Lifetime of the Bond Network and Gel-Like Anomalies in Supercooled Water

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We analyze the distribution of bond lifetimes in simulations of liquid water using a novel bond definition. We find that the characteristic lifetimes of the bonds and of the "gel" network itself both increase strongly when temperature is decreased—and even appear to diverge at a temperature well below the freezing temperature—thereby providing an appealing physical picture of the anomalous behavior of water in the supercooled region.

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The molecular structure of liquid water, as well as its dynamic evolution, is an open question. The instantaneous structure of the liquid can be described as a "gel"—a random network of hydrogen bonds (HB's) of macroscopic extent[1-6]—which is continually restructuring due to the rapid breaking and reforming of the HB's on a picosecond time scale. In recent years an increasing body of experimental evidence has been accumulating to suggest power-law behavior in the temperature dependence of both thermodynamic and dynamic properties of liquid water, which has been interpreted as evidence for a singularity at an unattainably low value of the temperature (the "Angell temperature" T_A of about $-46\,^{\circ}\mathrm{C}$).[2] The connection between this *apparent* singularity and the structure and dynamics of the HB network that distinguishes water from other liquids has been difficult to elucidate.[3-6]

Here we present evidence suggesting that the *dynamic* anomalies observed in the vicinity of T_A may be related to a region of power-law behavior of the characteristic lifetimes of the bonds and the connectivity properties of the entire bond network or "gel." Our evidence is based upon an analysis of the distribution of bond lifetimes obtained—for five different temperatures—from extensive molecular-dynamics (MD) simulations using a widely used microscopic model of liquid water, the ST2 intermolecular potential.[7]

The main difficulty in studying bond properties—such as local and global connectivity, or HB dynamics—using MD simulations arises from the high degree of arbitrariness in the definition of a bond for systems such as water that have a continuous range of interaction energies. Moreover, in the case of water, further arbitrariness arises from the high directionality of the interaction and the substantial libration (hindered rotation) which modulates the time evolution of the interaction. The most common ways to define a bond—according to the instantaneous geometric or energetic properties of a pair of water molecules[3,6,7]—cannot strictly be extended to dynamics because of this fast librational motion. Only limited information on the dynamics has been extracted from the simulations, although such information would be particularly relevant to the description of the restructuring of the HB gel.

In this work, we use a bond definition recently introduced by Sciortino and Fornili[8] (SF) who consider the complete set of all interactions which have a negative interaction energy V_{ij} between molecules i and j, and an oxygen-oxygen distance r_{ij} less than the maximum distance[9] that allows a HB (3.5 Å). In the following, we shall call such interactions "bonds" to make clear that the interactions considered here are quite distinct from standard[3,6] definitions of a hydrogen bond.

Our configurations are obtained by MD simulations of 216 ST2 particles in a cubic box of edge 18.6 Å, with periodic boundary conditions. The system density is 1 g/cm^3 and the integration time step is 0.001 ps. The starting configurations used are the final configurations from an earlier MD simulation by Geiger *et al.*,[10] and the same computer program is run in order to produce 200 ps of configurations. The configurations from the last 100 ps are recorded on tape and are analyzed. Five different temperatures, ranging from 350 to 235 K, are studied.[11]

We first test the plausibility of the SF criterion by demonstrating that a representative activation energy can be associated with the bond, and that this activation energy is related to the bond *lifetime* in a conventional Arrhenius fashion (as expected for simple bond-breaking processes[12]). We choose the activation energy to be the average energy $\langle E_{ij}\rangle$ associated with the bond, where[13]

$$E_{ij} \equiv 2V_{ij} + \sum_{k\neq i,j} V_{ik} + \sum_{k\neq i,j} V_{jk} \,. \tag{1}$$

Thus for each bond present in a selected configuration we record the sequences of values assumed by E_{ij} during the time interval between the first appearance of the bond and its first dissociation. To each bond we associate (i) a lifetime, given by the number of consecutive configurations in which the same bond is present, and (ii) a value for $\langle E_{ij}\rangle$.

Figure 1 is a semilog plot showing the dependence on bond lifetime τ of $\langle E_{ij}\rangle$, averaged over all bonds with the same lifetime. The observed straight-line behavior supports an exponential dependence of τ on $\langle E_{ij}\rangle$, and the increase of the slope with temperature is as expected

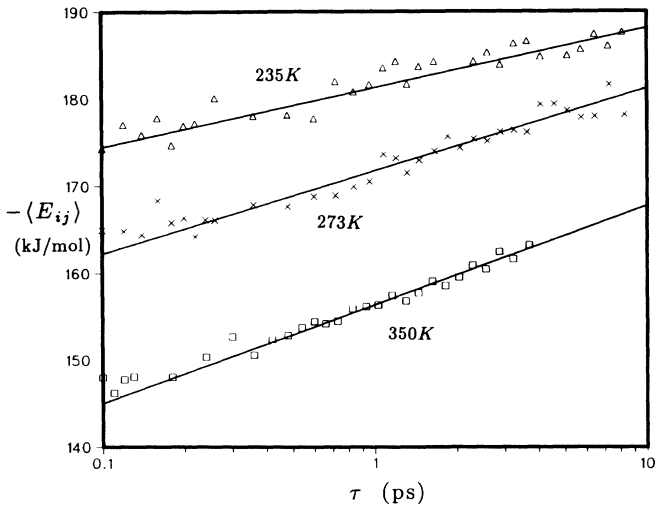

FIG. 1. Semilog plot of $\langle E_{ij}\rangle$ (the average of the recorded values of E_{ij} during the existence of the bond) as a function of bond lifetime τ. Each point is the average over all the bonds with the same lifetime. Only three of the five studied temperatures are reported: $T=235$ K (△), $T=273$ K (×), and $T=350$ K (□). Note that the energies shown are the sum of *all* the interaction energies of the two molecules sharing the bond ij.

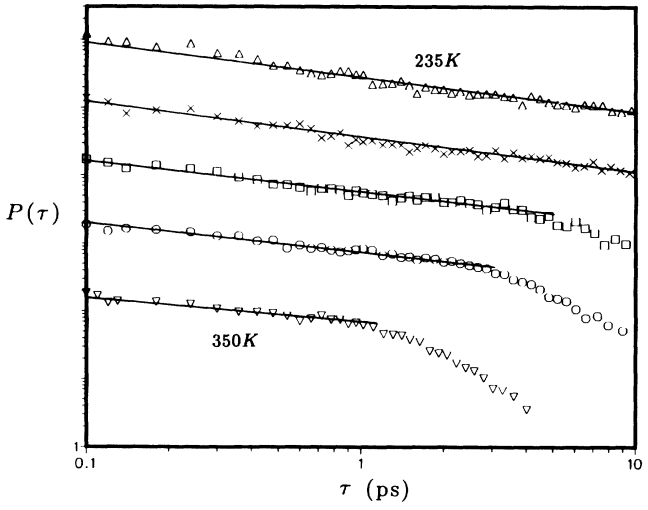

FIG. 2. The distribution $P(\tau)$ of bond lifetimes. Shown are data for all five temperatures studied, with the top four curves each shifted by one decade for clarity. Reading from top to bottom, the curves correspond to $T=235$ K (△), $T=247$ K (×), $T=299$ K (□), $T=273$ K (○), and $T=350$ K (▽).

from the Arrhenius kT factor. The large time interval (almost two decades) over which such an exponential relationship exists supports the SF criterion and explains the finding of correlation in the dynamic properties of bonds connected to the same molecule.[11]

We first measure the bond lifetime distribution $P(\tau)$ (Fig. 2) by making a histogram of the number of bonds in a given configuration with lifetime τ. We observe a remarkably large power-law region in this log-log plot, with the same exponent (-0.5 ± 0.1) independent of temperature. This power-law region is followed by a faster decay, and the range of the power law *increases* toward larger times when we supercool. This latter behavior, which is typical of scaling for dynamical critical phenomena,[14] is consistent with the possibility of a critical region in ST2 water.

Figure 3 shows the temperature dependence of the average bond lifetime $\langle\tau\rangle$ calculated from $P(\tau)$.[15] Since experimental data are frequently analyzed by making the assumption of a singularity at T_A, we attempt to fit our data for $\langle\tau\rangle$ by a power-law behavior of the form $(T-T_A)^{-\alpha}$. A least-squares fit results in the values $T_A=229\pm5$ K $(=-44\pm5°\,\mathrm{C})$ and $\alpha=0.7\pm0.2$ (see inset of Fig. 3), values consistent with experimental findings.[2,16] It is possible that the fit of the experimental data by a power law in $T-T_A$ arises from the temperature-dependent cutoff to the power-law distribution of bond lifetimes. In this sense, the claimed absence of a genuine transition could be related to a limitation in the maximum value assumed by the cutoff.

Next we analyze the effect of bond dynamics on the *connectivity* properties of the system, with the aim of extending the concept of the lifetime of a *single bond* to the lifetime of the entire *gel network*. The fraction of bonds in liquid water is always well beyond the percolation threshold and almost all the molecules in the system be-

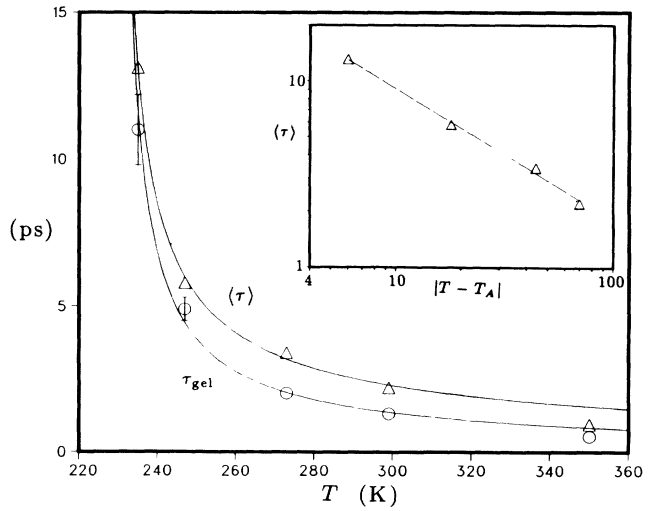

FIG. 3. Temperature dependence of the average bond lifetime $\langle\tau\rangle$ (△) and the average lifetime of the spanning cluster τ_{gel} (○) (defined as the time interval after which the fraction of original bonds still alive becomes equal to the bond-percolation threshold value, and evaluated by measuring the position of the maximum in the mean cluster size S). Inset: A Double-logarithmic plot of the average bond lifetime $\langle\tau\rangle$ vs $|T-T_A|$, with $T_A=229$ K; the slope of the least-squares fit is $-\alpha=-0.71$.

long to the same "infinite cluster."[17] Therefore an order parameter associated with the static instantaneous connectivity cannot be connected to the collective behavior observed in the supercooled region. We focus instead on the time interval over which the spanning cluster restructures itself, i.e., on the lifetime τ_{gel} of the entire bond network or "gel." To this end, we follow the development *in time* of the connectivity properties by analyzing the properties of the clusters formed by bonds that have existed without interruption since the start of a given "observation interval," and ignoring bonds that are newly formed during this interval. The standard percolation functions[14]—such as the fraction of sites belonging to the spanning cluster P_∞ and the mean cluster size S —*thus become functions of time.*

Figure 4 shows $P_\infty(t)$ for five different temperatures.[18] We define τ_{gel} as the time at which the initial cluster ceases to span or, equivalently, to be the position of the maximum in $S(t)$. Our results, shown in Fig. 3, have the same qualitative and quantitative behavior as $\langle\tau\rangle$. The two quantities τ_{gel} and $\langle\tau\rangle$ are not completely independent, both being related to the actual distribution of bond lifetimes. However, the spatial correlation among the bonds and the topological structure of the pseudolattice formed by the oxygen position are taken into account only in the τ_{gel} value. The approach to the apparent transition is reflected also in an increase of correlation among bonds, as we found in the progressive reduction of the mean number of bonds needed to form a spanning cluster when the system is supercooled.

In summary, from MD simulations using the ST2 potential, we have found evidence for (a) a power-law decay in the bond-lifetime distribution function $P(\tau)$ followed by a faster decay, (b) a sharp increase as T decreases in the average bond lifetime $\langle\tau\rangle$, and (c) a similar temperature dependence of the lifetime of the spanning cluster τ_{gel}. Our ST2 results may provide a microscopic interpretation for the experimental evidence that suggests a region of power-law behavior in the dynamic properties of liquid water. Indeed, the MD calculations —showing that the characteristic lifetime τ_{gel} of the bond network gives the impression of diverging to infinity—provide an appealing physical picture of the anomalous behavior of water in the presently investigated range of supercooling.

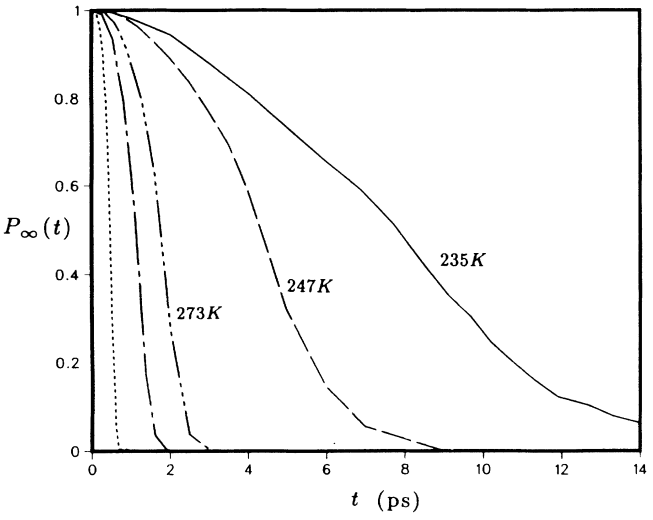

FIG. 4. The fraction $P_\infty(t)$ of molecules belonging to the spanning cluster. At the beginning of the observation interval, all the molecules belong to the same cluster; during the interval we consider only the bonds "still alive" and neglect newly formed bonds. From left to right, $T=350$, 299, 273, 247, and 235 K.

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[1]For general background, see D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford Univ. Press, New York, 1969).

[2]R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976). More recent work is reviewed in C. A. Angell, in *Water: A Comprehensive Treatise,* edited by F. Franks (Plenum, New York, 1981), Vol. 7; Annu. Rev. Phys. Chem. **34**, 593 (1983); Nature (London) **331**, 206 (1988).

[3]The implications of the fact that HB networks in water are above the percolation threshold are described in A. Geiger, F. H. Stillinger, and A. Rahman, J. Chem. Phys. **70**, 4185 (1979); see also the earlier work of P. D. Fleming and J. H. Gibbs, J. Stat. Phys. **10**, 157 (1974).

[4]H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980); R. L. Blumberg, H. E. Stanley, A. Geiger, and P. Mausbach, J. Chem. Phys. **80**, 5230 (1984).

[5]Recent work on dynamics of HB network includes (a) F. X. Prielmeier, E. W. Lang, R. J. Speedy, and H.-D. Lüdemann, Phys. Rev. Lett. **59**, 1128 (1987); (b) D. Bertolini, M. Cassettari, M. Ferrario, P. Grigolini, G. Salvetti, and A. Tani, J. Chem. Phys. **91**, 1179 (1989); (c) D. Bertolini, P. Grigolini, and A. Tani, J. Chem. Phys. **91**, 1191 (1989); (d) J. Teixeira, M.-C. Bellissent-Funel, S.-H. Chen, and B. Dorner, Phys. Rev. Lett. **54**, 2681 (1985).

[6]M. Mezei and D. L. Beveridge, J. Chem. Phys. **74**, 622 (1981).

[7]F. H. Stillinger and A. Rahman, J. Chem. Phys. **60**, 1545 (1974). Our numerical results would of course be modified if we were to include quantum effects, three-body interactions, or intramolecular interactions, but there are numerous studies suggesting that the qualitative effects of classical two-body MD simulations are basically correct since they can reproduce

many of the static and dynamic features of liquid water and the trends observed in the supercooled region; see, e.g., W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983). We have begun to test the robustness of the conclusions of this Letter using different rigid and flexible potentials; recent work on SPC and TIP4P potentials (to be presented elsewhere) confirms the basic conclusions of the present work.

[8]F. Sciortino and S. L. Fornili, J. Chem. Phys. **90**, 2786 (1989).

[9]I. Olovson and P. J. Jonsonn, in *The Hydrogen Bond,* edited by P. Schuster, G. Zundel, and C. Sandorfy (North-Holland, Amsterdam, 1976).

[10]A. Geiger, P. Mausbach, J. Schnitker, R. L. Blumberg, and H. E. Stanley, J. Phys. (Paris) **45**, C7-13 (1984).

[11]It is well known that MD simulations using ST2 water —and many other commonly used water potentials—do not reproduce the experimental value for the pressure. The source of this disagreement may be traced to the computational problem of evaluating the pressure for systems with long-range interactions as well as to the inaccuracy of the model used (Ref. 10). It is customary to hold the density constant when studying different temperatures, but some authors change the density as the temperature is varied [Ref. 5(b)]. Our choice of the first tactic is supported by two considerations: (1) The experimental density change in the temperature range studied here is less than 0.05 g/cm^3, and studies of ST2 water as a function of density with constant temperature [A. Geiger, P. Mausbach and J. Schnitker, in *Water and Aqueous Solutions,* edited by G. W. Neilson and J. E. Enderby (Adam Hilger, Bristol, 1986)] show that a decrease in density from 1 to 0.95 g/cm^3 produces negligible structural and dynamical changes. Therefore we expect that changes in temperature are the principal source of the effects we find. (2) Experimental studies of supercooled water as a function of the pressure show that on increasing the pressure the magnitude of the anomalies is reduced. Therefore we expect that the power-law behavior we find would only be more pronounced were we to undertake a constant-pressure simulation.

[12]O. K. Rice, *Statistical Mechanics, Thermodynamics and Kinetics* (Freeman, New York, 1966), p. 495.

[13]We choose the energy E_{ij} associated with a bond to be of the form given in (1) in order to incorporate the influence of neighboring molecules on the bond-breaking process. The relevant activation energy is related to the properties of the potential well formed by the energy function E_{ij}. Some evidence was presented in Ref. 8 suggesting that the lifetime of the bond must be related to the total number of bonds in which the two linked molecules are directly involved, i.e., with a quantity related to the total potential energy of the pair. We chose the average of E_{ij} to take into account the modification of the potential well during the bond lifetime.

[14]D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).

[15]The average bond lifetimes reported in Fig. 3 are 1 order of magnitude larger than the lifetimes obtained from analysis of depolarized Rayleigh scattering spectra [W. Danninger and G. Zundel, J. Chem. Phys. **74**, 2769 (1981); O. Conde and J. Teixeira, J. Phys. (Paris) **44**, 525 (1983)]. The reason for this difference is that the experiments are sensitive to the linearity of the bond, which is related to the time-dependent changes of the bond polarizability. For example, large-amplitude librational motions contribute to the depolarized Rayleigh spectrum but are not counted as bond breaking in our definition. Our definition is in fact related to the sharing of the same proton by two different oxygen atoms, almost independently from the degree of bending and in this sense should be more appropriate for describing the gel-like properties of the water network. That is, the present definition should be more appropriate for studying the gel-like properties since such fluctuations are not counted as breaking the bond. This distinction may be quite important since the lifetimes obtained from depolarized Rayleigh scattering display an Arrhenius temperature dependence, while the lifetimes obtained from the present bond definition display a power-law temperature dependence. In fact, by using a computational bond definition related to the degree of bond bending, one can reproduce the depolarized Rayleigh scattering data and the Arrhenius temperature dependence (Ref. 10).

[16]In principle, we would expect T_A and α to depend on density, and further work on this subject is in progress. A. Geiger (private communication) has noted that possibly the pressure increase that occurs at constant density shifts T_A to lower values, which *compensates* the known tendency of ST2 water to overestimate the temperature; e.g., the melting point in ST2 water at ambient pressure is at about 300 K [F. H. Stillinger and T. A. Weber, J. Phys. Chem. **87**, 4277 (1983)] and the density maximum is at about the same temperature (Stillinger and Rahman, Ref. 7). For this reason, the agreement between our calculations and the experimental values of T_A and α should perhaps be regarded as a qualitative confirmation of our approach.

[17]For the diamond lattice, which has approximately the same connectivity as oxygens, the critical number of bonds per site is 1.55 (Ref. 3).

[18]Finite-size effects broaden the decay of P_∞ but, as has been checked by evaluating the same quantities for smaller systems, do not modify the τ_{gel} values.