Slow Dynamics of Water Molecules in Supercooled States

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We perform long molecular dynamics simulations of liquid water in normal and supercooled states for times up to 50 ns. We observe the onset of a cage effect at 0.25 ps followed by diffusion at much longer time. The diffusion constant has a power-law temperature dependence. The long-time single-particle dynamics of supercooled water is dominated by a two-step process, beta and alpha relaxations, familiar in the mode-coupling theory of supercooled simple liquids. Over length scales comparable to the cage size alpha decay is characterized by a relaxation rate having a q^2 to q crossover close to the kinetic glass transition temperature.

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There has been a well documented set of thermodynamic and transport properties of supercooled H_2O which indicates that specific volume, sound velocity, isobaric specific heat, and isothermal compressibility of supercooled water increase moderately strongly in the vicinity of $T_S = 228$ K or 49 deg below the temperature of maximum density (TMD). It has been noted by Speedy and Angell [1,2] that the T dependence of many thermodynamic quantities can be fitted, at some distance away from T_S, to a power-law divergence of the type $(T/T_S - 1)^{-x}$. The values of x depend on the measured quantity and span an interval between 0.024 and 0.35 [2–5]. Transport properties, such as static shear viscosity η, inverse self-diffusion coefficient D^{-1}, and various experimental relaxation times τ, on the other hand, diverge strongly on approaching T_S with an exponent in the range 1.5 to 2.5 [2–5]. In particular, it has been noted [6] that two scaling relations are valid. The products $D\eta/T$ and $D\tau$ remain temperature independent within the investigated temperature range.

Interpretation of the thermodynamic origin of T_S can be cast in three widely discussed classes [3]. The first class suggests that the divergence of thermodynamic quantities is due to the existence of a reentrant spinodal line which crosses the ambient pressure line at T_S [1,7,8]. The second class predicts the existence at ambient pressure of low temperature inflections in the liquid isotherms, connected to the formation of a low-density structure in the liquid [8,9]. The third one predicts extrema in the response function but no divergence upon supercooling at any pressure [10,11]. The second and third classes associate the predicted maximum in the response function on cooling to the formation of patches of four-coordinated hydrogen-bonded water molecules, i.e., to the development of a structure similar to the low-density amorphous ice structure. It is relevant to point out here that a recent neutron diffraction experiment of supercooled D_2O has shown that at -31.5 °C the structure factor tends toward that of the corresponding low-density amorphous ice [12]. Moreover, recent small angle scattering experiments indicate that the correlation length of the density fluctuations in water, even at -34 °C, does not extend more than 3.8 Å [13]. Thus, the apparent anomaly of the isothermal compressibility at T_S may not be due to a thermodynamic instability.

In this Letter we present evidence, based on molecular dynamics (MD) simulations, that T_S may be associated with a temperature of structural arrest due to the cage effect that appears in deeply supercooled liquids. We find that the single-particle dynamics in this hydrogen-bonded liquid is consistent with the predictions of the idealized mode-coupling theory (MCT) for supercooled liquids [14], suggesting the identification of T_S as the MCT glass transition temperature [15].

Thus the nature of the singularity in transport properties of water is at least partially dynamic in origin. We conducted MD simulations in the *NVE* ensemble, with 216 molecules. The model potential used is the SPC/E [16], which models a single water molecule as a rigid set of interaction sites. The electrostatic long range interactions have been taken into account using the reaction field method [17]. Further details of the simulations are described [18]. The SPC/E potential has been explicitly parametrized to reproduce also the experimental value of the self-diffusion constant at ambient temperature and density 1 g/cm^3 and it has been widely studied in recent years [19,20]. Moreover, this potential is able to reproduce a pressure-dependent TMD [9,20,21]. As shown in [20] the SPC/E 1 bar isobar is characterized by a TMD of 235 K and a corresponding density of 1.026 g/cm^3. The -40 MPa isobar is instead characterized by a TMD of about 250 K and a corresponding density of 1.000 g/cm^3 [21], in agreement with the experimental pressure dependence of the TMD line. We have decided to study a negative pressure isobar, so that the density at the simulated points never exceeds 1 g/cm^3. Seven simulations have been performed at the state points indicated in Table I, ranging from 35 deg above the TMD to 45 degrees

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TABLE I. Simulated state points.

T (K)	ρ_s (g/cm^3)	E (kJ/mol)	P (MPa)	D (10^{-5} cm^2/s)
284.5	0.984	-48.1	-73 ± 11	$(1.3 \pm 0.1)\ 10^{0}$
258.5	0.986	-50.0	-76 ± 12	$(5.2 \pm 0.5)\ 10^{-1}$
238.2	0.987	-51.6	-80 ± 10	$(1.4 \pm 0.1)\ 10^{-1}$
224.0	0.984	-52.6	-75 ± 15	$(4.4 \pm 0.4)\ 10^{-2}$
213.6	0.977	-53.4	-78 ± 14	$(1.1 \pm 0.4)\ 10^{-2}$
209.3	0.970	-53.8	-99 ± 18	$(5.1 \pm 0.9)\ 10^{-3}$
206.3	0.966	-54.2	-90 ± 23	$(1.8 \pm 1.1)\ 10^{-3}$

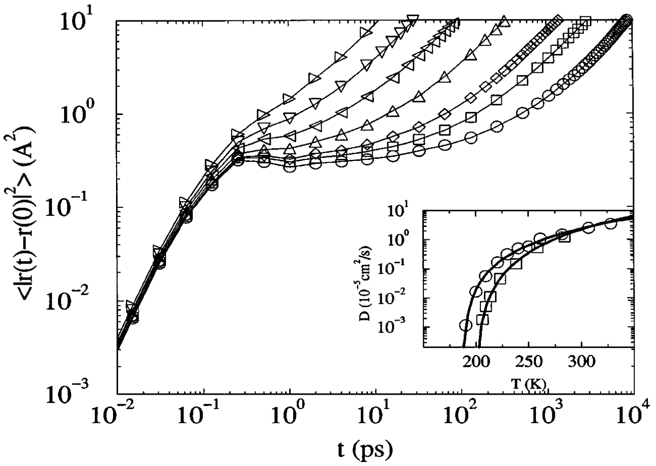

FIG. 1. MSD of the center of mass vs time. (○$T = 206.3$ K, □ $T = 209.3$ K, ◇ $T = 213.6$ K, △ $T = 224.0$ K, ◁ $T = 238.2$ K, ▽ $T = 258.5$ K, ▷ $T = 284.5$ K). The curves show the cage effect, starting at 0.25 ps, followed by the eventual diffusion of the molecule. The inset shows D vs T for two isobars. □'s are from Table I, ○ from [20]. Full lines are power-law fit, respectively, given by $D = 13.93(T/198.7 - 1)^{2.73}$ and $D = 7.39(T/186.3 - 1)^{2.29}$ where D is in cm^2/s and T is in K.

below, thus covering both the normal and supercooled states of water, for time periods ranging from a few hundreds of ps at high T to 50 ns at the lowest T [22].

Several previous water MD simulations, starting from the pioneering work of Rahman and Stillinger [23], have analyzed the single molecule dynamics and its relation to incoherent neutron scattering [23–25]. References [23–25], based on a rather limited simulated time scale (up to 10 ps at most) and limited temperature range, have shown that (i) the intermediate scattering function for the center of mass $F_s(Q,t)$ is non-Gaussian [23], (ii) the diffusive behavior of water molecules is not describable by a discrete jump diffusion [23,25], (iii) the major low frequency translational peaks are centered at 55 and 175 cm^{-1} [23,24], and (iv) the decay of $F_s(Q,t)$ has a fast and a slow component, the time scale of which becomes increasingly disparate upon supercooling [25].

In the following we present the most significant results of the analysis of our long time scale and deeply supercooled MD simulations. We focus on those quantities which are traditionally examined when studying dynamic behavior of supercooled viscous liquids undergoing a kinetic glass transition *á la* mode coupling [14,26]. The reason for this parallel is that the dynamic properties of water near T_S show many analogies with respect to the phenomena near the temperature of structural arrest T^* as discussed by MCT [14,15,26]. These analogies will be discussed as we proceed. A more detailed account of the present work will be published in a separate paper. In Fig. 1 we show the mean square displacement (MSD) of the center of mass as a function of time for different temperatures. The curves have been plotted in a log-log scale in order to display better the flattening-out behavior of the MSD at intermediate times. For lower temperatures the molecules appear trapped in a cage for a considerable amount of time before starting to diffuse away. For the lowest temperature the MSD becomes almost flat starting from 0.25 to about 100 ps; thus the particle remains trapped for three decades in time. Note that the onset of the cage effect appears always at the same time, 0.25 ps, regardless of temperature. This is completely analogous to the recent results [27] obtained for a binary mixture of Lennard-Jones spheres close to the ideal glass transition. The values of D extracted from the asymptotic behavior of MSD are shown in the inset of Fig. 1 together with the fitted curve to the power-law temperature dependence $D = D_o(T/T^* - 1)^{\gamma}$. We also show the values of D from [20]. For both isobars, the temperature dependence of D is well described by a power law, as in real experiments [4]. T^* and γ are pressure dependent. The difference between T^* and the corresponding TMD is always about 50 K. We note also that the difference between T_S and TMD in real water is also about 50 K. Henceforth we suggest the possibility of interpreting T_S as the temperature of structural arrest. The differences in γ between real water and the two simulated isobars are consistent with the experimentally observed sensitivity of γ on pressure (see Ref. [4]).

In Fig. 2 we present $F_s(Q,t)$ in the time interval $10^{-3} < t < 10^{4}$ ps. In the T range investigated, the decay of $F_s(Q,t)$ is clearly described by two relaxation processes. The time scale of the two relaxations becomes more and more disparate as water is supercooled. We fit all the curves rather well by the following equation:

$$F_s(Q,t) = [1 - A(Q)]e^{-(t/\tau_s)^2} + A(Q)e^{-(t/\tau_l)^{\beta}}, \quad (1)$$

where $A(Q)$ is the Debye-Waller factor arising from the cage effect, τ_s is the short relaxation time, and τ_l is the long relaxation time. For all temperatures, $A(Q) = e^{-a^2Q^2/3}$, with $a = 0.50 \pm 0.03$ Å suggesting that during the fast process the center of mass of the water molecule is constrained in a cage of radius a.

Note that $A(Q)$, which plays the role of a nonergodicity factor [14], is such that at low Q we mainly see the

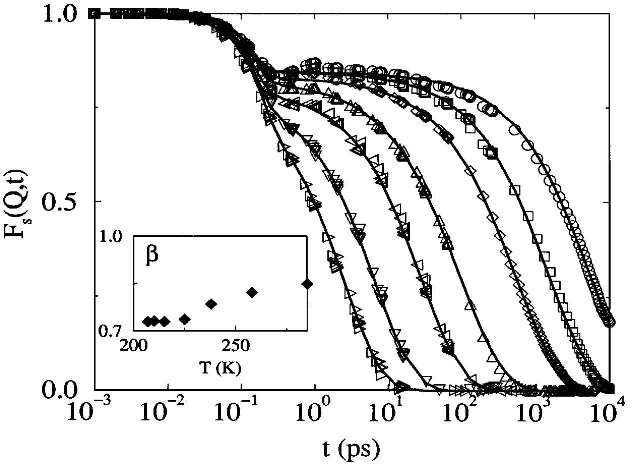

FIG. 2. $F_s(Q_{\max}, t)$ vs time (symbols as in Fig. 1). Solid lines are calculated according to Eq.(1). The inset shows the T dependence of the exponent β associated with the slow relaxation.

slow relaxation, while at the peak of the structure factor $Q_{\max}$, we see both the fast and the slow relaxations. Clearly the Gaussian form of the fast relaxation can be only an approximate one, because the short time behavior of $F_s(Q,t)$ would have to reflect all the low frequency spectral features of translational motion of water molecules, which were extensively investigated before [23–25]. The novel point discovered for the first time in our simulation is that, around and above $Q_{\max}$, the slow relaxation part of the $F_s(Q,t)$ changes gradually from an exponential behavior at high T to a well defined stretched exponential decay. The stretch exponent approaches the value 0.73 as T approaches T^*. Its T dependence for $Q = Q_{\max}$ is shown in the inset. The Q dependence of β is such that β goes to 1 as Q goes to 0. Both the T and the Q dependence of β are thus in agreement with the prediction of MCT [14], in spite of the fact that water is a hydrogen-bonded molecular liquid.

It is remarkable to observe that at $Q_{\max}$ the slow relaxation is already clearly visible 12 deg below the TMD which is easily realizable in a quasielastic neutron scattering (QENS) experiment of bulk water. Figure 3 gives $1/\tau_l$ vs Q in a log-log plot. It is seen that the data follow a straight line within the interval of Q of practical interest. At the highest temperature the slope is 2 and at lower temperatures the slopes gradually change to 1. In the inset we show the degree of validity of the constancy of the product $\tau_l D q^2$ as a function of T and Q. It is seen that at higher T this product is nearly constant but, for the last two lowest Ts, it deviates significantly from a constant at high Q. In real water, $D\tau$ is constant [6]. Our MD results give additional information on Q dependence which can be tested by scattering experiments. We note here that the MCT of kinetic glass transition predicts that D^{-1} and the α-relaxation time τ_l diverge with the same exponent near T^*. However, as Q increases, one expects to have Q-dependent τ_l and we suggest that in the case of water this scaling relation may be modified by including the Q-dependent factor as shown above. We also examined in some detail the intermediate time behavior of $F_s(Q,t)$. In MCT, the initial part of the α relaxation is given by a power law in time with exponent b, and b is a function of γ, the power-law exponent of D vs $T - T^*$. We fitted the run at the lowest temperature by the von Schweidler power-law decay in the range from 4 to 800 ps and obtained $b = 0.5$ which, using the universal scaling relations of MCT, leads to $\gamma = 2.75$. This value is consistent with our analysis of D.

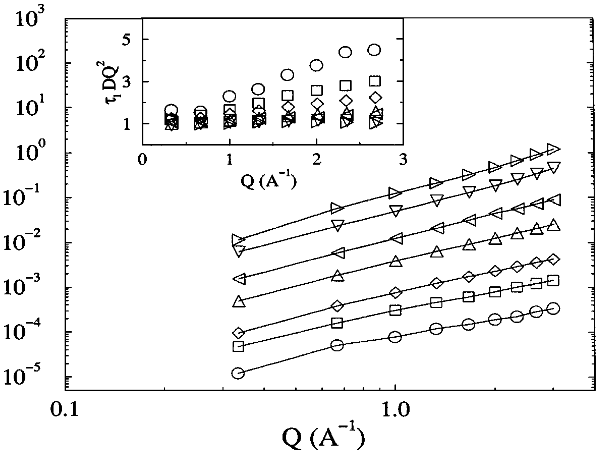

FIG. 3. $1/\tau_l$ vs Q. Solid lines are guides for the eye. Inset is $\tau_l DQ^2$ vs Q at different T. (Symbols as in Fig. 1.)

In summary, we have shown that the experimentally observed power-law T dependence of D may be related to cage effects similar to the one observed in simple liquids close to their MCT glass transition T [14,15,27]. Thus, our findings support the view that no thermodynamic instability is required to explain the anomalous behavior of transport properties in supercooled water near T_S. We have also shown that the long-time behavior of the single-particle dynamics is characterized by a two-step process where the indices b and γ are connected by the MCT universal relations. We propose a simple model for $F_s(Q,t)$ that can also be used to analyze the line shape of future high resolution QENS experiments to extract the Q and T dependence of the correlation time τ_l.

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[18] Periodic boundary conditions are used. The time step for the integration of the molecular trajectories is 1 fs. Specific sites on different molecules in SPC/E interact via either Lennard-Jones or Coulomb potentials. The interaction between pairs of molecules is calculated explicitly when their separation is less than a cutoff distance r_c of 2.5σ, where σ is the length scale in the Lennard-Jones part of the SPC/E. The contribution due to Coulomb interactions beyond r_c is calculated using the reaction-field method, as described by Steinhauser [17]. Also, the contribution of Lennard-Jones interactions between pairs separated more than r_c is included in the evaluation of thermodynamic properties by assuming a uniform density beyond r_c. The MD code used here to calculate the SPC/E trajectories is the same used in Ref. [21] where further details are given. During the equilibration time, $t_{\rm eq}$, a heat bath [H.J.C. Berendsen *et al.*, J. Chem. Phys. **81**, 3684 (1984)] has been used to allow for heat exchange. Simulations at low T have been started from equilibrated configurations at higher T. Equilibration has been monitored via the time dependence of potential energy. In all cases $t_{\rm eq}$ was longer than the time needed to enter in the diffusive regime (see Fig. 1), i.e., $\langle r^2(t_{\rm eq})\rangle$ larger than 10 Å^2.

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