Experimental Observation of the α Relaxation in Supercooled Water

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(Received 22 February 2000)

Intermediate scattering functions for density fluctuation in D_2O contained in pores of a Vycor glass have been measured using an improved neutron spin-echo spectrometer at two supercooled temperatures. The measurements cover the time range from 1 to 2300 ps with the Q range spanning the first diffraction peak of water. The time correlation functions can be fitted to a stretched exponential relaxation function with a Q-dependent amplitude. Both the stretch exponent and the relaxation time peak approximately at the Q value corresponding to the first diffraction peak, confirming the validity of the mode coupling idea in supercooled water.

PACS numbers: 61.12.Ex, 61.20.Lc, 64.70.Pf

Studies of quasielastic and inelastic coherent scattering of neutrons from D_2O at room temperature were made by Bosi *et al.* [1] and Teixeira *et al.* [2] a number of years ago mainly for showing the existence of a collective, propagating high frequency soundlike excitation. The collective excitation appears as shoulders on both sides of the quasielastic peak in the frequency domain technique used in these studies. The existence of these short wavelength sound waves in water was reconfirmed recently by high resolution, coherent inelastic x-ray scattering experiments of Ruocco *et al.* [3]. However, inspection of these neutron and x-ray scattering spectra reveals the presence of a rather striking common feature, in addition to the so far emphasized frequency-shifted side peaks (the Brillouin component). The Rayleigh-Brillouin triplet, characteristic of these coherent scattering spectra at high Q (the magnitude of scattering vector), is dominated by an unusually intense Rayleigh (quasielastic) component, the width of which is essentially resolution limited. This is in sharp contrast to the well-known fact [4] that the Rayleigh peak observed with light scattering (at low Q) in room temperature water is usually rather small compared to the Brillouin component, because near room temperature the ratio of specific heats, $\gamma = C_p/C_v$, is very close to unity [5]. Since the Q range in which these neutron and x-ray scattering spectra were measured corresponds to a length scale of the order of the intermolecular distance, this high Q nonpropagating density fluctuation process which gives rise to the quasielastic peak is likely to be related to the local structural relaxation. Considering that the neutron and x-ray spectrometers which were used to measure these spectra have the best resolution of about 1.5 meV, the local structural relaxation time for water above the freezing point must be in the order of 1 ps or longer. In this Letter we report a direct measurement of this relaxation time in supercooled temperatures for the first time using a time-domain technique called neutron spin-echo spectroscopy.

In 1997, Sciortino, Fabbian, Chen, and Tartaglia (SFCT) published a result of a computer molecular dynamics (CMD) study of supercooled water (H_2O) based on the SPC/E model potential [6]. These authors computed the coherent intermediate scattering function (ISF) at a series of temperatures ranging from 43° below the temperature of maximum density (TMD) to 35° above the TMD (corresponding to real water at 4 °C). They showed that, while above the TMD the model water exhibits a single, fast (sub-picosecond) relaxation, below the TMD it shows a clear, time-separated, two-step fast-slow relaxation. The two relaxation processes are separated in time by a plateau, and the level of it is Q dependent. Furthermore, the slow relaxation, or the long-time tail, can be well fitted by a stretched exponential function, known in the literature as the α relaxation. The relaxation time associated with the α relaxation grows longer as the water is increasingly supercooled, generally longer than 1 ps. According to the mode coupling theory (MCT) of supercooled liquids [7], the α relaxation is related to the local structural relaxation and is a manifestation of a "cage effect" that a typical molecule is increasingly subjected to in supercooled states. One striking result of the SFCT paper was that, as far as the long time part ($t > 1$ ps) of the normalized ISF is concerned, it is accurately describable by a function,

$$\frac{F_L(Q,t)}{S(Q)} = A(Q)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \tag{1}$$

where $A(Q)$ is the Debye-Waller factor, β the stretch exponent, and τ the cage relaxation time. All three parameters are Q dependent and their Q dependences are oscillatory with their peak positions coinciding approximately with the peak positions of the O-O partial structure factor of water. This is in complete agreement with predictions of the MCT.

In order to formulate a theory which accounts for the complete time dependence of the ISF, short time as well

0031-9007/00/85(17)/3644(4)$15.00

as long time, Liao, Sciortino, and Chen [8] have recently proposed a phenomenological formula for the normalized ISF,

$$\frac{F(Q,t)}{S(Q)} = \left[[1 - A(Q)]\frac{F_{\mathrm{GET}}(Q,t)}{S(Q)} + A(Q)\right] \times \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad (2)$$

where $F_{\mathrm{GET}}(Q,t)$ is the in-cage collisional relaxation function calculated using the generalized Enskog kinetic equation [5], with a correction due to the confinement effect [8]. This approximate theory takes into account the short-time in-cage collisional dynamics of the water molecule by the kinetic theory and the eventual relaxation of the cage at long time by the stretched exponential function. These authors were able to analyze all the CMD data of SFCT successfully using this model. Liao, Chen, and Sette have further applied this theory to the analysis of a set of inelastic x-ray scattering data of supercooled water at 259 K with satisfactory results [9]. The cage effect and the associated long cage relaxation time were predicted by the MCT which was originally formulated for a hard-sphere liquid and also for simple atomic liquids with a Lennard-Jones interatomic potential. The applicability of the MCT to a complex, hydrogen-bonded molecular liquid, like water, is uncertain from a theoretical point of view. In fact, the concept of the "cage" in water is qualitatively different from the one in the simple liquids. As water is supercooled, the probability of formation of a tetrahedrally coordinated, hydrogen-bonded configuration around a typical molecule increases. Since this configuration is an open structure, the density of water actually decreases upon supercooling. On the other hand, in simple liquids, the density increases upon supercooling. The cage effect arises in water because the tetrahedrally coordinated structure is a more stable structure and its lifetime is longer. Thus a direct experimental demonstration of the existence of an α relaxation is of great relevance not only to confirmation of the approximate validity of the earlier CMD work but to a further development of the MCT for molecular liquids.

The neutron scattering measurements have been performed at the Orphée reactor of the Laboratoire Léon Brillouin in Saclay, France. We used a new neutron resonance spin-echo (NRSE) spectrometer MUSES installed on the guide G1bis. Although conceptually different from the "classical spin-echo spectrometer" [10], NRSE [11] allows the measurement of the same normalized intermediate scattering function, $F(Q,t)/S(Q)$. We alternatively used an incoming neutron beam with two different average wavelengths of 4.0 and 4.8 Å, respectively, with a wavelength spread of 15%. The range of Fourier time covered in the experiment was from 1.0 to 2300 ps. The resolution of the spectrometer has been measured with a quartz sample (fully coherent scatterer). In the wave vector range of the measurements (near the maximum of the D_2O structure factor) the polarization of the scattered beam $P(Q,t=0)/P^{\mathrm{res}}(Q,t=0) \sim 0.93$, therefore we neglected the incoherent contribution of D_2O. The total intermediate scattering function has then been deduced by simple division of the normalized spectra by the normalized resolution. The total intermediate scattering function contains two contributions: a time dependent contribution due to D_2O and a time independent plateau arising from the elastic scattering of Vycor (see Fig. 1). The count rate was of 2100 counts min^{-1} near the maximum of the structure factor of D_2O with 4.8 Å.

A sample of D_2O used in the experiment is contained in a porous glass "Vycor" in the form of a fully hydrated Vycor (0.25 g D_2O per g of dry Vycor). Vycor brand porous glass No. 7930 is a product of Corning Glass Works. It is made by heating a homogeneous mixture of boron oxide and silica glass above the melting point and then quenching the mixture to a temperature below the spinodal line where the mixture phase separates into mutually interpenetrating boron oxide-rich and silica-rich regions (a bicontinuous structure). At a certain stage of the preparation, the boron-rich regions are leached out by acid, leaving behind a silica skeleton with a characteristic distribution of pore sizes (with an average pore size of 50 Å) having a pore volume fraction of 28%. The sample consists of a flat rectangular plate 1.9 mm in thickness.

Figure 1 presents the long-time portion of the normalized ISF at $T = 259$ K, for four Q values in the vicinity of the first diffraction peak (located between $Q = 1.8$ and 2.0 Å^{-1}) of the neutron structure factor. Note that by definition the normalized ISF has a value unity at $t = 0$, independent of Q. Even though the measured Fourier time spans more than three decades, covering 1.0 to 2300 ps, it still cannot reach the short-time region where the normalized ISF aproaches unity. According to the CMD data for the temperature 12° below the TMD [6], the normalized

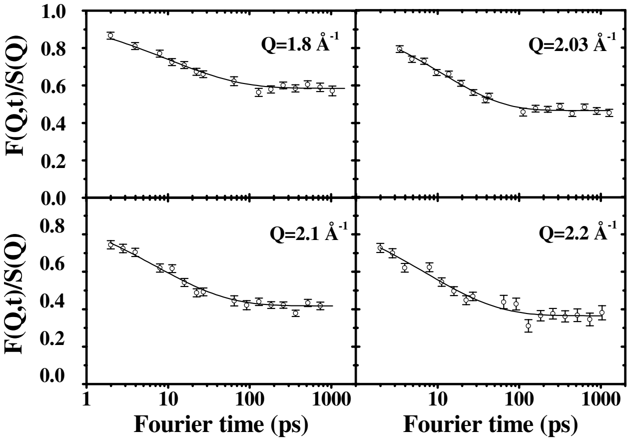

FIG. 1. Intermediate scattering functions at four different Q values in the vicinity of the first diffraction peak of the neutron structure factor of heavy water. Temperature of the sample was 259 K. The symbols with error bars denote experimental data and the solid lines are the best fits using Eq. (3) (see text).

ISF is essentially flat and unity up to 0.02 ps, followed by a β-relaxation range where the ISF decays according to a power law, reaching the plateau level at about 0.3 ps [6]. The plateau persists until about 1 ps and from there on the α relaxation commences. Unfortunately, the spin-echo spectrometer MUSES cannot be operated with the Fourier time shorter than 1 ps without having to use thermal neutrons which are not transmitted by the guide G1bis. Therefore we were unable to measure the plateau region of the normalized ISF. The solid lines are the best fits using equation,

$$\frac{F(Q,t)}{S(Q)} = p(Q) + [1 - p(Q)]A(Q) \times \exp\left[-\left(\frac{t}{\tau(Q)}\right)^{\beta(Q)}\right], \tag{3}$$

where

$$p(Q) \simeq \frac{S_{\mathrm{SiO_2}}(Q)}{S_{\mathrm{SiO_2}}(Q) + S_{\mathrm{D_2O}}(Q)}.$$

Agreement between the theory and experimental data is seen to be satisfactory over three decades of time.

Figure 2 shows the Q dependences of the three extracted model parameters at two temperatures, $T = 259$ K and $T = 262$ K. Also shown is the neutron structure factor of D_2O, as measured at the $t = 0$ limit of the normalized ISF (upper left panel) at $T = 259$ K. It should be noted that the neutron structure factor of heavy water is dominated by the O-D and D-D partial structure factors which are different from the center-of-mass structure factor measured by x-ray diffraction. The fitted stretch exponent $\beta(Q)$ (lower left panel) and cage relaxation time $\tau(Q)$ (lower right panel) are seen to show a maximum, within the error bars, at the position of the peak of the structure factor. These features have been predicted by the MCT [7] and were also shown clearly in the CMD work of SFCT. Because of the unavailability of the experimental plateau levels mentioned above, the uncertainty in the extracted Debye-Waller factor $A(Q)$ is large, and we are unable to see a clear maximum which was also predicted by the MCT.

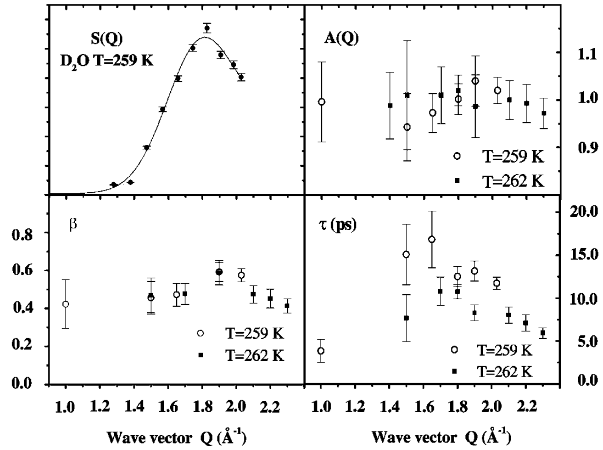

FIG. 2. The values of the three fitted parameters, $A(Q)$, $\beta(Q)$, and $\tau(Q)$, according to the α-relaxation model. Also shown (upper left panel) is the experimental structure factor obtained from the elastic scan of the sample (with the signal due to the Vycor subtracted) at 259 K using MUSES. The peak position is in agreement with an independent neutron diffraction measurement [12].

Detailed investigation of structural relaxation above the predicted MCT critical temperature has been performed by neutron spin-echo spectroscopy in different glass forming systems including molten mixed salts [13], molecular liquids [14], or polymer systems [15] (see [16] for a recent review). Much of the MCT prediction on the structural relaxation has been tested, with careful attention paid to the MCT time-temperature superposition principle. However only a small number of experiments investigates the details of the wave vector dependence of the Kohlrausch-Williams-Watt parameter by coherent neutron scattering [13,17]. Such an investigation has to be performed by high resolution neutron spectroscopy and preferably in the time domain, since the analysis of the peak shape is strongly dependent on convolution effects in the frequency domain. Unfortunately water is very difficult to supercool to lower temperatures than 260 K (for D_2O), whereas apparent divergence of the transport properties appears near 225–230 K [18]. As a consequence the structural relaxation is not easy to separate experimentally from other dynamical processes. At the deepest temperature measured in this experiment (259 K), the α-relaxation time remains of the order of 20 ps. This prevents us from any detailed analysis of the temperature dependence of this relaxation. However two basic features appear from the data: first the parameter $\tau(Q)$ and $\beta(Q)$ oscillate in phase with the structure factor. Such behavior was observed by solving the mode coupling equations for hard-sphere systems [19] and refining the structural relaxation decay with Kohlrausch function. It is a direct consequence of the MCT equations [7]. The second observation is the nontemperature dependence of the parameter $\beta(Q)$, although observed in a tiny temperature range, which is similar to the time-temperature superposition principle. Another point worth mentioning here is that the single particle dynamics of H_2O contained in Vycor has also been studied by us [20]. The spectral analysis verified that the incoherent ISF followed the stretched exponential form. At $T = 258$ K, the measured relaxation time and the stretch exponent at $Q = 1.8$ Å^{-1} were 9 ps and $\beta = 0.56$, comparable to the above values obtained by a coherent quasielastic scattering.

In summary, we have carried out the state of the art neutron spin-echo measurements of the ISF of supercooled D_2O contained in a porous glass and the results establish clearly the existence of the α relaxation with the relaxational parameters consistent with that of CMD data of SPC/E model water. These observations suggest that the dynamics of supercooled water can be described in the general frame of the MCT scheme of glass forming liquids.

The research work of S. L. is supported by a grant (No. 03PESTUM6) of the BMBF. The research of S. H. C. on water is supported by a grant from the Materials Chemistry Program of the USDOE. He would also like to acknowledge receiving a NATO collaborative Research grant for travel support which made this collaborative work across the Atlantic possible.

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