Experimental Determination of the Structural Relaxation in Liquid Water

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(Received 10 August 1998)

The transition from normal to fast regimes of the longitudinal sound velocity has been studied by inelastic x-ray scattering in liquid water as a function of momentum transfer (1–12 nm^{-1}) and temperature (260–570 K), using pressure (0–2 kbar) to keep the density at $\rho \approx 1$ g/cm^3. As in many glass-forming liquids also in water this transition is induced by the structural (α) relaxation. The relaxation time τ, however, when close to the melting point, is 2 orders of magnitude shorter than in glass formers. The activation energy, deduced from the Arrhenius behavior of τ, suggests that such relaxation is associated to the rearrangement of the local structure induced by the hydrogen bond. [S0031-9007(98)08332-X]

PACS numbers: 63.50.+x, 61.10.Eq, 78.70.Ck

The investigation of large wave vector excitations in liquid water has shown the existence of a positive dispersion in the velocity of sound. This dispersion has been inferred in the pioneering computational [1] and experimental [2] studies of the dynamic structure factor, $S(Q,E)$, and has been recently assessed by inelastic x-ray scattering (IXS) [3,4]. Using IXS, the transition of the longitudinal sound velocity from the adiabatic value, $c_0 \approx 1500$ m/s, to a value more than twice larger, $c_\infty \approx 3200$ m/s, was studied at $T = 5\,^\circ\mathrm{C}$. Here, the transition is observed for the acousticlike excitation with wave vector $Q_t \approx 2\ \mathrm{nm}^{-1}$ and energy $\hbar\Omega_t \approx 3$ meV [4,5]. This sound velocity dispersion is qualitatively similar to that observed in glass-formimg liquids. There, the transition between the two dynamic regimes is determined by the coupling of the propagating density fluctuations with the dynamics of the structural rearrangements of the particles in the liquid. The complex dynamics of such a rearrangement can be described by a relaxation process with a characteristic time τ. The transition takes place when the condition $\Omega_t\tau \approx 1$ is fulfilled. In glass-forming liquids τ has a very steep temperature dependence; its typical values are in the *nano*second range when close to the melting point and dramatically increases near the calorimetric glass transition temperature T_g [6]. This relaxation process (α process) has a cooperative nature and the density fluctuations are differently influenced in the two opposite frequency limits: the system has a solidlike elastic behavior for $\omega\tau \gg 1$, and a viscous one for $\omega\tau \ll 1$. One could speculate that also in liquid water the physical mechanism responsible for the dispersion of the sound velocity is an α relaxation process. Contrary to glass formers, however, in water the existence of a liquid to glass transition, predicted to be in the 130–140 K region, has not yet been firmly established. The situation is even more involved as extrapolation of experiments made at $T > 245$ K and molecular dynamics simulations seem to indicate the presence of a relaxation time that diverges at $T \approx 230$ K [7]. A further quantitative difference is found in the characteristic time, which in water is in the *pico*second range at the liquid to crystal transition, corresponding to a value much faster than in glass formers.

The experimental characterization of the α process is typically obtained by the determination of the dispersion of the sound velocity as a function of T and at a constant Q transfer value. At the inflection point ("t") of such an "S"-shaped curve the condition $\Omega_t(Q,T)\tau(T) \approx 1$, with $\Omega(Q,T) = c_{\mathrm{app}}(Q,T)Q$, is fulfilled. In glass-forming liquids, this condition is met by Brillouin light scattering (BLS) measurements close to melting, and by ultrasonic (US) methods close to T_g. Indeed, the typical frequencies allowed by these two techniques are such that $\Omega_t(Q,T)\tau(T) \approx 1$ is met for values of τ in the 100 ps (BLS) and 1 μs (US) ranges. In the case of water, as a consequence of the small value of τ close to melting, the BLS cannot access the relevant excitations energy region, although, in the highly supercooled liquid, it was possible to detect by BLS a deviation of c_o towards a higher value, i.e., towards c_∞ [8]. The complete determination of the S-shaped curve as a function of either T or Q requires, however, the use of IXS [4].

In this Letter, we report on an IXS study of the temperature dependence of the transition from normal to fast sound in liquid water in the $T = 260$–570 K and $Q = 1$–$12\ \mathrm{nm}^{-1}$ regions. In order to emphasize the thermal effects and to minimize the modification of the hydrogen bond dynamics due to large variations of the excluded volume, the density was kept in the range $\rho = 0.94$–1.07 g/cm^3. This was obtained adjusting the pressure in the 0–2 kbar range. The existence of a relaxation process is demonstrated by the observation that the transition takes place at increasing Q values with increasing temperatures. The associated time scale extends into the sub*pico*second region with increasing temperature. The analogy with the glass-formers phenomenology implies that the fast relaxation process found here can be identified with an α process. The derived values of τ are consistent with previous estimations: they roughly follow an Arrhenius behavior with an activation energy comparable to the hydrogen bond energy. This suggests that, in water, the α process is associated with the rearrangement of molecular structures kept together by the hydrogen bond.

The experiment has been carried out at the very high energy resolution IXS beam line (BL21-ID16) at the European Synchrotron Radiation Facility. The instrument consists of a backscattering monochromator and five independent analyzer systems, held one next to each other with a constant angular offset on a 7-m-long analyzer arm. We utilized the Si(11 11 11) configuration, giving a total instrumental energy resolution of 1.6 meV full width half maximum (FWHM) [9], and an offset of 3 nm^{-1} between two neighbor analyzers. The momentum transfer, $Q = 2k_0 \sin(\theta_s/2)$, with k_0 the wave vector of the incident photons and θ_s the scattering angle, is selected by rotating the analyzer arm. The Q resolution is 0.4 nm^{-1} FWHM. Energy scans, performed by varying the monochromator temperature with respect to that of the analyzer crystals, took about 150 min, and each Q point was obtained by typically averaging five scans. The data were normalized to the intensity of the incident beam. The liquid sample ($\approx 1\ \mathrm{cm}^3$) was contained inside a INCONEL-751 cell, which can be pressurized by a hand pump up to 5 kbar and heated up to 700 K. The x-ray beam passed through two 1-mm-thick diamond single crystal windows with a 2.3-mm-diameter aperture. The distance between the two windows, i.e., the sample length along the x-ray beam was 10 mm: this allowed us to cover the 0°–25° scattering angle range with a sample length comparable to the x-ray photoabsorption length. The pressure stability was better than ±5 bars at 2 kbar. The transverse dimensions of the focused x-ray beam are $0.15 \times 0.3\ \mathrm{mm}^2$.

The IXS spectra were measured at different (Q, T, P) points. The Q dependence was studied in the $1-12\ \mathrm{nm}^{-1}$ region at the temperatures of 278, 373, and 493 K. The T dependence was studied at the Q values of 2, 4, and 7 nm^{-1} in the 260–570 K region. The pressure, selected according to the equation of state (EOS) [10], was varied to keep the density, $\rho \approx 1.00\ \mathrm{g/cm}^3$. The points at $T < 270$ K ($T > 410$ K) were taken at $P =$ 2 kbar, corresponding to $\rho \approx 1.02-1.07\ \mathrm{g/cm}^3$ ($\rho \approx 1.00-0.96\ \mathrm{g/cm}^3$). These measurements were performed, therefore, at constant density and not along the coexistence curve.

An example of the evolution observed in the IXS spectra as a function of temperature is reported in Fig. 1 for $Q = 2$ and 4 nm^{-1} and three selected temperatures. The spectra were fitted by the convolution of the experimentally determined resolution function with a phenomenological model function made by the sum of a Lorentzian and of a damped harmonic oscillator (DHO) [11]. The Lorentzian accounts for the quasielastic contribution to $S(Q, E)$ and the DHO for the two side peaks, whose energy position is $\hbar\Omega(Q)$. The fit to the data are also shown in Fig. 1, together with the two individual contributions. The energy dispersion of the inelastic signal with Q is in agreement with the dispersion previously reported for liquid water at $T = 278$ and 300 K [3,4]. This can be seen in Fig. 2, where we report the Q dependence of the fitting parameter $\Omega(Q)$ at the selected temperatures of 278, 373 and 493 K. In this figure, the values of $\Omega(Q, T)$ have been scaled by the ratio $c_0(278\ \mathrm{K})/c_0(T)$, where c_0 is the adiabatic sound velocity [10], and the full line represents the adiabatic sound dispersion $\Omega(Q) = c_0(278\ \mathrm{K})Q$. For completeness, we also show the dispersion relations obtained from representative molecular dynamics simulations [5,12], where the dispersion of the sound velocity was reported. It is evident from the figure that the transition of the apparent sound velocity $\Omega(Q)/Q$ from the adiabatic c_0 value to the high frequency limit, c_∞ (the "fast" sound), takes place at a Q value which is strongly temperature dependent: in the dispersion at $T = 278$ K, the deviation from c_0 is already observable at $\approx 1\ \mathrm{nm}^{-1}$, while, at $T = 373$ K and $T = 493$ K, this deviation is observed at Q values larger than 3 and 6 nm^{-1}, respectively. This behavior indicates that the mechanism underlying the observed transition has a dynamical origin and is likely to be due to a relaxation process. The temperature

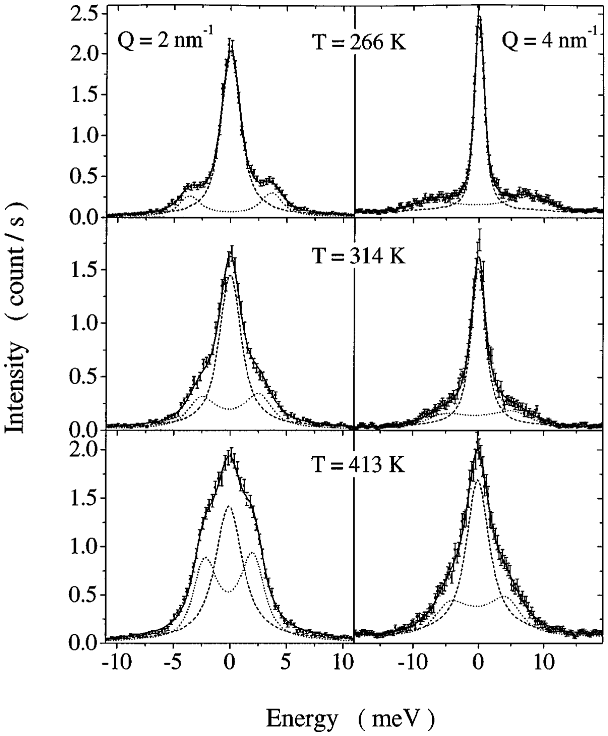

FIG. 1. Example of IXS spectra of liquid water at the indicated Q values (●) shown together with the total fits and the individual components, as explained in the text. The spectra at $T = 266$ (314, 413) K were taken at $P = 2$ (0.3, 2) kbar corresponding to a density $\rho = 1.02$ (1.00, 0.98) $\mathrm{g/cm}^3$.

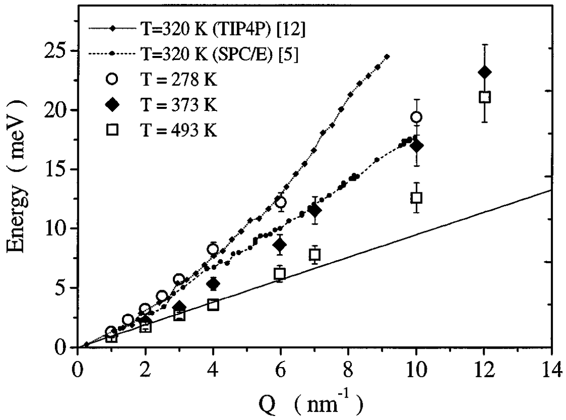

FIG. 2. Dispersion relation of the DHO energy position parameter $\hbar\Omega(Q,T)$ as a function of Q at the indicated temperatures. Two dispersion relations, obtained by molecular dynamics simulation, respectively, at $T = 300$ K [12] and $T = 4$ °C [5]. The excitation values have been scaled by the factor $c_0(278\text{ K})/c_0(T)$, with $c_0(T)$ values as obtained from the EOS [10]. This has been done to emphasize in the same plot the departure of the dispersion relation from the $c_0(T)Q$ law, shown by the solid line, which is valid in the $Q \to 0$ limit. This departure takes place at increasing Q values with increasing temperatures.

dependence of its characteristic relaxation time, τ, is then the cause of the strong temperature dependence of the Q value, Q_t, at which the transition is observed.

An estimate of both Q_t and τ can be obtained by defining the apparent longitudinal elastic modulus: $M = \rho c_{\text{app}}^2(Q,T)$. In the simple Debye approximation for the relaxation process, the frequency dependence of M, leading to the dispersion from its low frequency value $M_0 = \rho c_0^2$ to its high frequency one $M_\infty = \rho c_\infty^2$, is given by [13]

$$M = M_\infty + \frac{M_0 - M_\infty}{1 + i\omega\tau}. \qquad (1)$$

Introducing the reduced apparent modulus

$$M_r = \frac{M - M_0}{M_\infty - M_0}, \qquad (2)$$

the values of τ can be determined by the condition $\text{Re}(M_r) = 0.5$. The calculation of $M_r(Q,T)$ from the spectroscopic parameters requires the knowledge of c_0 and c_∞. For $c_0(T)$, we used the values from the EOS [10] and we assumed them to be Q independent; this hypothesis is justified by the small variation of the static structure factor in the considered Q range [1,14]. We also assumed a T and Q independent value of $c_\infty = 3200$ m/s (derived from the IXS measurements at $T = 278$ K [4]). In deriving $M_r(Q,T)$, one must also consider that the $c_{\text{app}}(Q,T)$ could depend on the utilized model for the $S(Q,\omega)$. Within these approximations, we obtained from the data reported in Fig. 2, the M_r values shown in Fig. 3. This allows us to determine the momentum transfer value Q_t from the condition $M_r = 0.5$ at the considered temperature. The values for $\tau(T)$ are then derived as $\tau(T) = \Omega(Q_t,T)^{-1}$, where $\Omega(Q_t,T)$ is obtained interpolating the $\Omega(Q,T)$ reported in Fig. 2. The lines superimposed to the data correspond to the representation of Eq. (2) using the derived values of τ. Similarly, from the sets of measurements performed at $Q = 2$, 4, and 7 nm^{-1} as a function of temperature, we obtained the $\Omega(Q,T)$ values which lead to the $M_r(Q,T)$ values reported in Fig. 4. Here, from the condition $M_r(Q,T) = 0.5$, one obtains the temperature T_t, where the selected momentum transfer becomes Q_t. Therefore $\tau(T) = \Omega(Q,T_t)^{-1}$, where $\Omega(Q,T_t)$ is obtained interpolating the $\Omega(Q,T)$.

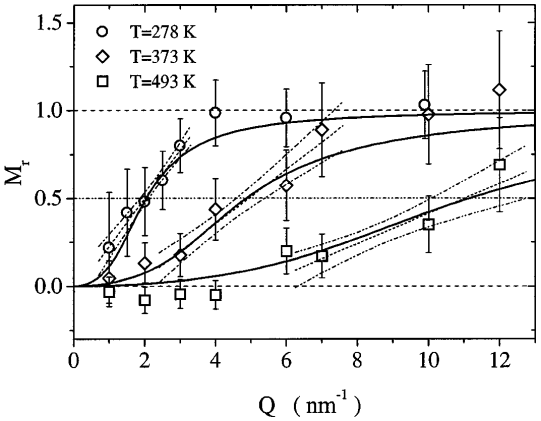

FIG. 3. Q dependence of the reduced apparent modulus M_r at the indicated temperatures. The Q_t values have been determined by the condition $M_r = 0.5$. This has been found by the linear fits to the data, shown (dashed lines) together with their $\pm 1\sigma$ prediction bands (dot-dashed lines). The full lines represent the real part of Eq. (2) with the obtained values of τ and $\omega = c_{\text{app}}(Q)Q$.

The values of $\tau(T,Q)$ derived from Figs. 3 and 4 are reported in an Arrhenius plot in Fig. 5. This quantity changes from 1.3 ps at 280 K to 0.2 ps at 490 K. In spite of the fact that the present measurements were performed at constant density, the derived τ values are

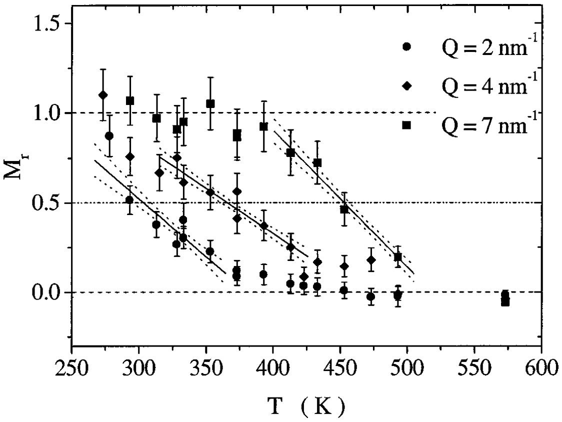

FIG. 4. T dependence of the reduced apparent modulus M_r at the indicated Q values. The T_t values have been determined as the Q_t values in Fig. 3.

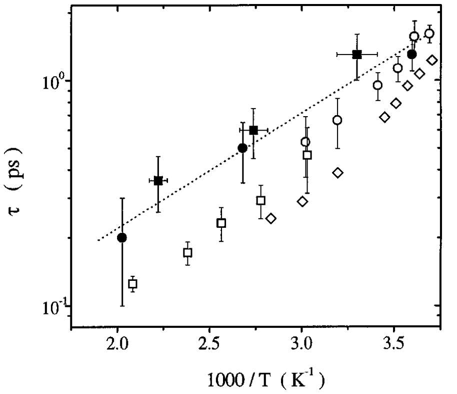

FIG. 5. Arrhenius plot of the relaxation time $\tau(T,Q)$ as obtained from the analysis of the apparent reduced moduli reported in Figs. 3 (●) and 4 (■), and from Refs. [15] (○), [16] (□), and [17] (◇). The dotted line is the best linear fit to the whole data set, and its slope gives an activation energy of 2.5 ± 0.5 kcal/mole.

consistent with other determinations performed along the coexistence curve. This is shown in Fig. 5, where are also reported the τ values obtained either from the linewidths [15,16], or from a mode coupling theory analysis [17] of the depolarized Raman scattering. These values are also comparable to those obtained from ultrasound absorption and viscosity measurements [18], Brillouin light scattering data [8], and from molecular dynamics simulations [12,19]. In the considered temperature and momentum transfer region, we also observe that τ does not have a marked Q dependence, and when fitted to an Arrhenius behavior gives an activation energy $\Delta E = 2.5 \pm 0.5$ kcal/mole. This value is consistent with the other determinations along the coexistence curve, where a relevant deviation from the Arrhenius behavior is observed only at temperature below 280 K.

In conclusion, we have shown that in liquid water the transition between the low frequency adiabatic sound velocity towards its high frequency limit takes place at a Q_t value which is strongly temperature dependent. This demonstrates that such transition is due to a relaxation process. The phenomenology reported here resembles the one observed in glass-forming liquids undergoing the α relaxation process, although on a much faster time scale. This similarity leads to suppose that also in water, the considered relaxation process is due to a rearrangement of the local molecular structure. This rearrangement takes place on a time scale of the order of τ: The response of the system to a density fluctuation is either hydrodynamiclike for frequencies smaller than $1/\tau$ or solidlike in the opposite limit. This interpretation is in agreement with the observed equivalence of the high frequency dynamics in liquid and solid water [20].

We acknowledge I. Vogl for his help during the IXS measurements, and D. Gibson and L. Melesi (ILL, high pressure group) for their help in the high pressure cell construction and testing. We also acknowledge U. Balucani and R. Pick for useful discussions.

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