Low frequency scattering excess in supercooled confined water

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Inelastic neutron scattering data on water confined in Vycor glass are presented for temperatures ranging from 268 to 220 K and hydration levels of 12% and 8%. The data have been analyzed in the framework of the mode coupling theory, in the region of the β relaxation. Strong deviations from the theoretical predictions are found and ascribed to the existence of a low frequency scattering excess. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1367284]

I. INTRODUCTION

Due to its ubiquitous role on earth, water is the subject of numerous studies in various fields. In particular, over the last decade the study of the glass-like features of this bizarre element has attracted considerable attention. Below the melting temperature all liquids exist as such only in a metastable state, namely the supercooled one.[1] Water does not make any exception in this respect. Nonetheless, while in most liquids it is possible to reach the glassy state by deeply supercooling, in water homogeneous nucleation prevents this direct observation. This last phenomenon is believed to be triggered by the presence of impurities. Due to this problem, while numerical simulations can go down deep into the supercooled metastable region, the range of temperatures tested by the experiments is much more limited. As a consequence the signatures of glassy behavior in real water were, at the beginning, very weak.[2,3] More recent molecular dynamics (MD) simulations on simple point charge/extended (SPC/E) water[4,5] clearly showed the behavior typical of a glass former approaching the crossover temperature of the mode coupling theory (MCT).[6] Low frequency Raman spectra of supercooled bulk water have also been interpreted as due to the existence of a MCT relaxing cage.[7]

As experimental resolution of instruments progressed and physicists experimented new thermodynamic states for water upon confinement in small volumes, a new impulse to the experimental verification of the possibility of vitrification of water was given. Upon confinement water offers, in fact, the invaluable possibility of a much deeper supercooling with respect to the bulk. The dynamical behavior of confined water is of particular interest not only for its relation with the bulk, but also because of the relevant role that confined water plays in many situations of interest for biology and geology. In particular, it is believed that the protein functionality could be crucially dependent on the presence of water on its surface.[8]

Nowadays it is quite commonly accepted that water, when confined, develops upon supercooling a slow dynamics typical of a glass former. In particular, a detailed MD study on SPC/E water confined in a pore of Vycor glass showed the appearance of glassy features at higher temperatures with respect to the bulk case and a behavior *à la mode coupling*.[9–13] Moreover, high resolution quasielastic neutron scattering (QENS) and neutron resonance spin–echo (NRSE) studies of the slow relaxation region, α, have been recently performed on water confined in Vycor glass[14–17] and confirmed the MCT behavior of the α relaxation region.[16,17] Both experiments and simulations of water close to the surface of proteins also evidenced features typical of a glass former.[18–21] In particular, in the range of frequency that corresponds to the β relaxation region, evidence from both MD and QENS has been found of an excess of vibrational intensity for water close to the surface of proteins.[18,19,21] This excess has been related to a typical feature of a strong glass former, namely the boson peak.

In this paper we performed an inelastic neutron scattering (INS) experiment to test the behavior of the fast relaxation region, β, for supercooled water confined in Vycor glass. In the next section we describe the MCT scenario for water and the theoretical predictions for the correlator that has been measured in our experiment. In the third section we turn to the description of the experiment and to the data analysis procedure, and in the fourth section we discuss the results. The last section is devoted to the concluding remarks.

II. THE STATE OF THE ART FOR WATER IN THE FRAMEWORK OF MCT

On supercooling a glass former liquid below its melting temperature, one reaches, well above the calorimetric glass transition temperature, T_g, an important crossover temperature T_C. On approaching T_C from above, the ideal version of MCT is capable of predicting a precise behavior for the density correlators measured in a neutron scattering experiment. In particular, for simple glass formers a transient caging of

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J. Chem. Phys., Vol. 114, No. 22, 8 June 2001

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the particle due to the nearest neighbors is responsible for the separation in two time scales of the correlator and for the stretching of the slow relaxation law. The time scale separation appears most evident at wave vectors Q around the first peak of the static structure factor. This behavior has been successfully tested for many glass formers.[6] For simple glass formers the transient caging is induced by the increase of the density. Water does not rank in the category of typical glass formers, being a network forming molecular liquid. In water in fact there is no substantial increase of density upon super-cooling. The caging seems to be most likely induced by the enhanced stiffness of the hydrogen bond network on lowering the temperature.[17] Due to the development of a two-step relaxation dynamics when approaching T_C from the liquid side, the space Fourier transform of the density correlator, the self-intermediate scattering function, SISF, $F_S(Q,t)$ after a fast decay at short times enters a plateau region, β relaxation, corresponding to the rattling of the particle in the nearest-neighbor's cage. In this region the SISF is predicted to have a power law behavior

$$F_S(Q,t) - f_Q \sim (t)^{-a}. \tag{1}$$

After a time interval, which becomes longer on approaching T_C, the function $F_S(Q,t)$ decays to zero, α relaxation. The region of departure from the plateau is also predicted to have a power law behavior, namely the von Schweidler law

$$F_S(Q,t) - f_Q \sim (t)^{b}, \tag{2}$$

where f_Q is the Q-dependent height of the plateau also known as the Lamb–Mössbauer factor. The last part of the α relaxation region has a stretched exponential decay.[6]

An INS experiment on an incoherent scatterer measures the space–time Fourier transform of the density correlator, namely the self-dynamic structure factor, $S_S(Q,\omega)$. This correlator multiplied by the frequency is proportional to the response function $\chi(Q,\omega)$, which exhibits a minimum between two regions asymptotically approaching $\chi \sim \omega^{-b}$ and $\chi \sim \omega^a$. The analytic shape of this correlator as a function of the temperature around the susceptibility minimum follows a scaling law when normalized to the values of the function in the minimum between the two peaks

$$\chi / \chi_{min} = A \times (\omega/\omega_{min})^{a_{eff}} + B \times (\omega/\omega_{min})^{-b}. \tag{3}$$

Equation (3) is the interpolation formula for an *ad hoc* data fitting procedure used for the β-relaxation scaling law test. In fact, if the high-frequency tail of the α peak follows the von Schweidler law $\chi_1''(\omega) \sim \omega^{-b}$ with $0 < b \leq 1$, then the low-frequency part of the β peak can be described by an effective power law $\chi_2''(\omega) \sim \omega^{a_{eff}}$. This interpolation formula obeys the MCT β-relaxation scaling law if both b and a_{eff} are temperature independent and $a_{eff} = a \leq a_{max} \sim 0.395$.[6,22]

III. EXPERIMENTAL DETAILS

Vycor brand porous glass n.7930 is a product of Corning Glass Works, which offers to water a network of cylindrical pores of average diameter of 40 Å and a hydrophilic surface. The procedure for cleaning the Vycor glass substrate and preparing the hydrated samples must be performed with great attention as Vycor glass behaves like a sponge for or-

TABLE I. Details of the experimental runs: percentual hydration level, h, temperature, and instrument used.

Run number	h	T (K)	Instrument
1	8%	248	MARI
2	12%	248	MARI
3	12%	268	MARI
4	8%	220	IN5
5	8%	248	IN5
6	8%	268	IN5

ganic substances that are immediately absorbed.[23] It is therefore crucial that the samples are kept isolated from the external atmosphere. The samples are first accurately cleaned through a full immersion in a solution of hydrogen–peroxide heated at a temperature of 90 °C for ca. 3 h. In order to remove residues of peroxide from the glasses, they are washed with H_2O. Samples are then kept in pure H_2O until used. A full hydration is defined as 0.25 g of water per g of Vycor. Partially hydrated samples are obtained by exposing the fully hydrated ones to a dehydrating powder, P_2O_5, in a glove box with flushing of an inert gas while monitoring the weights. For the dry sample, once the weight stabilizes, the remaining water is eliminated by using a vacuum pump. Due to the low water content there is no risk at this point of breaking the sample because of ice formation inside the pores. At the end of this procedure the nonbridging oxygens on the Vycor surface are saturated by hydrogens and their number is ca. 14% of the total atoms in the dry slab.[23]

We performed two series of INS experiments. The first series was taken at the ISIS facility on the MARI[24] spectrometer and the second at the ILL facility using the IN5[25] spectrometer. MARI is a direct geometry chopper spectrometer which uses a Fermi chopper to monochromate the incident neutron beam. Available incident energies are in the range of 10 to 2000 meV and the instrument is equipped with a detector bank that continuously covers the angular range from 3 to 135 deg. In our experiment the selected incident energy was $E_i = 24$ meV. The energy resolution is between 1%–2% $\Delta E/E$, constant for all the detector banks. IN5 is a general purpose direct geometry time-of-flight spectrometer, designed to study low-energy transfer processes as a function of momentum transfer. It uses four disk choppers to produce a monoenergetic neutron beam in the range 0.3 to 25 meV. The detector bank covers the range from 2 to 130 deg. In our experiment the selected incident energy was $E_i = 3.3$ meV, corresponding to an energy resolution of 109 μeV. On both spectrometers we have used a thin flat aluminum sample container. The Vycor glass slabs used for the MARI and the IN5 experiments have dimensions of $50.6 \times 50.5 \times 3.1$ and $32 \times 36 \times 1.8$ mm^3, respectively. Details on the different experimental runs are reported in Table I. For the sake of the data analysis on each spectrometer a dry Vycor spectrum has been measured. We have, however, verified that in the energy and temperature range investigated the dry Vycor spectrum is not sensitive to temperature changes. Moreover, both multiple scattering and absorption are negligible, given the thickness of our samples. The calibration of runs has been obtained by recording the spectrum of a vanadium slab, at
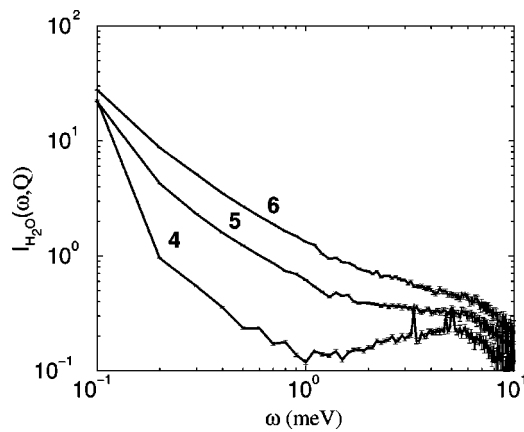
FIG. 1. Log–log plot of the raw data from the IN5 runs 4,5,6 interpolated at $Q = 1.9 \, \text{Å}^{-1}$. Hydration level is 8% and temperatures from bottom to top are $T = 220$, 248, and 268 K.
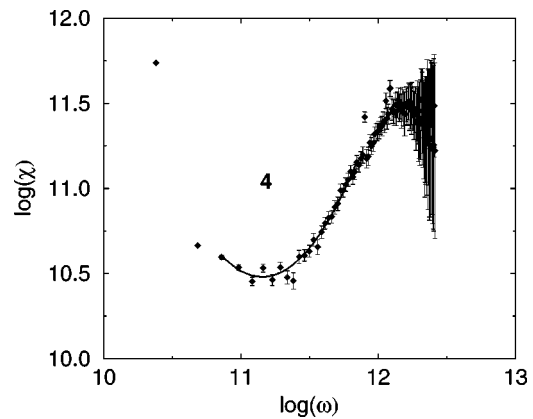

FIG. 2. The logarithm of the χ (in arbitrary units) vs the logarithm of the frequency (in Hz). The experimental data are reported with the error bars, while the continuous line represents a polynomial fit around the minimum, performed to evaluate, for each run, χ_{min} and ω_{min}. The experimental data reported here as an example correspond to run number 4 (see Table I), namely $T = 220$ K, hydration level of 8%, and $Q = 1.9 \, \text{Å}^{-1}$.

ambient temperature on both MARI and IN5.

The raw data for water, $I_{H_2O}(Q, \omega)$, plotted in Fig. 1, have been obtained by subtracting the signal of the dry Vycor, $I_{dry}(Q, \omega)$, from the total scattered intensity

$$I_{exp}(Q, \omega) = c_1 I_{H_2O}(Q, \omega) + c_2 I_{dry}(Q, \omega), \qquad (4)$$

where c_1 and c_2, reported in Table II, represent the molar fraction of water and Vycor glass, respectively, as evaluated from the composition and weight of the individual samples.[23] Conversion of the experimental intensity to the self-dynamical structure factor, $S_S(Q, \omega)$, has been obtained through the vanadium calibration runs. Constant Q data for $S_S(Q, \omega)$ have been interpolated at Q values of 1.7, 1.9, and $2.1 \, \text{Å}^{-1}$. These values have been selected in the vicinity of the first peak of the oxygen–oxygen static structure factor where MCT features are most evident.

IV. DATA ANALYSIS AND RESULTS

Figure 1 shows, as an example, the experimental intensity for three selected data set at $Q = 1.9 \, \text{Å}^{-1}$. All the data show, after the short frequency decay, a feature centered at about 5 meV, best resolved at the lowest temperature. This feature is closely reminiscent of that observed in the dynamical structure factor of hydration water confined around a protein macromolecule[18,19] and interpreted in terms of an excess of vibrational modes, associated with the amorphous character of hydration water[26] in analogy with what is found in amorphous ice.[27] However, it has to be mentioned that the neutron and Raman spectra of bulk water also show a contribution at about the same frequency: this is best visible, and centered at about 7.5 meV, when the spectra are multiplied by ω^2.[28,29] This well-known translational band is sometimes referred to as the O–O–O bending mode.[30]

TABLE II. Hydration dependence of the coefficients defined in Eq. (4).

h	c_1	c_2
8%	0.2	0.8
12%	0.27	0.73

In order to test our data against the MCT predictions, we have estimated the response function $\chi(Q, \omega)$ at the three selected Q values for each sample run and performed a polynomial fit around its minimum. In Fig. 2 we have reported the experimental data for run number 4, together with its fit, as an example. The values of χ_{min} and ω_{min} obtained from the polynomial fit have been used to rescale all the experimental data at the minimum of the response function. Rescaled data at $Q = 1.9 \, \text{Å}^{-1}$ are shown in Fig. 3. The bottom panel shows the data at the highest hydration, taken on MARI, and the top one all the data at the lowest hydration, independently on the spectrometer used. In particular, run 1 and 5 have been performed at the same hydration and temperature on different spectrometers and using Vycor slabs of different thickness; nevertheless, scaled data compare very well to each other above the minimum of the response function. The low-frequency region of the data taken on MARI, corresponding to the α relaxation, is completely obscured by the instrumental resolution. The resolution of IN5 in the chosen setup is better, although still too low to study the α relaxation dynamics. We notice that the region where the response function follows the universal behavior reported in Eq. (3) becomes shorter as the temperature decreases, as already found in the case of supercooled glycerol.[31]

We have performed a fit to Eq. (3) for all the curves shown in Fig. 3. We have fixed the value of the b exponent to 0.4. This value was estimated from simulations[13] and has, however, little influence in our fit. In fact, the α relaxation region is completely, or almost completely buried in the experimental resolution, depending on the spectrometer. As an example, two fits to Eq. (3) are shown in Fig. 4. These two runs correspond to the same hydration level and temperature of the sample and are taken on the two different spectrometers. In spite of the slight difference in the frequency windows accessible by the two spectrometers, we do find the same value of the exponent a_{eff} within the error bar. This confirms the reliability of the fits performed on the β region on both spectrometers. The values of a_{eff} are reported in Fig. 5 for three selected Q values close to the peak of the
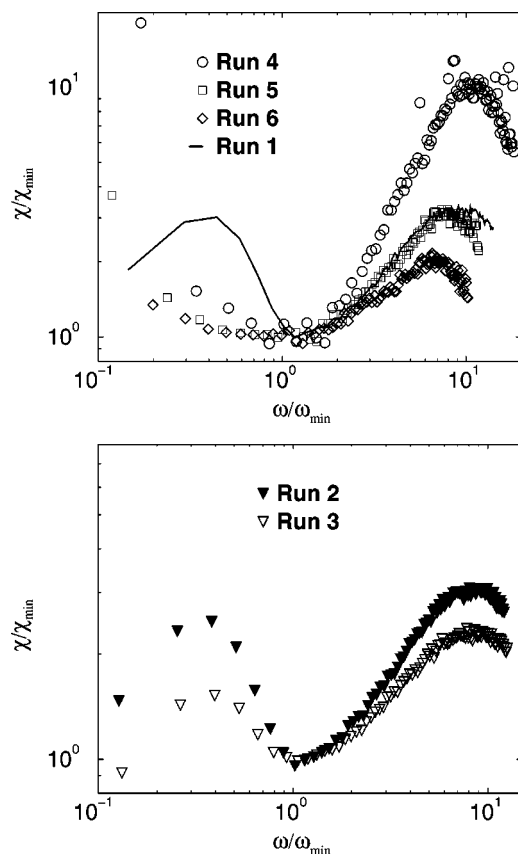
FIG. 3. Log–log plot of χ/χ_{min} vs ω/ω_{min} at $Q = 1.9$ Å^{-1}. The experimental uncertainty is within the symbol size except for the very high frequency region around the maximum (see Fig. 2). The different resolution of the two spectrometers clearly emerges from the low-frequency behavior. The run numbers correspond to temperatures and hydration levels listed in Table I.

oxygen–oxygen structure factor. As we note, $a_{eff} > 1$ for all the Q investigated, while MCT indicates for this exponent a topmost value of 0.395. As already stated in the Introduction, the existence of an MCT α relaxation region has been clearly
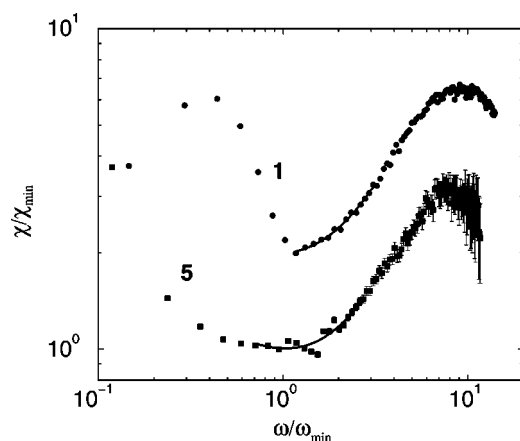
FIG. 4. Log–log plot of χ/χ_{min} vs ω/ω_{min} (symbols) for run numbers 1 and 5 at $Q = 1.9$ Å^{-1}, together with their fit (continuous lines), performed according to Eq. (3). Data for run 1 have been arbitrarily shifted upward for the sake of clarity. These two runs correspond to the same hydration and temperature and the data are closely superimposed, as can be seen in Fig. 3. Data collected on MARI (run 1) show a lower resolution but a higher statistical accuracy.
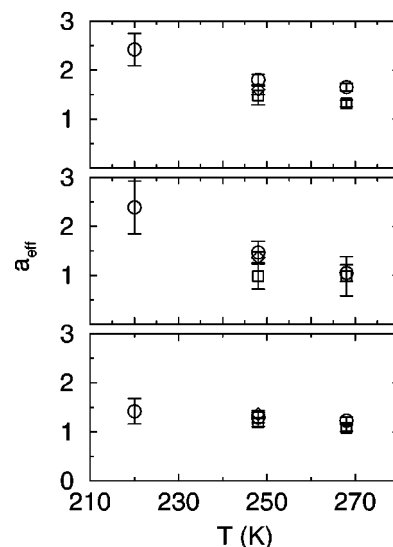
FIG. 5. Values of the exponent a_{eff} of Eq. (3) extracted from the fit to the experimental data at three Q values around the first peak of oxygen–oxygen static structure factor, namely $Q = 1.7$, 1.9, and 2.1 Å^{-1} from top to bottom. Circles correspond to IN5 runs, diamonds correspond to run 1, and squares correspond to runs 2 and 3.

shown for water in Vycor both with experiments and simulations.[9–17] Therefore, given the present state-of-the-art on the subject, our finding appears to be compatible with the existence of a low-frequency scattering excess (LFSE) analogous to that observed already in strong glass formers.[22,31,32] We notice that a_{eff} shows a slight Q dependence, best evident at the lowest temperatures. Moreover, the value of a_{eff} increases with decreasing temperature, as expected for the LFSE.

V. CONCLUDING REMARKS

We presented the results of an INS experiment on water confined in Vycor glass at low temperatures and hydration levels. The data have been analyzed in the framework of MCT. As far as the α relaxation region is concerned, the MCT behavior has already been successfully tested both experimentally[14–17] and with MD simulations[9–13] on the same system. We performed a β-relaxation scaling law test on our data. The data show a marked deviation from MCT predictions about the exponent a_{eff} which is to be ascribed to the presence of an LFSE. The nature of this LFSE is still under debate in the literature. It is a feature that starts appearing in liquids forming strong glasses upon deeply supercooling and then becomes most evident in the amorphous solid. It can possibly be related to the tail of the BP feature appearing at higher frequency. Another possible source of the LFSE could be attributed to localized vibrational motions, induced by molecular mechanisms or disorder effects. It is worth noting that for high density amorphous ice this LFSE has been recently detected and found to be due to localized oscillations of short chains and isolated water molecules.[33] An overshoot in the α-relaxation region of the SISF, which could possibly be related to the LFSE, has also been observed in the MD simulation of water in a Vycor pore[9–13] and of water close to the surface of proteins.[18,19,21]

In our case, due to the strong hydrophilicity of the inner surfaces of the pores of Vycor glass, water at low hydration level is already in a sluggish state at relatively high temperatures.[9–13] Therefore, not surprisingly deviations from MCT in the β region appear not very far from ambient in the low hydrated samples. It is important to stress that an enhancement of vibrational contributions for water upon supercooling favors the hypothesis recently appearing in the literature[34] of a fragile-to-strong transition of confined water upon supercooling.

ACKNOWLEDGMENTS

[1] For a review on metastable liquids and water in particular, see P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, 1997).

[2] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).

[3] E. W. Lang and H. D. Lüdeman, Angew. Chem. Int. Ed. Engl. **21**, 315 (1982); F. X. Prielmeir, E. W. Lang, R. J. Speedy, and H. D. Lüdeman, Phys. Rev. Lett. **59**, 1128 (1987).

[4] 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).

[5] F. W. Starr, F. Sciortino, and H. E. Stanley, Phys. Rev. E **60**, 6757 (1999); F. W. Starr, S. T. Harrington, F. Sciortino, and H. E. Stanley, Phys. Rev. Lett. **82**, 3629 (1999).

[6] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992); W. G. Götze, in *Liquids, Freezing and Glass Transition*, Les Houches Session LI, 1989, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North Holland, Amsterdam, 1991).

[7] A. P. Sokolov, J. Hurst, and D. Quitmann, Phys. Rev. B **51**, 12865 (1995).

[8] J. A. Rupley and G. Careri, Adv. Protein Chem. **41**, 37 (1991), and references therein.

[9] P. Gallo, M. A. Ricci, M. Rovere, C. Hartnig, and E. Spohr, Europhys. Lett. **49**, 183 (2000).

[10] P. Gallo, M. Rovere, M. A. Ricci, C. Hartnig, and E. Spohr, Philos. Mag. B **79**, 1923 (1999).

[11] P. Gallo, Phys. Chem. Chem. Phys. **2**, 1607 (2000).

[12] P. Gallo, M. Rovere, and E. Spohr, Phys. Rev. Lett. **85**, 4317 (2000).

[13] P. Gallo, M. Rovere, and E. Spohr, J. Chem. Phys. **113**, 11324 (2000).

[14] S.-H. Chen, P. Gallo, and M. C. Bellissent-Funel, Can. J. Phys. **73**, 703 (1995).

[15] S.-H. Chen, P. Gallo, and M. C. Bellisent-Funel, in *Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials*, edited by M. Giordano, D. L. Leporini, and M. P. Tosi (World Scientific, Singapore, 1996), p. 186.

[16] J.-M. Zanotti, M.-C. Bellissent-Funel, and S.-H. Chen, Phys. Rev. E **59**, 3084 (1999).

[17] M.-C. Bellissent-Funel, S. Longeville, J. M. Zanotti, and S.-H. Chen, Phys. Rev. Lett. **85**, 3644 (2000).

[18] A. Paciaroni, A. R. Bizzarri, and S. Cannistraro, Phys. Rev. E **57**, R6277 (1998).

[19] A. Paciaroni, A. R. Bizzarri, and S. Cannistraro, Phys. Rev. E **60**, R2476 (1999).

[20] M. Settles and W. Doster, Faraday Discuss. Chem. Soc. **103**, 269 (1996).

[21] M. Tarek and D. J. Tobias, J. Am. Chem. Soc. **121**, 9740 (1999).

[22] For a discussion on this analysis, see W. Götze, J. Phys.: Condens. Matter **11**, A1 (1999).

[23] F. Bruni, M. A. Ricci, and A. K. Soper, J. Chem. Phys. **109**, 1478 (1998).

[24] Detailed information on the MARI spectrometer can be found at the web site: www.isis.rl.ac.uk

[25] Detailed information on the IN5 spectrometer can be found at the web site: www.ill.fr

[26] A. R. Bizzarri, A. Paciaroni, and S. Cannistraro, Phys. Rev. E **62**, 3991 (2000).

[27] A. I. Kolesnikov, J. Li, S. F. Parker, R. S. Eccleston, and C. K. Loong, Phys. Rev. B **59**, 3569 (1999).

[28] P. A. Madden and R. W. Impey, Chem. Phys. Lett. **123**, 502 (1986).

[29] A. De Santis, M. Sampoli, V. Mazzacurati, and M. A. Ricci, Chem. Phys. Lett. **133**, 381 (1987).

[30] G. E. Walrafen, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972), Vol. 1.

[31] J. Wuttke, J. Hernandez, G. Li, G. Coddens, H. Z. Cummins, F. Fujara, W. Petry, and H. Sillescu, Phys. Rev. Lett. **72**, 3052 (1994).

[32] H. Z. Cummins, G. Li, W. Du, Y. H. Hwang, and G. Q. Shen, Prog. Theor. Phys. Suppl. **126**, 21 (1997).

[33] J. S. Tse, D. D. Klug, C. A. Tulk, E. C. Svensson and I. Swainson, Phys. Rev. Lett. **85**, 3185 (2000).

[34] R. Bergman and J. Svenson, Nature (London) **403**, 283 (2000).