Effect of Environment on Hydrogen Bond Dynamics in Liquid Water

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In a series of molecular dynamics calculations we simulate the dynamics of forming and breaking a hydrogen bond in liquid water at room temperature. We show that this dynamics is clearly nonexponential, yet virtually uncorrelated with the fluctuations of neighboring bonds.

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It is generally accepted that the distinctive properties of water can be ascribed to hydrogen bonding [1]. The fundamental dynamical process of the liquid is the making and breaking of hydrogen bonds. This dynamics, however, is far from being completely understood. Experiments such as infrared absorption and Raman scattering [2], depolarized light scattering [3], and inelastic neutron scattering [4] probe hydrogen bond dynamics indirectly and can be interpreted in only a qualitative way [5]. While limited to classical models, the method of molecular dynamics can be used to explore hydrogen bond dynamics at the microscopic level [6]. Factors controlling the dynamics can be determined from trajectory calculations of correlation functions. Different types of hydrogen bond correlation functions, as proposed by Stillinger [7], have been computed for liquid water. Different conclusions for the long time relaxation have been drawn. Some workers conclude this relaxation is purely exponential; others conclude it is nonexponential [8]. In this Letter, we demonstrate that the long time dynamics of a single hydrogen bond in ambient liquid water is indeed characterized by significant nonexponential relaxation, and this complex relaxation is essentially uncorrelated to the specific bonding patterns near the tagged hydrogen bond.

Our results are based upon an analysis of a large number of molecular dynamics simulations employing the single point charge (SPC) [9] intermolecular potential model for liquid water. A configurational criterion for whether a particular pair of water molecules is bonded allows the construction of a hydrogen bond population operator, h. It is unity when the particular tagged pair of molecules is hydrogen bonded, according to the adopted definition [10], and is zero otherwise. Two water molecules are chosen as being hydrogen bonded only if their interoxygen distance is less than 3.5 Å, and simultaneously the O—H ... O angle is less than 30° [11]. The average number of hydrogen bonds in an equilibrium of N water molecules is $\frac{1}{2}N(N-1)\langle h\rangle$, where $\langle h\rangle$ denotes the time average of h. In the dynamical equilibrium of liquid water, the hydrogen bond population operator fluctuates in time. These fluctuations are characterized by the correlation function

$$c(t) = \langle h(0)h(t)\rangle/\langle h\rangle \,. \tag{1}$$

This function is the probability that the hydrogen bond is intact at time t, given it was intact at time zero. At equilibrium, the probability that a specific pair of molecules is bonded in a large system is negligibly small. Thus, $c(t)$ relaxes to zero. The rate of relaxation to equilibrium is characterized by the reactive flux correlation function,

$$k(t) = -dc/dt = \langle j(0)\,[1 - h(t)]\rangle/\langle h\rangle \,, \tag{2}$$

where $j(0) = -dh/dt|_{t=0}$ is the integrated flux departing the hydrogen bond configuration space at time zero. The function $k(t)$ is the average of this integrated flux for those trajectories where the bond is broken at a later time t, thus the terminology "reactive flux." Its zero time value is the statistical transition state theory estimate of the rate of relaxation [12].

The $k(t)$ determined from our simulation of room temperature water [13] is shown in Fig. 1. An assortment of motions leading to hydrogen bond breaking is evident. At short times, $k(t)$ quickly changes from its initial value, indicating many recrossings in and out of the bonding region

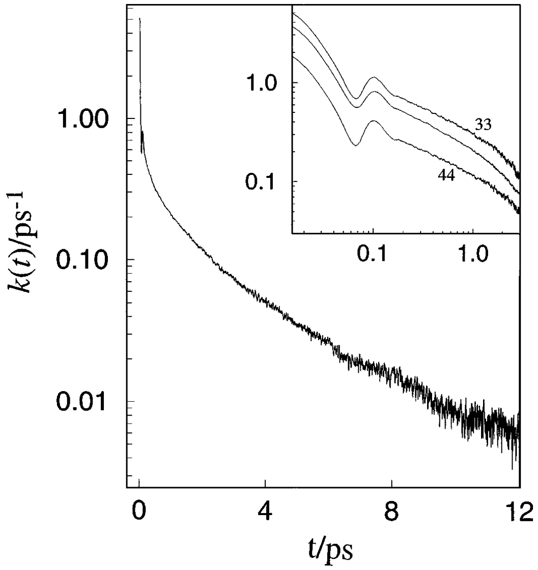

FIG. 1. The reactive flux hydrogen bond correlation function (semilogarithm plot) $k(t)$, for water at room temperature, calculated by molecular dynamics. The present data are obtained from ten consecutive trajectories, each of 24 ps in length. The inset panel shows the log-log plot of the same function, and conditional reactive fluxes $k_{44}(t)$ (labeled 44) and $k_{33}(t)$ (labeled 33).

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on a time scale of less than 0.1 ps. The dynamics on this time scale is primarily due to librations. Interoxygen vibrations are also evident, in this case on the time scale of 0.1–0.2 ps. Beyond this transient period, $k(t)$ decays monotonically. To the extent that each hydrogen bond acted independently of other hydrogen bonds and also independently of other processes of similar time scales, the long time decay of $k(t)$ would be that of first order kinetics. That is, one might expect $k(t) \sim (1/\tau)\exp(-t/\tau)$, with τ corresponding to the average hydrogen bond lifetime. As seen in Fig. 1, however, $k(t)$ does not relax exponentially. Beyond the transient period, the slope of $\log k(t)$ increases monotonically with time. The log-log plot demonstrates that this behavior does not coincide with a power law decay over the period of time that we have examined [14].

The long time relaxation referred to in Fig. 1 is invariant with respect to the specific definition of a hydrogen bond. To understand this fact, consider two different but reasonable choices of hydrogen bond definition. The surfaces in configuration space dividing bonded and nonbonded states are different for the two different definitions. But if both definitions are physically reasonable, the dividing surfaces will lie close to each other. Trajectories pass quickly between nearby surfaces. Alteration of the dividing surface will thus affect the short time transient decay and the amount of recrossings, but not the longer time reactive flux. Thus, the post-transient relaxation illustrated in Fig. 1 is not an artifact of the specific hydrogen bond definition employed in the calculation. It is therefore a property of liquid water. The assignment of ~0.3 ps as the end of the transient period would coincide with the arbitrary temporal definition of a hydrogen bond, used by Sciortino and Fornili [8(e)].

Others [8(c),14,16] have noted that hydrogen bond dynamics is not characterized by a single relaxation time. For room temperature water, the physical origin of this complexity at long times can be understood in terms of the coupling of hydrogen bond dynamics to diffusion. In particular, two molecules can diffuse apart only after the hydrogen bond between them breaks, and a broken bond can reform if a molecule reverses its direction and diffuses back to its partner. This aspect of hydrogen bond dynamics clearly introduces a continuum of relaxation times, as we have quantified elsewhere [17]. Here, we focus instead on the effects of correlations between different hydrogen bonds. Previous work would suggest that these correlations may also play a significant role [8(a),8(e),14,16,18]. We can unambiguously examine their role by partitioning the trajectories that contribute to the reactive flux, $k(t)$, according to the particular environment of the hydrogen bond. In particular, we define conditional reactive flux correlation functions,

$$k_{mn}(t) = \langle p_{mn} j(0)[1 - h(t)]\rangle / \langle p_{mn} h\rangle, \qquad (3)$$

where p_{mn} is unity when one of the water molecules in the tagged pair is participating in m hydrogen bonds, and the other is participating in n hydrogen bonds; otherwise, p_{mn} is zero.

The indices m and n serve to characterize the bonding state of the tagged pair of water molecules. $k_{mn}(t)$ is the reactive flux for the subset of equilibrium trajectories where the initial bonding state is (m, n). That is, it is the average integrated flux crossing out of the bonding region given the initial bonding state (m, n) and given the bond is broken a time t later. The ratio $\langle p_{mn} h\rangle / \langle h\rangle$ is the probability that (m, n) is the environmental state of the tagged bond. To within small statistical uncertainties (1%–3%), the simulation results give $\langle p_{mn} h\rangle / \langle h\rangle \propto (2 - \delta_{mn}) m P_m n P_n$ where P_ℓ is the probability that a single water molecule participates in ℓ hydrogen bonds [10(b)]. This proportionality indicates that the number of hydrogen bonds around a specified water molecule is uncorrelated with that number around a bonded nearest neighbor. Further, we find only small deviations from ideal tetrahedral configurations in that $|m - 4| + |n - 4| = 0$, 1, and 2, have relative occurrences 24%, 41%, and 26%, respectively. Hence, spontaneous fluctuations in water structure at room temperature are not large, as is consistent with mean field models of water [19].

As for the dynamical consequences of these fluctuations, we have evaluated the fifteen conditional reactive fluxes with $1 \le m, n \le 5$, all others being statistically negligible. For studying the long time relaxation, we computed the reactive flux functions out to times 2 orders of magnitude longer than the transient time. Some of the representatives are given in Fig. 2 and the inset panel of Fig. 1.

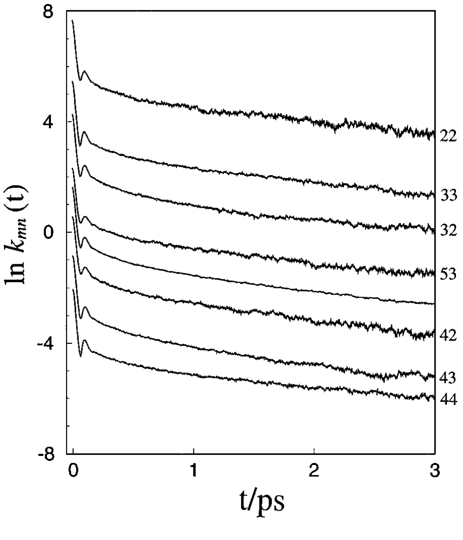

FIG. 2. Logarithm of the conditional reactive fluxes, $k_{mn}(t)$. The data presented are obtained from 25 consecutive trajectories, each of 8 ps in length. The values of (mn) are indicated by labels at the right. For the sake of comparison, the total reactive flux, $k(t)$, is presented (unlabeled curve). To make separate viewing possible, the labeled curves have been shifted as follows: $\ln[k_{42}(t)/\mathrm{ps}^{-1}] - 1$, $\ln[k_{43}(t)/\mathrm{ps}^{-1}] - 2$, $\ln[k_{44}(t)/\mathrm{ps}^{-1}] - 3$, $\ln[k_{53}(t)/\mathrm{ps}^{-1}] + 1$, $\ln[k_{32}(t)/\mathrm{ps}^{-1}] + 1.5$, $\ln[k_{33}(t)/\mathrm{ps}^{-1}] + 3.5$, $\ln[k_{22}(t)/\mathrm{ps}^{-1}] + 4$.

The similarity between the different functions is remarkable. While the absolute values of these functions are different, their relative values, i.e., transmission coefficients,

$$\kappa_{mn}(t) = k_{mn}(t)/k_{mn}(0)\,, \tag{4}$$

are essentially identical for all m and n. The variation of decay rate with initial bonding state is thus a statistical effect and not a dynamical one. In the parlance of transition state theory [12], the transmission coefficients are independent of bonding state. At short times, each conditional reactive flux exhibits the same rapid transient decay to a value an order of magnitude smaller than its initial value. Beyond the transient, to within our statistical uncertainties, each function exhibits the same nonexponential relaxation. For statistically likely environments, inspection of Fig. 2 also shows that variation in the absolute values between different conditional reactive fluxes is not larger than a factor of 2.

The $\kappa_{mn}(t)$'s therefore demonstrate a lack of correlation between the dynamics of a tagged hydrogen bond and that of its neighboring bonds. As the correlation length in room temperature water is not large, correlations with more distant bonds are even less likely. Cooperative processes, where one bond is formed or broken depending upon the dynamics of its neighbors, are thus of little significance in room temperature water. This conclusion can be viewed in terms of the standard picture of water as a distorted random tetrahedral network of hydrogen bonds [20]. Each water molecule optimally participates in four hydrogen bonds. At standard liquid conditions, however, about half of the water molecules use only three of the four bonding sites [10(b)]. Thus, in the vicinity of a hydrogen bond, one or more neighboring water molecules can receive an additional bond. The average water environment therefore provides ample opportunity for the tagged hydrogen bond to disappear as water molecules switch allegiances [20]. A correlated fluctuation is not required. The creation of an unusual environment can, of course, affect the dynamics of the hydrogen bond. But our calculations demonstrate that the statistical significance of such events is small.

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[13] The system in the classical molecular dynamics simulation at room temperature contained 250 water molecules interacting through the SPC pair potential (Ref. [9]). The solvent density was that of the experimental bulk water at the corresponding temperature and 1 atm pressure. Dynamical results were obtained from running trajectories in the microcanonical ensemble for 240 ps after 100 ps runs were completed in the canonical ensemble. The Nosé-Hoover thermostat was used to control the temperature for the initial 100 ps portion. The equations of motion were integrated using the velocity predictor-corrector method with a time step of 0.5 fs. The time derivatives of the hydrogen bond correlation function were calculated every second time step. Periodic boundary conditions were used together with the minimum image convention for non-Coulombic interactions. Account of electrostatic in-

teractions was made using the Ewald summation technique. The simulation model ignores quantum effects and intramolecular flexibility. There is to be expected only a small increase in observed rates of dynamical processes in bulk water upon introducing intramolecular vibrations [D. E. Smith and A. D. J. Haymet, J. Chem. Phys. **96**, 8450 1992)].

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