larger than the rate of the reverse reaction. This rationalizes the shorter lifespan of the IBW2 species. Note that this ratio of eight in the rates of interconversion between IBW1 and IBW2 species will be reduced by the other reaction proceeding in the system, that is between IFW and IBW1. This too will add to the attrition in the lifetime of the IBW1 species. Fitting the S_{HB} data of lifetimes presented in Fig. 4 to multiexponential forms, we find that the average lifetime of the IBW2 species is 0.62 ps and that of the IBW1 species is 2.26 ps. Thus, the IBW1 species is around 3.6 times longer lived than the IBW2 species, which is not inconsistent with the arguments presented above.

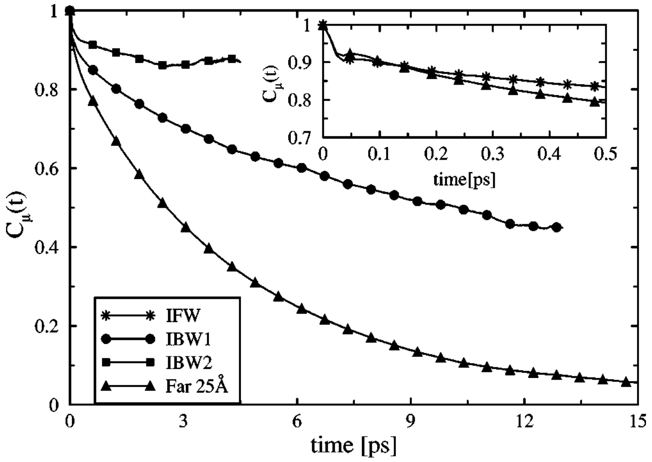

FIG. 5. Dipolar reorientational time correlation function $C_\mu(t)$ for the interfacial water molecules. The inset compares the data for the IFW water species and for water molecules that are at least 25 Å away from the micellar surface. The latter behave like water in bulk. The time resolution of the underlying trajectory used in this calculation is 12 fs. Numerical data points are shown infrequently for clarity.

C. Reorientational dynamics of interfacial water

Having determined the intrinsic lifetimes of these interfacial water species and of the strong hydrogen bonds that they form with the polar head groups of the surfactant molecules that constitute the micellar surface, we turn our attention now to their single-particle dynamics, namely, their ability to reorient. The behavior of the dipolar reorientational TCF of the individual bound water species illuminates our understanding on the important issue of the slow decay observed in our simulations earlier [22,25,47]. With this objective, we have calculated the dipole-dipole TCFs of the IFW, IBW1, and IBW2 species, which are compared to the function for water molecules far away from the micelle in Fig. 5. These data were obtained with a time resolution of 12 fs. The data for water molecules that are at least 25 Å away from the micellar surface shows that they behave just like bulk water molecules. The inset to the figure shows the very fast decay of the curve corresponding to the IFW species, very similar to that of water far from the micelle. This validates our christening this species as free interfacial water, IFW. The plot also displays the corresponding TCF for the IBW1 and IBW2 species. The reorientation of the IBW1 water, possessing a single, strong hydrogen bond with the PHG is slowed down relative to that of the IFW species, while the IBW2 water species being in a constrained environment is able to rotate only within a narrow cone. This is borne out by the plateauing of the dipolar TCF after a few picoseconds, found in the data for the IBW2 species. The strict definitions of a water-PHG hydrogen bond precludes us from probing the TCFs any further than the durations shown in the figure, as

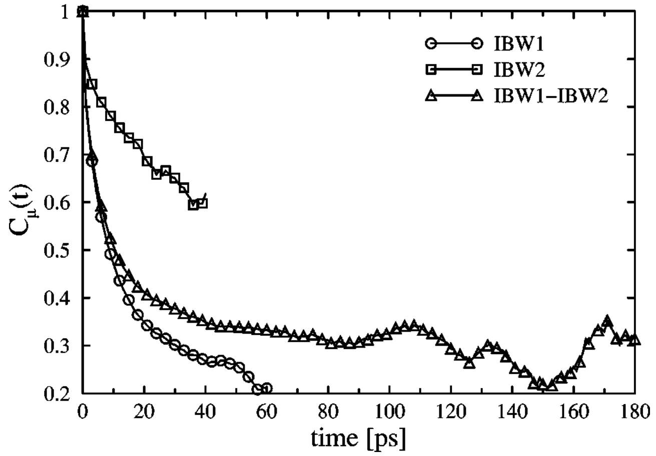

FIG. 6. Dipolar reorientational time correlation function $C_\mu(t)$ for bound water molecules. The data denoted by the legend, IBW1-IBW2, correspond to all bound water molecules irrespective of their being in state IBW1 or IBW2. The time resolution of the underlying trajectory used in this calculation is 1 ps. Numerical data points are shown infrequently for clarity.

these species themselves cease to survive, a few picoseconds beyond the maximum times for which the TCFs have been displayed. However, a bound water is unlikely to lose its memory of orientation, once it has ‘‘broken’’ its w-PHG hydrogen bond. It is more likely that its orientation is preserved for some longer duration and that the strict definition of the existence of the bound nature of water prevents one from probing the orientation any further. This indicates that we could continue to probe the dipolar TCFs of these waters for a longer duration, if we relax the conditions on the nature of the bound water species. We describe such a calculation below.

Water molecules within a 10-Å hydration layer around the micelle exhibit a pronounced slowing down in their reorientation [22,47]. The long-time behavior of the $C\mu(t)$ shows a near-constant value, indicating that the molecules are not able to explore fully the all possible orientations. In our simulations, the near-constant value of $C\mu(t)$ extends to a few hundred picoseconds and appears to be a general feature to interfacial water near hydrophilic surfaces in complex systems. This observation may seem apparently inconsistent with the data presented in Fig. 4 or Fig. 5, where the bound water of either the IBW1 or IBW2 type, is seen to lose their identity within few tens of picoseconds. The resolution of this apparent conflict, lies, as we discussed earlier, in the rather strict definition of the lifetime of the bound species. We have calculated the same functions exhibited in Fig. 5, with a coarser resolution of 1 ps, and displayed them for the bound water species in Fig. 6. Shown here are the $C_\mu(t)$ functions obtained from a trajectory where the coordinates of all the atoms were stored every 1 ps, instead of the 12 fs used in Fig. 5. This effectively allows for the consideration of reformation of the w-PHG hydrogen bond, thus extending the lifetime of the bound water species. We are thus able to observe the reorientational TCFs of these species for a much longer duration than what was possible in Fig. 5. Such a data, presented in Fig. 6 clearly shows the existence of very slow dynamics in the time scales of hundreds of picoseconds. More importantly, the reorientational TCF obtained for all bound water species, irrespective of the IBW1 or the IBW2 type, exhibits a plateau followed by a slow decay. These results shows that exchanges between the IBW1 and the IBW2 states of water molecules artificially prevents one from obtaining the dipolar reorientational TCF of either of these individual species for times longer than their ‘‘intrinsic’’ lifetimes. However, the TCF for all bound water species, irrespective of their type, clearly proves the existence of a long-lived plateau running probably into hundreds of picoseconds. As mentioned earlier, these results should be of relevance to other hydrophilic surfaces as well [46].

It is thus clear that the long-time slow decay in the dipolar reorientational TCF arises out of (i) the orientational locking-in of the IBW2 species due to its two strong w-PHG hydrogen bonds, (ii) the interconversion between the IBW1 and IBW2 species.

The latter, a secondary process, merits further discussion. From the TCFs shown in Fig. 6, one can obtain average time constants for the relaxation of the reorientation of the dipole. This is certainly valid if a water molecule, for example, was of the IBW1 type at time zero, and remained so thereafter. However, the average lifetime of the w-PHG hydrogen bond is of the order of 2 to 40 ps (see Fig. 3), and hence one can expect a fair number of water molecules to interconvert between the IFW, IBW1, and IBW2 states within the interfacial layer. Hence, the said IBW1 water molecule may form an additional w-PHG bond and change its nature to that of a IBW2 type. This would, in effect, set the clock for reorientation of its dipole to the dipolar TCF corresponding to the IBW2 type shown in Fig. 6, which is much slower than that for the IBW1 species. Such interconversions between the interfacial water species will add to the slow decay of the intrinsic species shown in Fig. 6 and would contribute, specifically, to the intermediate time scales (tens of picoseconds) in the TCF, while the orientational locking-in of the IBW2 species will contribute to the long-time slow decay (hundreds of picoseconds). Further, a few members of the IBW2 type can be long lived, and they too would contribute to the long-time behavior of the total dipolar reorientational TCF. It is the sum effect of these processes that we had observed earlier in our preliminary investigations of the reorientations of interfacial water molecules. This interpretation of the exchange between the species present at the interface to contribute to the slow dynamics is consistent with the postulates of Nandi and Bagchi [29,15].

IV. VIBRATIONAL SPECTRUM OF INTERFACIAL WATER AND DENSITY OF STATES

Thus far, we have provided microscopic evidence for the slowdown in the dynamics of interfacial water due to the presence of the polar, fluctuating micellar surface. The interface influences not only the single-particle quantities, such as the dipolar reorientation of the water molecules, but it also affects the ability of water molecules to librate (hindered rotation), and their ability to alter the hydrogen bond network through bond bending excitations. We probe such molecular motions through calculations of the velocity time correlation function of the water molecules and the density of states of the respective motions.

Low frequency Raman and neutron scattering experiments on aqueous protein solutions have shown the presence of *excess density of states*, called the *boson peak*, at around 3 meV (24 cm^{-1}) [48], which has been corroborated by molecular dynamics simulations [7,20,49]. This boson peak arises from the hydration layer around biomolecules. In the present work, however, we concentrate on excitations of relatively higher frequencies. Specifically, we study the effect of the interface on the O···O···O bending, O···O stretching, and the librational modes of water, that are observed at around 50 cm^{-1}, 200 cm^{-1}, and at 500 cm^{-1} [50,51], respectively, in bulk water. Note that all the three are intermolecular vibrational modes and involve hydrogen bonding. All these modes play an important role in the dynamics of chemical processes in water, such as solvation dynamics and charge transfer [52,53].

We have obtained the velocity autocorrelation functions of both the oxygen and the hydrogen atoms of interfacial water molecules and have obtained their power spectra. The results indicate strong effects of the micellar surface.

The computed velocity correlation functions are presented in Fig. 7 where we have also compared them with corresponding functions for water molecules far away from the micelle. In Fig. 7(a), we present the $C_{\mathrm{vv}}^{\mathrm{O}}(t)$ for the oxygen atoms of the interfacial water species. As expected, there is a clear trend in the variation of this function, particularly, near the first minimum that corresponds to backscattering of the atoms. The minimum for IBW2 is deeper than that for the rest of the species, a direct consequence of the enhanced rigidity of its environment. The function for water molecules far away from the micellar surface is identical to its behavior in bulk. The function for IFW follows closely that of bulk water, however, it exhibits a shallower first minimum than bulk water. We had shown earlier [27] that the first coordination shell (up to a distance of 3.5 Å) around the IFW species contains 4.4 water molecules and 0.3 PHG oxygens, while that around the IBW1 species contains 4.1 water molecules and 1.2 PHG oxygens, and that of the IBW2 species contains 3.0 water molecules and 2.1 PHG oxygens. This marginal decrease in the coordination number around the IFW species could be a prime reason for the shallower first minimum in its $C_{\mathrm{vv}}^{\mathrm{O}}(t)$ than that for bulk water. These broad conclusions are substantiated by an analysis of the $C_{\mathrm{vv}}^{\mathrm{H}}(t)$ function for the hydrogen atoms of the interfacial water species presented in Fig. 7(b). The enhanced rigidity around IBW2 water manifests itself in a deeper minimum, and again, the data for IFW species mirrors closely the behavior for water in bulk. However, the value for the IFW species at the first minimum is less negative than that for bulk water. Lee and Rossky [2] had found a similar behavior for water molecules present near a hydrophobic surface. This indicates that the IFW species might be somewhat buried within the micelle, in proximity to the CF_2 groups adjacent to the polar head group. The data for IBW1, the abundant species in the interface lies between the functions for IFW and that of IBW2.

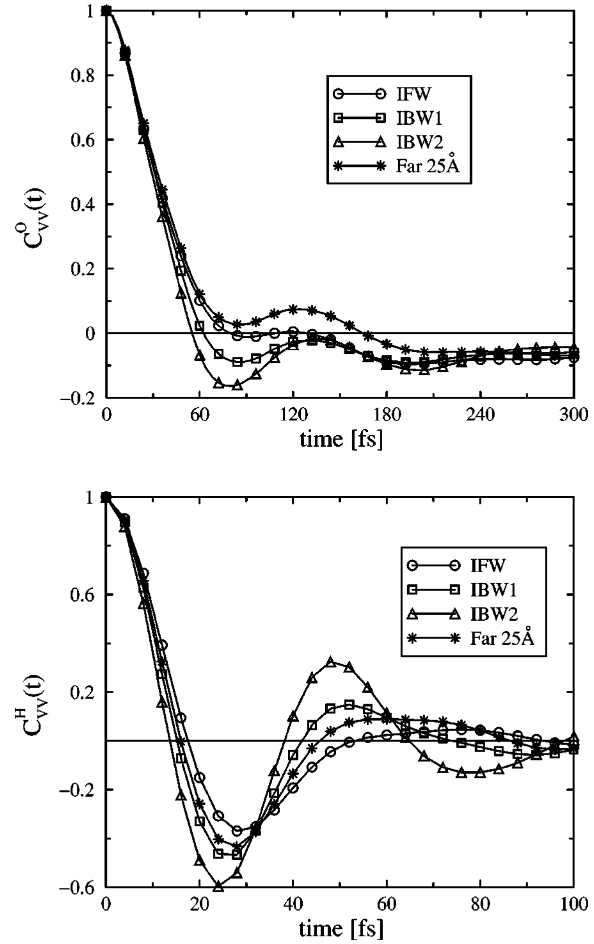

FIG. 7. (a) Normalized velocity autocorrelation function $C_{\mathrm{vv}}^{\mathrm{O}}(t)$ of the oxygen atoms for various interfacial water molecule types compared with that for water molecules that are at least 25 Å away from the micellar surface. The latter behave like water in bulk. Numerical data points are shown infrequently for clarity. (b) Normalized velocity autocorrelation function $C_{\mathrm{vv}}^{\mathrm{H}}(t)$ of the hydrogen atoms for various interfacial water molecule types compared with that for water molecules that are at least 25 Å away from the micellar surface. The latter behave like water in bulk. Numerical data points are shown infrequently for clarity.

The power spectra, obtained by a Fourier cosine transform of these velocity auto time correlation functions, are displayed in Fig. 8. In Fig. 8(a), we provide these data obtained from oxygen atoms, for all interfacial water species, i.e., for water molecules that reside within a distance of 4.5 Å from any of the surfactant head groups. Transforms of individual water species were noisy, and hence are not provided here. Relative to water in the bulk, we observe a clear blue shift in the frequency corresponding to the O···O···O bending mode by about 40 cm^{-1} for these interfacial water molecules, while the stretching mode seems not to be affected by the interface, consistent with earlier observations on aqueous protein solutions [54,20]. The most significant change in the vibrational spectrum occurs for the librational mode of the water molecules, which can be studied from the power spectrum for the hydrogen atoms of the

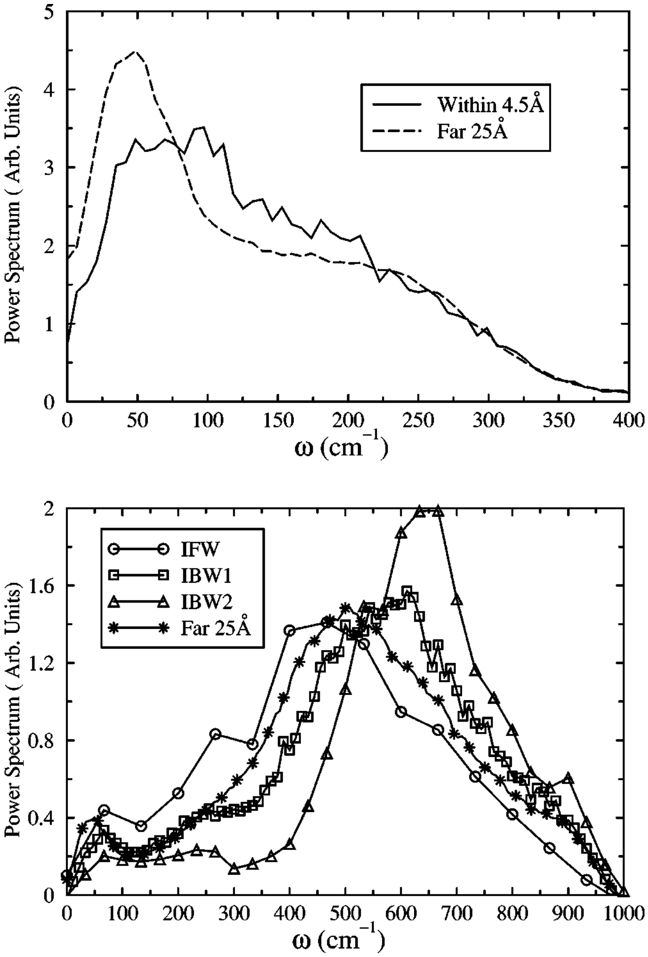

FIG. 8. (a) Power spectrum of the $C_{vv}^{O}(t)$ function for oxygen atoms of water molecules lying within 4.5 Å from any polar head group of the micelle compared with that for water molecules that are at least 25 Å away from the micellar surface. The latter behave like water in bulk. (b) Power spectrum of the $C_{vv}^{H}(t)$ function, for hydrogen atoms of various interfacial water molecule types compared with that for water molecules that are at least 25 Å away from the micellar surface. The latter behave like water in bulk.

interfacial water species. Again, the trend observed in Fig. 7(b) is seen in their power spectra. The librational mode of IBW2 is most affected, and is shifted considerably, by about 150 cm^{-1}, whereas that of the IBW1 species is blue shifted by about 100 cm^{-1} relative to water bulk and is observed at 600 cm^{-1}. *These data agree well with recent incoherent, inelastic neutron scattering experiments on aqueous DNA and membrane solutions, where the vibrational signature of interfacial water molecules was found to be predominant in the* 400–600 cm^{-1} *range* [32]. The hydrogen atoms also contribute to the O⋯O⋯O bending mode at around 60 cm^{-1}, whose shift to higher frequencies is also observed from the oxygen spectrum. These frequency shifts in the bending and librational modes must arise from the strong and longer-lived w-PHG hydrogen bond. Evidence for the strength and the lifetime of these bonds have been provided earlier. Therefore, one may conclude that water structure on the surface is more rigid. While this is of course expected on simple arguments, the strong effect on bending and librations and the negligible effect on stretching were not anticipated, but are in agreement with IINS results. This needs further study.

V. CONCLUSIONS

The results of the present atomistic MD simulations provide microscopic explanation for several of the observations reported earlier [23–26]. We find that the hydrogen bonds between the bound water molecules and the polar headgroups are much longer lived, on the average, than the hydrogen bonds that water molecules form among themselves. The lifetime of the w-PHG hydrogen bond of the IBW2 type of water molecule is shorter than that of the IBW1 type. This can be rationalized in terms of the constrained nature of the environment around the IBW2 water molecule. This aspect is also reflected in the lifetimes of the intrinsic species. The IBW1 water is dynamically more stable than the IBW2 species, which is consistent with our observations on its concentration, energetics, and environment.

We have also calculated *individual* dipolar reorientational time correlation functions for the three species of interfacial water molecules and have compared them to the corresponding function for water molecules in bulk. The IFW water molecule is able to reorient in the same time scale as the bulk water. *Thus, the interfacial free water appears to be energetically, structurally, and dynamically rather similar to, albeit a bit slower than, the water in the bulk*. The bound water molecules exhibit very different dynamical properties. The IBW1 water molecule exhibits a slow relaxation with the longest component around several tens of picoseconds, while the IBW2 water molecule exhibits a long-lived plateau region in the time correlation function. This can be ascribed to the two strong w-PHG hydrogen bonds that this species makes, resulting in a significant loss of orientational freedom. About 10% of the interfacial water molecules are of the IBW2 type, and hence this plateau can be directly implicated in the long-time relaxation of the dipolar TCF of all the interfacial water molecules that we had reported earlier [23,25]. The current set of results thus explain, comprehensively, the microscopic origin of the slow decay in the reorientational TCF of interfacial water molecules in aqueous macromolecular solutions.

A significant finding of the present work is the modification in the vibrational spectral features of the interfacial water molecules. We observe a blue shift in the O⋯O⋯O bending mode of about 40 cm^{-1}. The librational mode of the water molecule at around 500 cm^{-1} undergoes a blue shift of about 100 cm^{-1}. Surprisingly, the 200 cm^{-1} translational, O⋯O stretching mode is entirely unaffected due to the interface. These results are somewhat surprising and indicate that the potential surface around the interfacial water molecules is more rigid along the orientational degrees of freedom rather than along the translational degrees. This conclusion is also consistent with observations on the relative effects of the interface on translational diffusion of water molecules and their orientational relaxation [24,55]. Our results on the vibrational spectra also adds support to the recent IINS data on aqueous membrane and DNA solutions, where the interfacial water molecules have an altered vibrational spectrum in the 400–600 cm^{-1} range [32]. We plan to probe these aspects further by a normal mode analysis of the potential energy hypersurface. This could explain the reason for the lack of change in the 200-cm^{-1} intermolecular vibrational mode. This point deserves further study.

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