

Hydrogen Bond Dynamics at Water/Organic Liquid Interfaces

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Hydrogen bond dynamics at the neat interface between water and a series of organic liquids are studied with molecular dynamics computer simulation. The organic liquids are nonpolar (carbon tetrachloride), weakly polar (1,2-dichloroethane), and polar (nitrobenzene). The effect of surface polarity and surface roughness is examined. The dynamics are expressed in terms of the hydrogen bond population autocorrelation functions and are found to be nonexponential and strongly dependent on the nature of the organic phase. In particular, at all interfaces, the dynamics are slower at the interface than in the bulk and sensitive to the location of the water molecules along the interface normal.

1. Introduction

Over the last several decades, hydrogen bonding structure and dynamics have been the focus of numerous experimental and theoretical papers.¹ Of particular recent interest, motivated in part by the ability to experimentally probe the dynamics on a femtosecond time scale,^{2–4} has been the effort to understand the time-scale and detailed dynamics involved in the process of making and breaking hydrogen bonds in bulk water and aqueous solutions.^{5–10}

With the recent development of broadband sum frequency generation spectroscopy¹¹ and its application to liquid surfaces,¹² there is a growing interest in understanding the hydrogen bonding dynamics at aqueous interfaces.^{13–17} Paul and Chandra have calculated the hydrogen bond dynamics at the air–water interface and the water/metal interface and found slower relaxation than in bulk water.¹⁶ However, using a polarizable water model, Liu, Harder, and Berne have shown that the hydrogen bond dynamics at the water liquid/vapor interface are in fact faster than those in bulk water.¹⁷ If, however, one removes the effect due to the much faster diffusion of water molecules at the liquid/vapor interface, the hydrogen bond lifetime is found to be longer at the interface. The hydrogen bond lifetime between water molecules and other groups in proteins and micelles was found to be slower than that in bulk water.^{13–15} However, no determination of water–water hydrogen bond lifetime was reported at the water/liquid interface.

In a number of publications,^{17–22} we and others have made the observation that although the average number of hydrogen bonds that an interfacial water molecule participates in (2–3) is smaller than the number in bulk water (3–4), the probability that an interfacial hydrogen bond is intact (calculated by dividing the number of hydrogen bonds of a tagged molecule by its coordination number) is larger at the interface than in the bulk. This was the case for both hydrophobic^{18,20,22} and hydrophilic surfaces^{19,21} and was interpreted²³ as suggesting that the hydrogen bond lifetime is longer at the interface. Besides the importance of confirming the above assertion, an additional motivation for the present work is to elucidate to what degree two fundamental characteristics of a liquid/liquid interface, namely its dynamical roughness and polarity, influence hydrogen bond dynamics. Results of molecular dynamics simulations²³ and experiments^{24,25} suggest that the liquid/liquid interface

region is quite narrow (1–2 nm), and that this width is the result of thermally excited nanometer scale capillary waves giving rise to a dynamically rough surface. Since the existence of these density fluctuations (water “fingers”) must involve a change in the local water coordination number, we expect that their dynamics will influence hydrogen bond lifetimes. We test for this effect by considering interfaces with different roughness and by utilizing external perturbations. Molecular dynamics simulations,^{26,27} theoretical calculations,²⁸ and recent experiments^{29–33} suggest that an important characteristic of a liquid/liquid interface is its polarity and its variation across the interface. We test for the importance of this concept here by considering a series of liquids with varying polarity and computing the “hydrogen bond lifetime profile” by looking at narrow slabs perpendicular to the interface.

2. Systems and Methods

The molecular systems studied in this work have been described in detail elsewhere. Briefly, in each system 1000 water molecules are used to form a liquid/liquid interface with several hundred organic liquid molecules (256 nitrobenzene or 500 CCl₄ or 500 1,2-dichloroethane). The molecules are placed in a “box” with dimensions $L_x \times L_y \times L_z$ ($L_x = L_y$, $L_z > L_x$). L_z is allowed to fluctuate to maintain a fixed normal pressure of approximately 1 atm. Periodic boundary conditions in the three dimensions give rise to two liquid interfaces at $Z = 0, \pm L_z/2$. The reaction field method ($\epsilon = 20$) is used to calculate the contribution of the long-range forces outside the switching distance of $r = L_x/2$.

The water is modeled by using a flexible SPC potential, which has been shown to describe reasonably well the interfacial properties of water.²³ While the hydrogen bond lifetime in bulk water calculated with this model ($\tau_{\text{Hx}} = 5$ ps, see below) is quite close to the value (5.26 ps) determined by using a polarizable water model,¹⁰ it will be interesting to reexamine the calculations presented below using a polarizable potential. This requires a reparametrization of the organic liquid intermolecular potentials, and this work is in progress.

The organic liquids are described by using a flexible, all-atom model with an intramolecular potential based on harmonic bond stretching and bending, and a cosine series for the torsion (and improper torsion in the case of nitrobenzene). The

intermolecular interactions are modeled by using the standard Lennard-Jones plus electrostatic terms. All the intramolecular and intermolecular potential parameters are given in previous publications.^{19,21,34} The Bertholet rule for mixtures³⁵ is used to determine the water–organic liquid Lennard-Jones parameters.

The hydrogen bond dynamics is followed by using Yamamoto's time correlation approach to calculate chemical reaction rate.³⁶ This method has been extensively used in recent years to examine the hydrogen bond dynamic in bulk water and in aqueous solutions^{5–10} and at interfaces,^{13–17} and it is outlined here only briefly.

To study the hydrogen bond dynamics, one needs a working definition of a hydrogen bond. While several such definitions are possible, the one selected in this paper is the same used by Luzar and Chandler,⁵ namely, two water molecules are considered hydrogen bonded if the distance between their oxygen atoms is less than 3.5 Å (the first minimum in the water OO radial distribution function) and the OHO angle is equal or less than $\pi/6$. The exact choice of these two structural parameters is not expected to significantly change the calculated hydrogen bond lifetimes.^{5,7,8} With this definition, a dynamical random variable h is defined as follows: If two *tagged* water molecules are hydrogen bonded at $t = 0$, $h(t)$ is equal to 1 if these two molecules are still bonded at a later time t , otherwise it is equal to 0 (but may become 1 again later if *these* two water molecules reformed their bond). An equilibrium correlation function $c(t)$ is defined by using the random variable h :

$$c(t) = \frac{\langle h(t)h(0) \rangle}{\langle h \rangle} \quad (1)$$

where the relation $\langle h(0)h(0) \rangle = \langle h \rangle$ has been used (since of course $h^2 = h$), and the ensemble average is over all pairs and all time origins. The function $c(t)$ has the physical meaning of the probability that a given hydrogen bond exists at time t given that it existed at time zero. Since it is unlikely that a particular pair of water molecules will remain hydrogen bonded as times progress, $c(t)$ starts at 1 and decays to 0. The reader is referred to a number of papers where the choice of this and other correlation functions is discussed.^{6–8}

To examine the hydrogen bond dynamics at the liquid/liquid interface, the simulation box is divided into slabs of thickness $d = 3.5$ Å perpendicular to the Z axis (parallel to the interface). This choice of d approximately corresponds to the thickness of one water "layer". $c_n(t)$ is calculated for the n th slab by including the contributions of all hydrogen bonds between pairs of water molecules where at least one of them belongs to the given slab. If a water molecule changes its initial slab during the simulation, its time history begins to contribute to the average in the new slab. We checked that this procedure gives consistent results by confirming that the $c(t)$ are identical to each other (within the statistical error, see below) in all the bulk slabs and to the $c(t)$ calculated for a bulk system containing 500 water molecules (this also shows no system-size dependence). The correlation function in eq 1 is calculated for each system by averaging the results of 40 independent 200 ps trajectories with initial velocities selected from a Boltzman distribution at $T = 298$ K. The configurations used are separated by 10 fs and are generated by using the velocity version of the Verlet algorithm with a time step of 0.5 fs.

3. Results and Discussion

Figure 1 shows the density profiles at the liquid/liquid interface region in the three systems. The Gibbs dividing surface

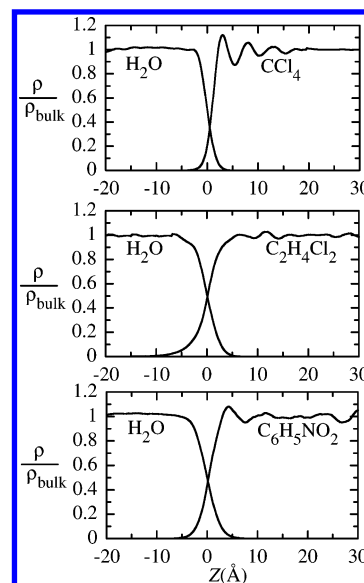


Figure 1. Density profiles of the neat liquid/liquid interfaces studied in this work. In all systems, $Z = 0$ is the location of the (water defined) Gibbs surface. Each profile is calculated by using a 4 ns trajectory at $T = 298$ K.

with respect to the water phase is located at $Z = 0$. The region where the water density varies the most (from 90% to 10% of the bulk value) is approximately 3.5, 5.4, and 5.3 Å for the water/CCl₄, water/DCE, and water/nitrobenzene interfaces, respectively. For the purpose of calculating the hydrogen bond lifetime, the Gibbs surface is taken to define the center of the region labeled G whose width is 3.5 Å. The two regions (whose widths are also 3.5 Å) next to this are labeled G+ and G− for the slabs on the organic side of the interface ($Z > 0$) and the water side ($Z < 0$), respectively. Thus

region G−: $-5.25 \text{ Å} < Z < -1.75 \text{ Å}$

region G: $-1.75 \text{ Å} < Z < 1.75 \text{ Å}$

region G+: $1.75 \text{ Å} < Z < 5.25 \text{ Å}$

The hydrogen bond dynamics are also followed in all the slabs with Z less than -5.25 Å to determine the extent of the surface effect, as well as for error analysis. While there are water molecules with $Z > 5.25$ Å, especially for the wider DCE and nitrobenzene interfaces, their number is too small for reasonable statistical accuracy, and the corresponding correlation functions are too noisy and are not reported.

The calculated $c(t)$ values for all the liquids are shown in Figure 2. The results are shown in a semilog plot to demonstrate the nonexponential character of the dynamics. In each panel, the $c(t)$ for the three interfacial regions are compared with the bulk. In the case of DCE and nitrobenzene, the $c(t)$ values for the slab just "below" the G− region (corresponding to $-8.75 \text{ Å} < Z < -5.25 \text{ Å}$) are also shown. The statistical errors are estimated (from the standard deviations of the data partitioned to 10 segments) to be less than or equal to the thickness of the lines for $t < 8$ ps, and 2–3 times the line thickness for $t > 8$ ps. The results in bulk water in the 7 different "bulk" slabs all fall within these error bars.

For each liquid, there is a gradual slowing down of the relaxation of $c(t)$ and a corresponding increase in hydrogen bond lifetime as one moves from bulk water to the water/organic liquid interface. Such distance-dependent behavior has been found in other interfacial systems.^{15,16} A comparison of the three liquids shows that the slowest relaxation takes place at the water/

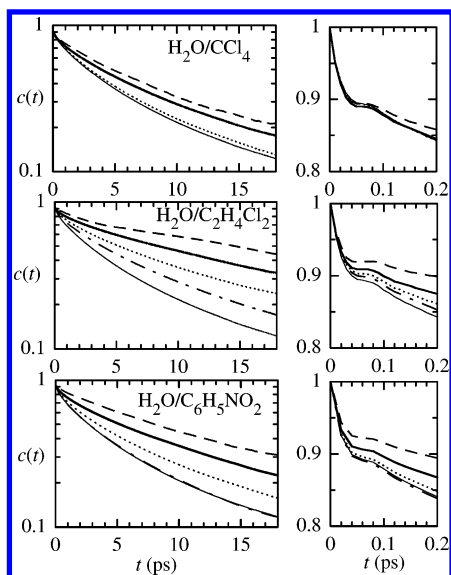


Figure 2. The hydrogen bond correlation function (eq 1) for the different interfaces shown using a semilog scale. In each panel, the thin solid, dotted, thick solid, and dashed lines correspond to bulk water and region G[−], G, and G⁺, respectively, as defined in the text. In the bottom two panels, the dashed–dotted line gives the relaxation in the slab “below” the G[−] slab. The panels on the right depict (linear scale) the short time behavior of $c(t)$. The data for each interface are calculated from an average of 40 trajectories of 200 ps each at 298 K.

TABLE 1: Decay Times of the Hydrogen Bond Correlation Function in the Different Regions and Different Systems

system	location ^a	τ^b (ps)
H ₂ O/CCl ₄	G ⁺	8.4 ± 0.3
	G	7.0 ± 0.2
	G [−]	5.3 ± 0.2
H ₂ O/nitrobenzene	G ⁺	13.7 ± 0.8
	G	9.6 ± 0.3
	G [−]	6.3 ± 0.2
	GB	4.8 ± 0.2
H ₂ O/1,2-dichloroethane	G ⁺	26 ± 3
	G	15 ± 1
	G [−]	9.6 ± 0.3
	GB	7 ± 0.2
bulk water		5 ± 0.1

^a Location key: G⁺, $1.75 \text{ \AA} < Z < 5.25 \text{ \AA}$; G, $-1.75 \text{ \AA} < Z < 1.75 \text{ \AA}$; G[−], $-5.25 \text{ \AA} < Z < -1.75 \text{ \AA}$; GB, $-8.75 \text{ \AA} < Z < -5.25 \text{ \AA}$. ^b τ is the time it takes for $c(t)$ to reach the value $1/e$.

DCE interface and the fastest (shortest lifetime) at the water/CCl₄ interface. If one uses (for comparison purposes) the time required for $c(t)$ to reach $1/e$ as an indication of the lifetime,⁸ the results in the Gibbs surface region G are $\tau_{\text{DCE}/\text{H}_2\text{O}} = 15 \pm 1$ ps, $\tau_{\text{NB}/\text{H}_2\text{O}} = 9.6 \pm 0.3$ ps, and $\tau_{\text{CCl}_4/\text{H}_2\text{O}} = 7.0 \pm 0.2$ ps, compared with those of bulk water, $\tau_{\text{H}_2\text{O}} = 5.0 \pm 0.1$ ps. Table 1 summarizes the lifetimes in the other slabs.

An examination of the short-time dynamics ($t < 0.2$ ps, right panels in Figure 2) reveals another interesting difference between the polar vs nonpolar organic liquids: The short-time dynamics at the water/CCl₄ interface is identical with that in bulk water, while the short time dynamics at the two polar liquid/water interfaces are almost identical to each other and already show significant deviation from bulk water.

As discussed by several authors,^{5,8–10,17} the relaxation of the correlation function $c(t)$ involves breaking an existing bond. The short-time dynamics reflect mainly librations and O–O vibrations, which are sensitive to the local intermolecular interactions. The longer time behavior involves rotational and translational diffusion, so that relaxation of $c(t)$ is possible if another water

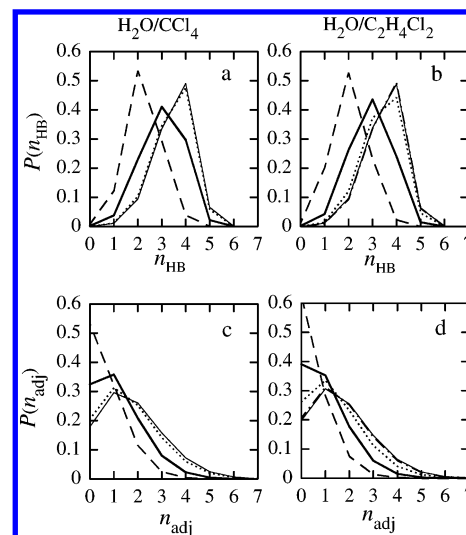


Figure 3. Top panels: The probability distribution of the number of hydrogen bonds per water molecule. Bottom panels: The probability distribution of the number of adjacent but non-hydrogen bonded water molecules. In each panel, the thin solid, dotted, thick solid, and dashed lines correspond to bulk water and regions G[−], G, and G⁺, respectively. For the water/DCE interface, the dashed–dotted line gives the distribution in the slab “below” the G[−] slab.

molecule is available to form a new bond. The source of the nonexponential behavior is the coupling between diffusion and the random dynamics of forming and breaking hydrogen bonds. At the interface, each water molecule is surrounded by fewer water molecules, and thus the probability of having a neighboring molecule form a bond decreases, which in turn increases the lifetime. This is demonstrated in Figure 3, which shows the distribution of the number of hydrogen bonds per water molecule at different locations (top panels), as well as the distribution of the number of adjacent but non-hydrogen bonded water molecules.

Given the above data, how then can one explain the differences between the three liquids? Consider first the case of the water/DCE vs water/CCl₄ interfaces. One clear difference between the structure of these two interfaces is the larger width of the water/DCE interface, as was demonstrated in Figure 1. The larger width is in part the result of thermally excited fingerlike water structures that are more pronounced in the case of water/DCE.¹⁹ This is possible because of the higher polarity of DCE and because the molecules of this liquid pack less efficiently (providing larger voids) than the spherical CCl₄ molecules, which is also clear from the oscillations in the density profile of CCl₄. The existence of this fingerlike structure increases the probability that all adjacent water molecules are hydrogen bonded (compare the dashed lines in panels c and d of Figure 3) with a corresponding dramatic increase in the hydrogen bond lifetime.

It is possible to demonstrate this effect by removing these types of structures from the system. A simple way to do this is by adding a weak external potential that penalizes a liquid molecule if it crosses the Gibbs surface toward the other phase. This creates a molecularly sharp interface, and the resulting density profiles are shown in Figure 4. The calculated $c(t)$ for the two sharp interfaces are shown in Figure 5. The results are consistent with the above interpretation: No change is observed in the case of the water/CCl₄ interface, while significant acceleration of the relaxation is observed in the case of the “top” slab of DCE. All the other slabs are not affected. The fact that the relaxation in regions G and G[−] are unaffected by the external perturbation and that the corresponding hydrogen bond

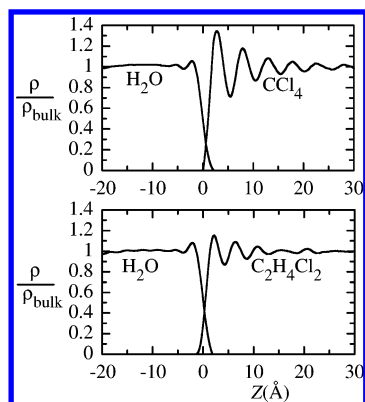


Figure 4. Density profiles of the two systems whose liquid/liquid surface is constrained to remain flat, as explained in the text.

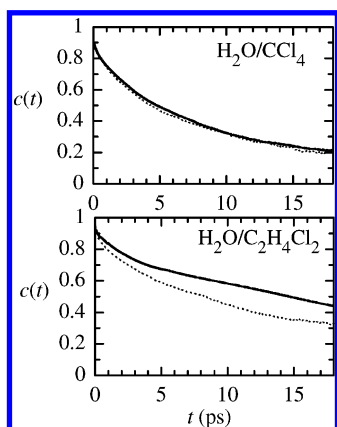


Figure 5. Comparison of the normal (solid line) vs flat (dotted line) hydrogen bonding correlation function in the G+ interface regions.

lifetime at the water/DCE interface is much longer than the lifetimes at the water/ CCl_4 interface in these regions suggest that the nature of the water–organic liquid intermolecular interactions also plays an important role. The stronger interactions between the water and DCE than between water and CCl_4 slow the diffusion of interfacial water molecules in the former case, which, as discussed by Luzar and Chandler⁵ and further demonstrated by Liu, Harder, and Berne for the water liquid/vapor interface,¹⁷ is an important mechanism contributing to the hydrogen bond relaxation dynamics. The stronger water–DCE intermolecular interactions manifest themselves in the observed effect on the water librations, while this motion is not affected at the water/ CCl_4 interface—explaining the short-time dynamics observed in Figure 2.

Given the above discussion, one would expect, contrary to the results shown in Figure 2, that the relaxation at the water/nitrobenzene interface would be slower than that at the water/DCE interface. The width of this interface is about the same as that of the water/DCE interface, and nitrobenzene molecules are more strongly interacting with water molecules, which will further slow their diffusion rate. However, the nitrobenzene–water system introduces the new feature of hydrogen bonding between the oxygen of the nitro group and the water hydrogens. The calculated radial distribution functions of interfacial nitrobenzene–water (Figure 6) indeed confirm this. The ability of interfacial water molecules to hydrogen bond with nitrobenzene molecules will hasten the relaxation because a neighboring nitrobenzene molecule can act as a “replacement”. This would shorten the lifetime below this of the water/DCE interface. It is impossible, however, to remove the possibility of hydrogen bonding without affecting the structure of the interface (such as the width). If we run a water/nitrobenzene system with the

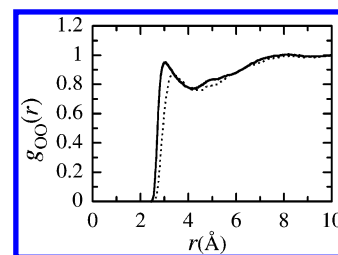


Figure 6. The water–nitrobenzene (oxygen–oxygen) pair correlation function for interfacial nitrobenzene molecules. Solid line: normal interface. Dotted line: the interface between water and nitrobenzene modeled without electrostatic interactions between the two liquids.

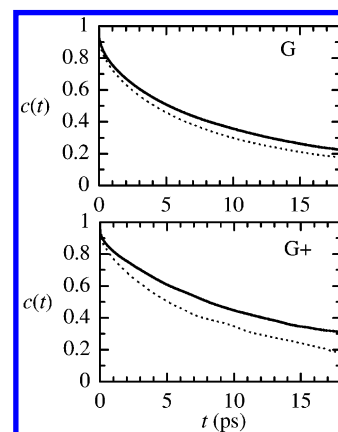


Figure 7. hydrogen bonding correlation function in the G+ and G interface regions of the normal water/nitrobenzene interface (solid lines) and the water/nitrobenzene interface modeled without interliquid electrostatic interactions (dotted lines).

water–nitrobenzene electrostatic interactions turned off, we turn off the hydrogen bonding. Figure 7 shows the effect that this has on the calculated $c(t)$ in regions G and G+. The faster relaxation causes the curves to be very similar to those at the water/ CCl_4 interface.

4. Conclusions

Hydrogen bond lifetimes are significantly longer at the interface between water and an organic liquid than in bulk water. The average lifetime of an interfacial hydrogen bond depends on the location along the interface normal and reaches the bulk water value at approximately two layers below the Gibbs surface. The slowest relaxation was found at the interface that is characterized by the tendency to form the most water “finger”-like structure. In this case, the lack of adjacent but non-hydrogen bonded molecules increases the time scale for a water molecule to “find” a new hydrogen bonding “partner”. This is consistent with the shortened lifetime calculated if the capillary fluctuations are removed.

In future studies, it would be interesting to perform the analysis of Luzar and Chandler⁵ to determine the rate constants for the formation and breakup of interfacial hydrogen bonds by taking into account the contribution of diffusion to the apparent dynamics.

Another issue that is under study is the effect due to the fluctuating charge in polarizable water models. This has been shown to be important at the water liquid/vapor interface,¹⁷ by making the relaxation faster than the fixed charge model (which overestimates the strength of the hydrogen bonding at the interface). Unlike the liquid/vapor interface, the organic phase is highly polarizable, and this in turn may make an important contribution.

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References and Notes

- (1) Nibbering, E. T. J.; Elsaesser, T. *Chem. Rev.* **2004**, *104*, 1887.
- (2) Gale, G. M.; Gallot, G.; Hache, F.; Lascoux, N.; Bratos, S.; Leicknam, J.-C. *Phys. Rev. Lett.* **1999**, *82*, 1068.
- (3) Asbury, J. B.; Steinel, T.; Stromberg, C.; Gaffney, K. J.; Piletic, I. R.; Goun, A.; Fayer, M. D. *Phys. Rev. Lett.* **2003**, *91*, 7402.
- (4) Fecko, C. J.; Eaves, J. D.; Loparo, J. J.; Tokmakoff, A.; Geissler, P. L. *Science* **2003**, *301*, 1698.
- (5) Luzar, A.; Chandler, D. *Nature* **1996**, *379*, 55.
- (6) Luzar, A.; Chandler, D. *Phys. Rev. Lett.* **1996**, *76*, 928.
- (7) Luzar, A. *J. Chem. Phys.* **2000**, *113*, 10663.
- (8) Starr, F. W.; Nielsen, J. K.; Stanley, H. E. *Phys. Rev. E: Stat. Phys. Plasmas, Fluids, Relat. Interdiscip. Top.* **2000**, *62*, 579.
- (9) Chandra, A. *Phys. Rev. Lett.* **2000**, *85*, 768.
- (10) Xu, H.; Stern, H. A.; Berne, B. J. *J. Phys. Chem. B* **2002**, *106*, 2054.
- (11) Vanderham, E. W. M.; Vrehen, Q. H. F.; Eliel, E. R. *Surf. Sci.* **1996**, *368*, 96.
- (12) Hommel, E. L.; Ma, G.; Allen, H. C. *Anal. Sci.* **2001**, *17*, 1325.
- (13) Balasubramanian, S.; Pal, S.; Bagchi, B. *Phys. Rev. Lett.* **2002**, *89*, 115505/1.
- (14) Tarek, M.; Tobias, D. J. *Phys. Rev. Lett.* **2002**, *88*, 138101.
- (15) Lopez, C. F.; Nielsen, S. O.; Klein, M. L.; Moore, P. B. *J. Phys. Chem. B* **2004**, *108*, 6603.
- (16) Paul, S.; Chandra, A. *Chem. Phys. Lett.* **2004**, *386*, 218.
- (17) Liu, P.; Harder, E.; Berne, B. J. *J. Phys. Chem. B* **2005**, *109*, 2949.
- (18) Linse, P. *J. Chem. Phys.* **1987**, *86*, 4177.
- (19) Benjamin, I. *J. Chem. Phys.* **1992**, *97*, 1432.
- (20) Michael, D.; Benjamin, I. *J. Phys. Chem.* **1995**, *99*, 1530.
- (21) Michael, D.; Benjamin, I. *J. Electroanal. Chem.* **1998**, *450*, 335.
- (22) Chang, T. M.; Dang, L. X. *J. Chem. Phys.* **1996**, *104*, 6772.
- (23) Benjamin, I. *Annu. Rev. Phys. Chem.* **1997**, *48*, 401.
- (24) Lee, L. T.; Langevin, D.; Mann, E. K.; Farnoux, B. *Phys. B* **1994**, *198*, 83.
- (25) Schlossman, M. L. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 235.
- (26) Michael, D.; Benjamin, I. *J. Chem. Phys.* **1997**, *107*, 5684.
- (27) Michael, D.; Benjamin, I. *J. Phys. Chem.* **1998**, *102*, 5154.
- (28) Benjamin, I. *J. Phys. Chem. A* **1998**, *102*, 9500.
- (29) Wang, H.; Borguet, E.; Eiseenthal, K. B. *J. Phys. Chem.* **1997**, *101*, 713.
- (30) Wang, H. F.; Borguet, E.; Eiseenthal, K. B. *J. Phys. Chem. B* **1998**, *102*, 4927.
- (31) Steel, W. H.; Walker, R. A. *Nature* **2003**, *424*, 296.
- (32) Zhang, X.; Steel, W. H.; Walker, R. A. *J. Phys. Chem. B* **2003**, *107*, 3829.
- (33) Steel, W. H.; Walker, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 1132.
- (34) Michael, D.; Benjamin, I. *J. Chem. Phys.* **2001**, *114*, 2817.
- (35) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic: London, UK, 1986.
- (36) Yamamoto, T. *J. Chem. Phys.* **1960**, *33*, 281.