Fast and Slow Dynamics of Hydrogen Bonds in Liquid Water

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We study hydrogen-bond dynamics in liquid water at low temperatures using molecular dynamics simulations, and find results supporting the hypothesized continuity of dynamic functions between the liquid and glassy states of water. We find that average bond lifetime ($\sim$1 ps) has Arrhenius temperature dependence. We also calculate the bond correlation function decay time ($\sim$1 ns) and find power-law behavior consistent with the predictions of the mode-coupling theory, suggesting that the slow dynamics of hydrogen bonds can be explained in the same framework as standard transport quantities. [S0031-9007(99)08707-4]

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Both experiments on [1–3] and simulations of [4–6] water have focused on understanding various aspects of hydrogen bond (HB) dynamics, such as the structural relaxation time τ_R and average HB lifetime τ_{HB}. Experiments show that characteristic relaxation times commonly obey power laws on supercooling, but that τ_{HB} follows a simple Arrhenius law [1–3]. Simulations are particularly useful for investigating supercooled water since nucleation does not occur on the time scale of the simulations. Furthermore, quantitative HB information is available in simulations. We find Arrhenius behavior (Fig. 1) of τ_{HB}, as expected from experimental results [3,7]. We also find complex behavior of τ_R (Fig. 2), consistent with the predictions of the mode-coupling theory (MCT) [1,8] and with the hypothesized continuity of the liquid and glassy states of water [9–11].

We perform lengthy molecular-dynamics simulations (up to 70 ns) at seven temperatures between 200 and 350 K [12] using the extended simple point charge (SPC/E) potential for water [13]. We calculate the HB dynamics by considering two definitions of an intact HB: (i) an *energetic* definition, which considers two molecules to be bonded if their oxygen-oxygen separation is less than 3.5 Å and their interaction energy is less than a threshold energy E_{HB}, and (ii) a *geometric* definition [6], which uses the same distance criterion but no energetic condition, instead requiring that the O–H$\cdots$O angle between two molecules must be less than a threshold angle θ_{HB}. We select these criteria to roughly reproduce the experimental value for the activation energy needed to break bonds through librational motion.

We calculate τ_{HB} using both bond definitions with threshold values $E_{\mathrm{HB}} = -10$ kJ/mol and $\theta_{\mathrm{HB}} = 30°$ over the entire temperature range simulated, and find Arrhenius behavior of τ_{HB} (Fig. 1). Measurements of τ_{HB} using depolarized light scattering techniques [3,7] find Arrhenius behavior [14]. The activation energy E_A associated with τ_{HB} has been interpreted as the energy required to break a HB via librational motion, a "fast" motion [3,7]. Comparison of experimental and simulated values of E_A provides a primitive test of the bonding criteria in our simulations; we obtain reasonable agreement between experimental and simulated values of E_A using thresholds of $E_{\mathrm{HB}} = -10$ kJ/mol for the energetic definition and $\theta_{\mathrm{HB}} = 30°$ [6] for the geometric definition. We find better quantitative agreement with experiments for τ_{HB} values obtained from the geometric definition than for τ_{HB} values obtained from energetic definition—possibly because the geometric bond definition, like the depolarized light scattering experiments, is highly sensitive to the linearity of the bond. We also calculate τ_{HB} using the

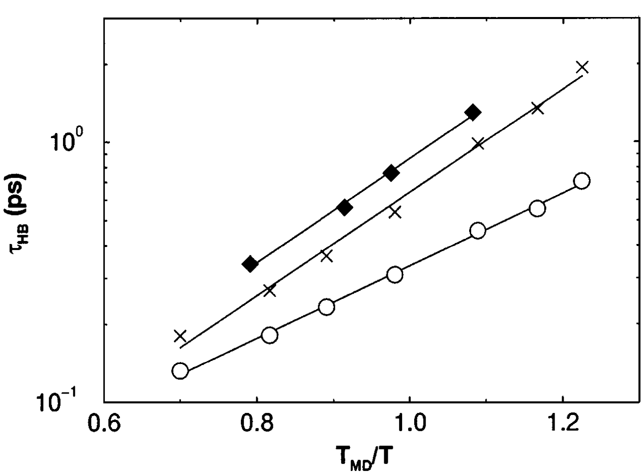

FIG. 1. Average HB lifetime τ_{HB} from (i) depolarized light scattering experiments [3] (◆) and from our simulations for the (ii) energetic (○) and (iii) geometric (×) bond definitions. We observe that each set of results can be fit by Arrhenius behavior, $\tau_{\mathrm{HB}} = \tau_0 \exp(E_A/kT)$, with activation energy: (i) $E_A = 10.8 \pm 1.0$ kJ/mol (experimental), (ii) $E_A = 8.8 \pm 0.8$ kJ/mol (energetic definition), and (iii) $E_A = 9.3 \pm 1.2$ kJ/mol (geometric definition). To facilitate comparison of the results, we scale the temperature of our simulation by $T_{\mathrm{MD}}^{\mathrm{SPC/E}} \approx 245$ K [15–17] and the temperature of the experimental data by $T_{\mathrm{MD}}^{\mathrm{H_2O}} = 277$ K.

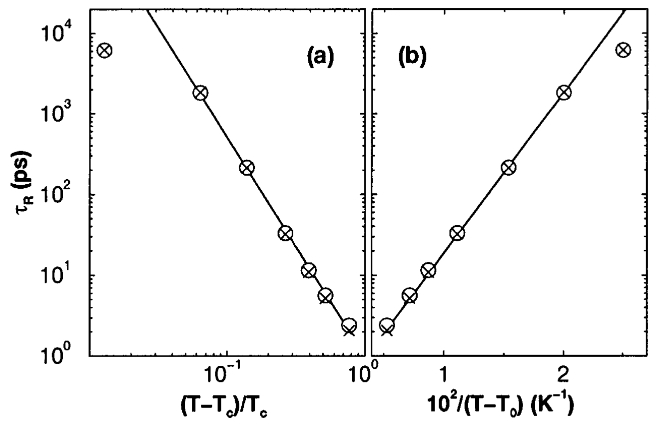

FIG. 2. Relaxation time τ_R of the bond correlation function $c(t)$ for the energetic (○) and the geometric (×) bond definitions. (a) Fit to the scaling form predicted by MCT (solid line) with $T_c = 197.5$ K. (b) Fit to the VFT form (solid line) with $T_0 = 160$ K. The possible significance of the deviation from both fitting forms at $T = 200$ K is discussed in the text.

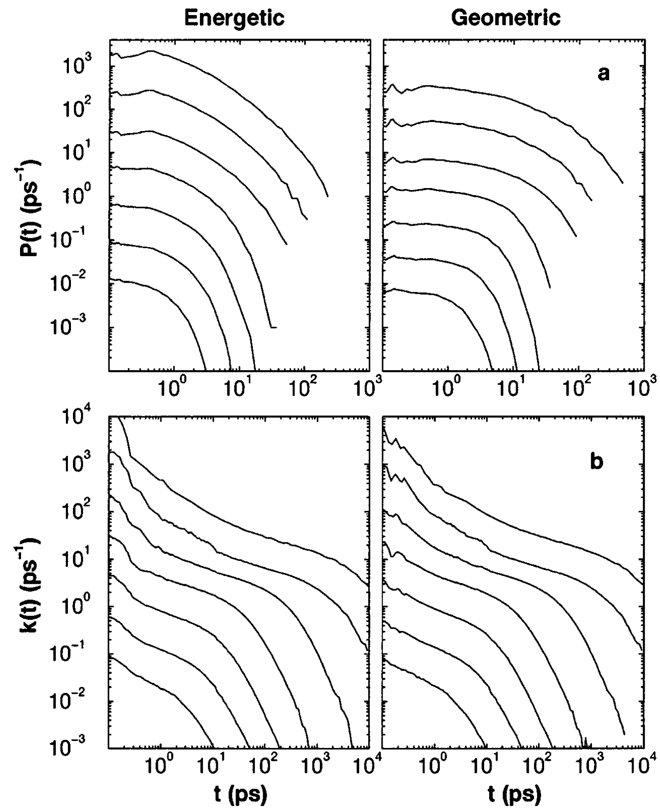

FIG. 3. Two relaxation functions, (a) the bond lifetime distribution $P(t)$ and (b) the reactive flux $k(t)$, for the energetic and geometric bond definitions. Each curve is offset by one decade for clarity. Reading from top to bottom: $T = 200$, 210, 225, 250, 275, 300, and 350 K. Note that $k(t)$ does not depend on the unbroken presence of a bond, so $k(t)$ decays less rapidly than $P(t)$. After a transient period of rapid librational motion up to $t \approx 0.3$ ps, $k(t)$ displays a region of power-law decay for $T \geq 250$ K. For $t \gtrsim 0.3$ ps, $k(t)$ is nearly identical for both bond definitions, not surprising since both definitions use the same distance criterion. We calculate $k(t)$ from the numerical derivative of $c(t)$, which is well approximated by a stretched exponential for $t \gtrsim 0.3$ ps. Our results for the geometric definition at $T = 300$ K are consistent with recent calculations for the SPC potential (see inset of Fig. 1 of Ref. [6]).

thresholds $E_{\mathrm{HB}} = 0$ kJ/mol and $\theta_{\mathrm{HB}} = 35°$ and find Arrhenius behavior, but with E_A roughly 30% smaller for the energetic definition and roughly 10% smaller for the geometric definition.

A previous study of HB dynamics using the ST2 potential found power-law behavior of τ_{HB} [5]. The difference between the results of Ref. [5] and the current study may arise from the fact that Ref. [5] used an energetic bond definition that requires a bond to be intact for a minimum threshold time in order to be considered a HB. Bond breaking by rapid librational motion is excluded by such a definition, so the HB dynamics are more closely related to diffusive motion, which is typically described by a power law—as we will also observe for HB correlation time. The power-law behavior, which might also be associated with the liquid-liquid critical point found in ST2, occurs at a temperature and pressure very close to the coldest state point studied in Ref. [5] ([9,18]).

The quantity τ_{HB} is one characteristic time—the mean—of the distribution of HB lifetimes $P(t)$, which measures the probability that an initially bonded pair remains bonded at *all times* up to time t, and breaks at t. $P(t)$ is obtained from simulations by building a histogram of the HB lifetimes for each configuration, since $\tau_{\mathrm{HB}} = \int_0^\infty tP(t)dt$ [19]. The behavior of $P(t)$ for the two bond definitions is different [Fig. 3(a)], likely caused by differences in sensitivity of the two definitions of librational motion. For both bond definitions, we find neither power-law nor exponential behavior.

We study τ_R ("slow" dynamics) for an initially bonded pair by calculating the bond correlation function $c(t)$, the probability that a randomly chosen pair of molecules is bonded at time t provided that the pair was bonded at $t = 0$ (independent of possible breaking in the interim time). To calculate $c(t)$, we define

$$c(t) \equiv \langle h(0)h(t)\rangle / \langle h^2\rangle, \tag{1}$$

where $h(t)$ is a binary function for each pair of molecules $\{i, j\}$, and $h(t) = 1$ if molecules $\{i, j\}$ are bonded at time t and $h(t) = 0$ if $\{i, j\}$ are not bonded at time t [6]. The angle brackets denote an average of all pairs $\{i, j\}$ and starting times. We define τ_R by $c(\tau_R) \equiv e^{-1}$. Short time fluctuations, due to the librational motion of molecules and choice of bond definition, do not strongly affect the long-time behavior of the "history-independent" quantity $c(t)$ (which *does not* depend on the continuous presence of a bond), but such fluctuations cause both qualitative and quantitative differences in the long-time behavior of the "history-dependent" $P(t)$ (which *does* depend on the continuous presence of a bond).

We can interpret the behavior of τ_R in terms of MCT for a supercooled liquid approaching a glass transition [1,8], which is known to describe the diffusive motion of the SPC/E model [10]. In accordance with MCT, we find—for both bond definitions—power-law growth for $T \geq 210$ K,

$$\tau_R \sim (T - T_c)^{-\gamma}. \tag{2a}$$

Here $\gamma = 2.7 \pm 0.1$ and $T_c = 197.5 \pm 1.0$ K, approximately 50 K less than the temperature of maximum density $T_{\rm MD}$ of SPC/E [Fig. 2(a)] [20]. Fits of experimental relaxation times to Eq. (2a) also find T_c at a temperature 50 K less than the $T_{\rm MD}$ of water [1,2]. In MCT, T_c is the temperature of the ideal kinetic glass transition and is larger than the glass transition temperature T_g. At $T = 200$ K, τ_R deviates from Eq. (2a), most likely because MCT does not account for activated processes which aid diffusion and reduce relaxation times at low T [21]. Typically, these activated processes become important near T_c, as we observe.

Our simulation results for τ_R can also be fit by the Vogel-Fulcher-Tammann (VFT) form [1] for $T \geq 210$ K,

$$\tau_R \sim e^{A/(T-T_0)}, \tag{2b}$$

with $T_0 = 160$ K [Fig. 2(b)] [22]. For typical liquids, we expect $T_0 < T_g$, so estimating T_0 and T_c provides lower and upper bounds for T_g. However, fits of experimental water data to Eq. (2b) (which are far above T_g) yield $T_0 > T_g$ [24]; hence we do not expect the T_0 value from our simulation to be a lower bound for T_g of the SPC/E model. Experimentally, T_g is defined as the temperature where the viscosity reaches 10^{12} Pa s or $\tau = 100$ s. Experiments near T_g often show a crossover from VFT to Arrhenius behavior [1]. While our simulations are still relatively far from T_g (based on the value of τ_R), a naive extrapolation, assuming that τ_R at $T = 210$ and 200 K follows Arrhenius behavior, yields $T_g \approx 105$ K [25]. The ratio $T_g/T_{\rm MD} \approx 0.43$ for the SPC/E model compares well to the experimental value $T_g/T_{\rm MD} = 0.49$ [2].

The experimental fact noted above that $T_0 > T_g$ might be accounted for by the existence of a continuous crossover from VFT or power-law behavior ("fragile liquid") for $T \gtrsim 220$ K to Arrhenius behavior ("strong liquid") for $T \lesssim 220$ K, thereby smoothly connecting the structural relaxation times of the liquid with those of the glass [26]. Our results support this possibility. A crossover from fragile to strong behavior in water has been previously suggested [27], and recent experimental results for the diffusion constant (proportional to τ_R^{-1}) for T closer to T_g may help to determine if such a crossover occurs [28].

The reactive flux, defined by the derivative

$$k(t) \equiv -dc(t)/dt\,, \tag{3a}$$

measures the effective decay rate of an initial set of bonds. At $T = 300$ K, nonexponential decay of $k(t)$ was found for the closely related SPC model using the geometric bond definition [6]. Our $k(t)$ calculations reveal a power-law region $k(t) \sim t^{-\zeta}$ for $T \geq 250$ K for both bond definitions, with an exponent $\zeta = 0.5 \pm 0.1$ [Fig. 3(b)]. The range of the power-law region increases from ≈ 1 decade at 350 K to ≈ 2 decades at 250 K.

The value of ζ can be interpreted using MCT, which predicts that $c(t)$ decays from a plateau value $c_{\rm pl}$ with power-law dependence

$$c_{\rm pl} - c(t) \sim t^b \tag{3b}$$

in the range where $k(t)$ appears to be power law [1,8]. From Eq. (3b), $k(t) \sim t^{b-1}$, so $b = 1 - \zeta$. We find $b = 0.5 \pm 0.1$, consistent with previous work [10], further suggesting that the HB behavior is consistent with MCT predictions for a glass transition [29]. For $T < 250$ K, $k(t)$ may be fit by Eq. (3b) if higher order terms are included. Our results suggest that the HB dynamics in water may be treated using the same theory, namely MCT, invoked to explain typical transport phenomena [10].

The *Arrhenius* behavior and short time scale of $\tau_{\rm HB}$ indicates that librational motion is a thermally activated process that is largely independent of structural slowing down. The *non-Arrhenius* behavior of τ_R and the *nonexponential* relaxation of $k(t)$ are consistent with the presence of the proposed ideal kinetic glass transition for SPC/E approximately 50 K below the $T_{\rm MD}$ of SPC/E water [10], which coincides with the temperature at which many experimental relaxation times appear to diverge [1,2]. It was hypothesized that the apparent singular temperature of liquid water observed experimentally may be identified with the T_c of MCT [10,30]; our results support this hypothesis. They also complement scenarios that account for the anomalous thermodynamic behavior, such as the liquid-liquid transition hypothesis [9,11,31,32] or the singularity-free hypothesis [33]. The behavior we observe appears not to be unique to water; short bond lifetimes that are thermally activated ("fast dynamics"), coupled with much slower network restructuring ("slow dynamics"), have been observed in a simple bonded hard-sphere system [34].

In summary, although the functional form of $\tau_{\rm HB}$ does not appear to be strongly dependent on bond definition, $P(t)$ is different for the two definitions—suggesting that $P(t)$ may not be the best function for studying HB dynamics. In contrast, $c(t)$ and $k(t)$—which include bond reformation—are largely independent of the bond definition at long times [35].

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[1] P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1996).
[2] C. A. Angell, in *Water: A Comprehensive Treatise,* edited by F. Franks (Plenum, New York, 1981).
[3] S.-H. Chen and J. Teixeira, Adv. Chem. Phys. **64**, 1 (1985).
[4] F. Sciortino and S. L. Fornili, J. Chem. Phys. **90**, 2786 (1989).
[5] F. Sciortino, P. H. Poole, H. E. Stanley, and S. Havlin, Phys. Rev. Lett. **64**, 1686 (1990).
[6] A. Luzar and D. Chandler, Phys. Rev. Lett. **76**, 928 (1996); Nature (London) **379**, 55 (1996).
[7] C. J. Montrose *et al.*, J. Chem. Phys. **60**, 5025 (1974); O. Conde and J. Teixeira, J. Phys. **44**, 525 (1983); Mol. Phys. **53**, 951 (1984); Y. Suzuki, A. Fujiwara, and Y. Tominaga (to be published).
[8] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[9] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992); Phys. Rev. E **48**, 3799 (1993); Phys. Rev. E **48**, 4605 (1993); S. Harrington, R. Zhang, P. H. Poole, F. Sciortino, and H. E. Stanley, Phys. Rev. Lett. **78**, 2409 (1997).
[10] P. Gallo, F. Sciortino, P. Tartaglia, and S.-H. Chen, Phys. Rev. Lett. **76**, 2730 (1996); F. Sciortino, P. Gallo, P. Tartaglia, and S.-H. Chen, Phys. Rev. E **54**, 6331 (1996).
[11] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).
[12] We simulate 512 water molecules with fixed density 1.0 $\mathrm{g/cm^3}$ at temperatures $T = 350$, 300, 275, 250, 225, 210, and 200 K interacting via the SPC/E pair potential [13]. We simulate two independent systems at 200 K to improve statistics. We equilibrate all simulated state points to a constant T by monitoring the pressure and internal energy. We equilibrate the system for times ranging from 200 ps (at 350 K) to 30 ns (at 200 K), followed by data collection runs ranging from 100 ps (at 350 K) to 40 ns (at 200 K). For additional simulation details, see Ref. [10].
[13] H. J. C. Berendsen, J. R. Grigera, and T. P. Stroatsma, J. Phys. Chem. **91**, 6269 (1987).
[14] The experiments of Refs. [3,7] were performed at constant pressure. The simulations we present are at constant density, thus a quantitative comparison on the lifetime values is not possible. However, the change in pressure along the 1.0 $\mathrm{g/cm^3}$ isochore is relatively small [16], and we still expect Arrhenius behavior.
[15] L. Baez and P. Clancy, J. Chem. Phys. **101**, 9837 (1994).
[16] S. Harrington, P. H. Poole, F. Sciortino, and H. E. Stanley, J. Chem. Phys. **107**, 7443 (1997).
[17] K. Bagchi, S. Balasubramanian, and M. L. Klein, J. Chem. Phys. **107**, 8651 (1997).
[18] If a liquid-liquid transition occurs in SPC/E, it has been estimated to terminate at a critical point located at 160 K and 200 MPa [16]. The present simulations should not be significantly affected by this critical point, as we are far from it.
[19] Since $P(t)$ depends on the unbroken presence of a bond, $P(t)$ is sensitive to the sampling frequency. Thus choosing a long time interval between sampled configurations corresponds to ignoring processes where a bond is broken for a short time and subsequently reforms. To calculate $P(t)$, we sample every 10 fs (shorter than the typical libration time, which could destroy a bond). We also measured $P(t)$ with a sampling frequency of 1 fs and observed no noticeable change in the decay of $P(t)$.
[20] The values T_c and γ depend on the pressure. Studying different dynamic properties, Ref. [10] independently calculated T_c and γ for the same potential and—depending on the pressure considered – obtained ($T_c = 186$ K, $\gamma = 2.3$) and ($T_c = 199$ K, $\gamma = 2.8$). Thus the HB dynamics appear to follow the same phenomenology as the commonly observed dynamic quantities.
[21] Other commonly observed dynamics quantities, such as the diffusion constant and the relaxation time of the intermediate scattering function, also show the same low temperature deviation from a power law. The discussion of τ_R appears to apply equally well to these other quantities.
[22] The VFT form is not predicted by MCT, but has been observed to fit a broad range of dynamic data. In the entropy theory of the glass transition [1,23], T_0 is associated with the Kauzmann temperature, the temperature where the extrapolated entropy of the supercooled liquid approaches the entropy of the solid.
[23] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[24] For reference, the experimentally observed values of the various temperatures discussed are $T_c \approx 225$ K, $T_0 \approx 175$ K, and $T_g \approx 135$ K at atmospheric pressure (see Ref. [2]).
[25] Evidence of a low temperature crossover to Arrhenius behavior in water has been found in simulations of the ST2 model [D. Paschek and A. Geiger, J. Phys. Chem. (to be published)].
[26] If such a crossover from fragile to strong behavior indeed exists, there is no need to hypothesize the presence of a reentrant spinodal to explain the apparent power-law behavior of dynamic quantities [R. J. Speedy, J. Chem. Phys. **86**, 892 (1982)].
[27] C. A. Angell, J. Chem. Phys. **97**, 6339 (1993).
[28] R. S. Smith and B. D. Kay (to be published).
[29] We expect the exponent b to vary slightly since we simulate along an isochoric rather than isobaric path.
[30] F. X. Prielmeier, E. W. Lang, R. J. Speedy, and H.-D. Lüdemann, Phys. Rev. Lett. **59**, 1128 (1987).
[31] C. J. Roberts, A. Z. Panagiotopoulos, P. G. Debenedetti, Phys. Rev. Lett. **77**, 4386 (1996); C. J. Roberts and P. G. Debenedetti, J. Chem. Phys. **105**, 658 (1996).
[32] M.-C. Bellissent-Funel, Europhys. Lett. **42**, 161 (1998).
[33] S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, Phys. Rev. E **53**, 6144 (1996).
[34] R. J. Speedy, Mol. Phys. **89**, 1121 (1996); R. J. Speedy and P. G. Debenedetti, Mol. Phys. **83**, 591 (1995).
[35] F. H. Stillinger, Adv. Chem. Phys. **31**, 1 (1975).