

Study of the β relaxation in supercooled confined water

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ABSTRACT

An inelastic neutron scattering experiment on water confined in Vycor glass has been performed to test the behaviour of the hydrogen dynamics against the predictions of the mode coupling theory, in the β -relaxation region.

§ 1. INTRODUCTION

The single-particle dynamics of bulk water have been extensively studied over a wide range of temperatures at ambient pressure. In particular, many investigations using different techniques have been performed in the supercooled regime, where the effects due to hydrogen bonding are dominant. However, in many relevant situations, water is not in its bulk form but is in contact with substrates or fills small cavities. Everyday examples are water in the interior of biological cells or on the surfaces of proteins; this is what we shall call 'confined water', as opposed to bulk water.

The possibility of vitrification of water is the subject of a long-standing scientific debate (Debenedetti 1997, Angell 1983). While in most liquids it is possible to reach the glassy state by deeply supercooling the system, homogeneous nucleation in water prevents the direct observation of the liquid-to-glass transition. As a consequence the range of temperatures investigated by experiments is small when compared with the range tested by numerical simulations that can go deep into the metastable supercooled regime, avoiding the nucleation phenomenon.

A comparison of the behaviour of the bulk liquid with the same liquid in a confined environment is highly interesting for the development of both biological and industrial applications. In particular, understanding how the dynamic behaviour of liquid water is modified by the interactions with hydrophilic and hydrophobic substrates at different levels of hydration is of fundamental value for the prediction

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of the stability and the enzymatic activity of biologically important macromolecules (Careri 1998). Last but not least, it is important to stress that, upon confinement, water offers the invaluable possibility of a much deeper supercooling with respect to its bulk counterpart.

It is a commonly accepted fact that confined and supercooled water exhibits slow dynamics that are typical of a glass former. In particular, detailed experimental investigations of the slow relaxation region α performed on water confined in Vycor glass (Zanotti *et al.* 1999, Bellissent-Funel *et al.* 2000) have evidenced mode coupling theory (MCT) behaviour. Added to this, molecular dynamics (MD) studies on simple point charge/extended (SPC/E) water confined in a pore of Vycor (Gallo *et al.* 1999, 2000a,b,c, Gallo 2000) have confirmed the presence of MCT behaviour and the appearance of glassy features at higher temperatures with respect to the bulk case. Typical features of a glass former have also been evidenced by both experiments and simulations performed on water close to the surface of proteins and, in the range of frequencies corresponding to the fast relaxation β an excess of vibrational intensity has been found (Settles and Doster 1996, Paciaroni *et al.* 1999, Tarek and Tobias 1999).

In this study we have performed an inelastic neutron scattering (INS) experiment in order to test the behaviour of the fast relaxation region β for supercooled water confined in Vycor glass. Such a system has been chosen because Vycor is characterized by a rather sharp distribution of pore sizes with a small average diameter (about $40 \pm 5 \text{ \AA}$), because the pore size does not depend on the hydration level and because the surface is strongly hydrophilic.

§ 2. THE MODE COUPLING THEORY SCENARIO

The idealized version of the MCT (Götze 1989, 1999, Götze and Sjögren 1992), in which hopping effects are neglected, introduces an important crossover temperature T_c , defined as the temperature of structural arrest. On approaching T_c from above, the theory is capable of predicting a precise behaviour for the density correlators that are measured in a neutron scattering experiment. MCT for supercooled liquids is a theory that takes into account the so-called cage effect which is associated with a transient trapping of the molecules on lowering the temperature or on increasing the density. Such a transient caging of the particle causes a two-step relaxation behaviour for the density correlator $\phi_Q(t)$ and a stretching of the slow-relaxation law. It is important to stress that the time scale separation is most evident for wave-vectors close to the first maximum Q_{\max} of the static structure factor $S(Q)$ or equivalently, in real space, for distances comparable with the interparticle distances in a liquid. On approaching T_c from the liquid side and after a fast decay at short times, $\phi_Q(t)$ enters a plateau region that corresponds to the rattling of the particle in the cage formed by its nearest neighbours. The approach to the plateau is described by a power law with exponent a :

$$\phi_Q(t) - f_Q^c \approx t^{-a}. \quad (1)$$

After a certain time interval, which becomes longer on approaching T_c , $\phi_Q(t)$ departs from the plateau as a power law with exponent b , namely the von Schweidler law:

$$\phi_Q(t) - f_Q^c \approx t^b, \quad (2)$$

where f_Q^c is the Q -dependent height of the plateau, also called the non-ergodicity factor. Around the crossover temperature T_c , some asymptotic solutions for the MCT equations have been found. These solutions predict that the dynamic susceptibility $\chi(Q, \omega)$, a quantity proportional to which is obtained in an INS experiment by multiplying the self-dynamic structure factor $S_{\text{self}}(Q, \omega)$ by the frequency, exhibits a minimum between two regions that approach and $\chi \approx \omega^{-b}$ and $\chi \approx \omega^a$. 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:

$$\frac{\chi}{\chi_{\min}} = A \left(\frac{\omega}{\omega_{\min}} \right)^a + B \left(\frac{\omega_{\min}}{\omega} \right)^b. \quad (3)$$

This interpolation formula obeys the MCT scaling law if both a and b are temperature independent and if $a \leq a_{\max} = 0.395$ and $0 < b \leq 1$ (Götze 1989, 1999, Götze and Sjögren 1992).

§ 3. EXPERIMENTAL DETAILS

Vycor glass is a product of Corning glass which is characterized by a network of cylindrical pores of small average diameter (40 Å) and by a hydrophilic surface. Vycor behaves like a sponge that rapidly absorbs the organic substances present in the external atmosphere; this is the reason why the procedures of cleaning and preparing the samples are of fundamental importance (Venturini *et al.* 2001).

INS measurements were performed at the ISIS facility on the spectrometer MARI and at the Institut Laue–Langevin facility using the spectrometer IN5. Details about the experimental set-up and sample preparation have been given by Venturini *et al.* (2001).

Measurements were performed at different hydration levels h of the samples (h is defined as the ratio $h = \text{grams of water/grams of Vycor}$) and at different temperatures (table 1). Added to this, on each instrument the spectrum of a dry Vycor sample was measured, in order to subtract the signal due to the non-hydrated slab from the total scattered intensity according to the formula

$$I_{\text{exp}}(Q, \omega) = c_1 I_{\text{H}_2\text{O}}(Q, \omega) + c_2 I_{\text{dry}}(Q, \omega). \quad (4)$$

The coefficients c_1 and c_2 are reported in table 2 for the different hydration levels; their values were determined from the composition and the weight of both the dry and the hydrated samples.

Table 1. Hydration levels h .

h (g H ₂ O (g Vycor) ⁻¹)	T (K)	Instrument
0.12	268	MARI
0.12	248	MARI
0.08	248	MARI
0.08	268	IN5
0.08	248	IN5
0.08	220	IN5

Table 2. Coefficients c_1 and c_2 for various hydration levels h .

h (g H ₂ O (g Vycor) ⁻¹)	c_1	c_2
0.08	0.2	0.8
0.12	0.27	0.73

The final conversion of the experimental intensity to the self-dynamic structure factor, $S_{\text{self}}(Q, \omega)$ was obtained through vanadium calibration runs.

§4. DATA ANALYSIS AND RESULTS

On a general basis the self-dynamic structure factor depends both on the wave-vector Q and on the energy transfer $h\omega$. In our study, because of an interpolation procedure, constant-wave-vector data were obtained for Q values equal to 1.7, 1.9 and 2.16 Å⁻¹. These values were chosen to be close to the first maximum in the O–O static structure factor. As an example, figure 1 shows the experimental scattered intensity for three different data sets; the temperatures are 220, 248 and 268 K (from bottom to top) and $Q = 1.9$ Å⁻¹. After a low-frequency decay all three of the spectra show a feature centred around 5 meV which is best resolved at low temperatures. This is the well-known translational contribution to the density of states of water. Such a feature appears at around 7.5 meV in the Raman and IF spectra of water when multiplied by ω^2 (Madden and Impey 1986, De Santis *et al.* 1987) and it is often referred to as the O–O–O bending (Walrafen 1972).

In order to test the MCT predictions for the dynamic susceptibility we have estimated a quantity proportional to $\chi(Q, \omega)$ at the three selected Q values for each experimental run and some polynomial fits have been performed around the minimum of these functions. The values of χ_{min} and ω_{min} obtained from such a

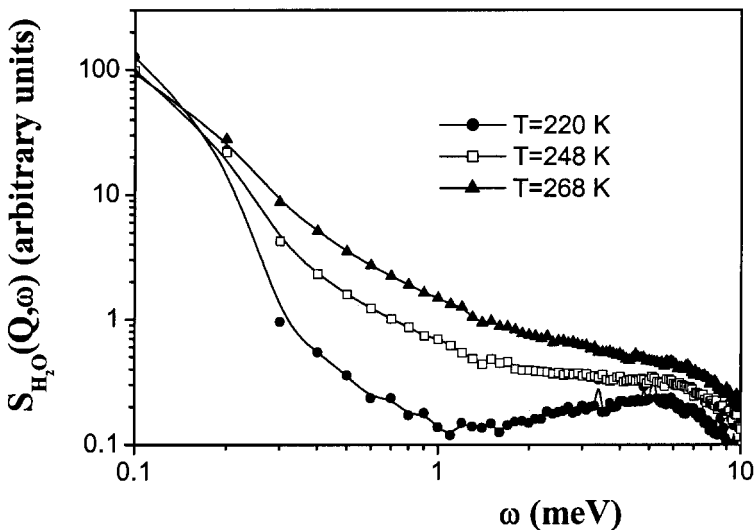
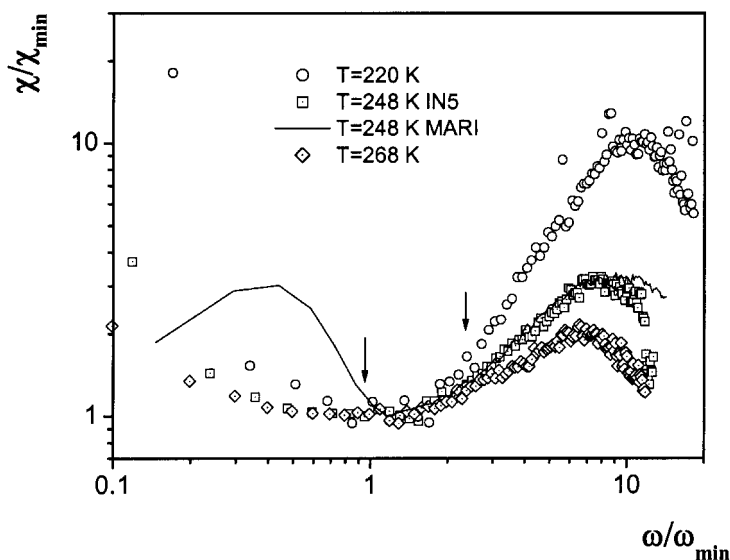
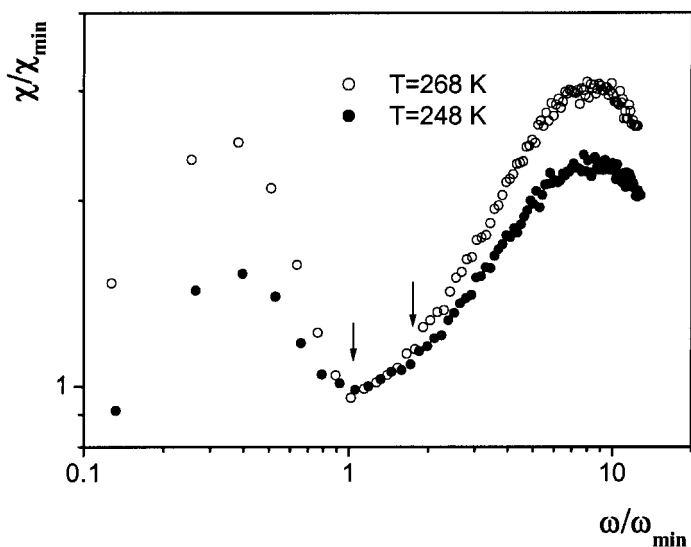


Figure 1. log–log plot of the raw data from IN5 for three selected experimental runs, namely at $T = 220, 248$ and 268 K, interpolated at $Q = 1.9$ Å⁻¹.



(a)



(b)

Figure 2. log-log plot of χ/χ_{\min} versus ω/ω_{\min} at $Q = 1.9 \text{ \AA}^{-1}$. (a) Data collected at 12% hydration on MARI; (b) data collected at 8% hydration. The arrows indicate the interval where the fit was performed.

procedure have subsequently been used to rescale all the experimental data at the minimum of the response function. Figure 2(a) shows the rescaled data at $Q = 1.9 \text{ \AA}^{-1}$ for the 12% hydrated sample measured on the spectrometer MARI, and figure 2(b) the experimental spectra of the 8% hydrated samples, independently of the instrument used. Moreover, for $T = 248 \text{ K}$ we report two sets of experimental data that refer to two analogous runs performed on the different spectrometers;

above the minimum of the response function (the β -relaxation region) the scaled data compare with each other extremely well and this confirms the reliability of our analysis. The low-frequency region, which corresponds to the α -relaxation region, is completely hidden by the experimental resolution of MARI. In the chosen experimental set-up the resolution of the spectrometer IN5 is better. Nevertheless, the experimental energy window still remains too small to include the slow relaxation. In both graphs the minimum that appears at intermediate frequencies indicates the beginning of the β -relaxation region, whereas the maximum that can be seen at higher frequencies corresponds to the O–O–O bending phenomenon. It can also be noted that, as the temperature decreases, the region in which the response function follows the universal behaviour described by equation (3) shortens. Similar results have already been found in the case of supercooled glycerol (Wuttke *et al.* 1994).

In the frequency range in which the spectra follow the MCT universal behaviour, some single fits of equation (3) were performed on all the sets of experimental data. Owing to the different resolutions of the instruments, the frequency interval mentioned above varies with the spectrometer and is slightly larger in the case of IN5. To perform the fits the value of the exponent b was kept fixed and equal to 0.4, as estimated from previous MD simulations performed on a similar system (Gallo *et al.* 2000a,b,c). On the contrary, the only constraint imposed on the exponent a that characterizes the fast relaxation is $a > 0$. As an example, figure 3 reports one of the fits performed. The data shown were measured on the spectrometer IN5; the level of hydration is such that $h = 0.08$, $T = 248$ K and $Q = 1.9 \text{ \AA}^{-1}$. The value of the exponent a obtained from the fit of the experimental data is $a = 1.47 \pm 0.23$, that is noticeably larger than the predicted theoretical value (Götze 1989, 1999, Götze and Sjögren 1992). The values of the exponent a obtained from the fits performed on all the experimental data relative to the 8% hydrated samples are reported in table 3.

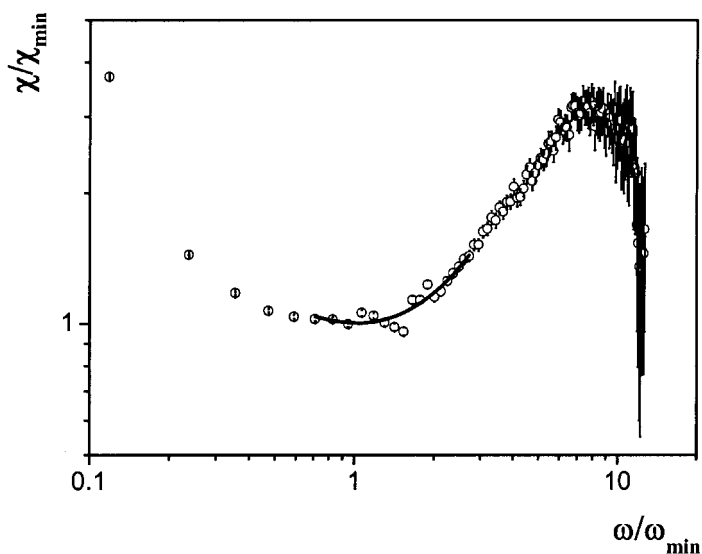


Figure 3. Experimental data at 8% hydration, $T = 248$ K and $Q = 1.9 \text{ \AA}^{-1}$, together with the fit.

Table 3. Values of the exponent a .

T (K)	a		
	$Q = 1.7 \text{ \AA}^{-1}$	$Q = 1.9 \text{ \AA}^{-1}$	$Q = 2.1 \text{ \AA}^{-1}$
220	2.42 ± 0.32	2.39 ± 0.54	1.42 ± 0.26
248 ^a	1.8 ± 0.1	1.47 ± 0.23	1.29 ± 0.11
248 ^b	1.56 ± 0.09	1.36 ± 0.12	1.36 ± 0.07
268	1.65 ± 0.08	1.05 ± 0.17	1.23 ± 0.07

^a IN5 spectrometer.^b MARI spectrometer.

In contrast with what is predicted by MCT, the value of a is always higher than unity within the experimental error. Furthermore, a similar behaviour has also been detected in the case of the 12% hydrated sample (not shown). Added to this and always in contrast with the theoretical predictions, the exponent a is temperature dependent. In particular, the value of the exponent increases as the temperature decreases. Such a behaviour is shown in figure 4 for the three different Q values that were investigated, namely $Q = 1.7, 1.9$ and 2.1 \AA^{-1} from top to bottom.

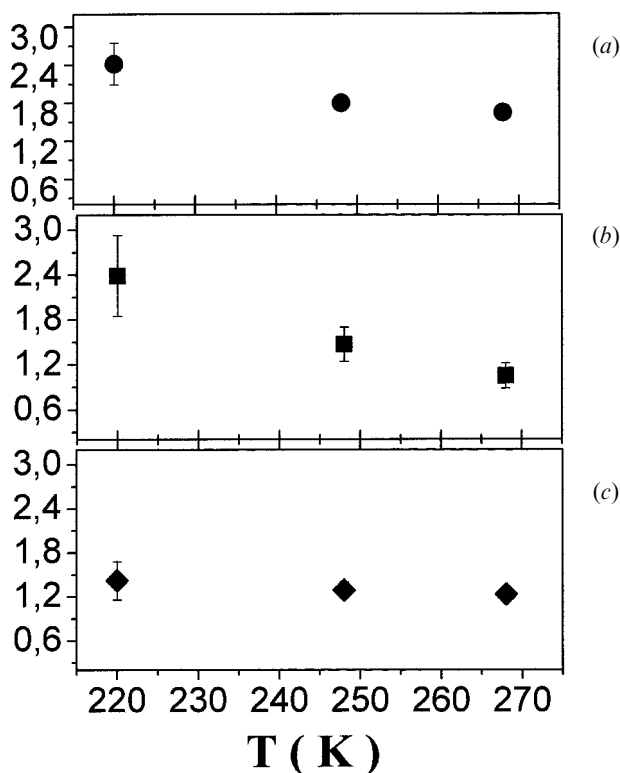


Figure 4. Values of the exponent a as a function of temperature at (a) $Q = 1.7 \text{ \AA}^{-1}$, (b) $Q = 1.9 \text{ \AA}^{-1}$ and (c) $Q = 2.1 \text{ \AA}^{-1}$.

§5. FINAL REMARKS

In this paper we have discussed the results of an INS experiment performed on supercooled water confined in Vycor glass. The data were analysed in the MCT framework. In the region that corresponds to the slow α relaxation a MCT behaviour has already been evidenced for the same system both experimentally (Zanotti *et al.* 1999, Bellissent-Funel 2000) and by means of MD simulations (Gallo *et al.* 1999, 2000a,b,c, Gallo 2000). In this study we focused our attention on the fast β relaxation. The analysed data show a qualitative agreement with the universal behaviour predicted for the dynamic susceptibility and described by equation (3). Nevertheless, on quantitative grounds, the obtained values of the exponent a in equation (3) are noticeably higher than the maximum value predicted by the theory (i.e. $a_{\max} = 0.395$). Moreover, the exponent shows a temperature dependence. These results appear to be compatible with the existence of a low-frequency scattering excess (LFSE) not considered by MCT and already experimentally detected in the case of non-fragile systems such as glycerol and B_2O_3 (Wuttke *et al.* 1994, Brodin *et al.* 1996). The nature of this LFSE is still widely debated in the literature and it is generally considered a typical characteristic of liquids that form strong glasses. In particular, the LFSE could possibly be related to the low-frequency tail of the boson peak (BP) feature that appears at higher frequencies. Without entering into the details of this effect that has already been observed in many glassy systems (Wuttke *et al.* 1994, Brodin *et al.* 1996, Hehlen *et al.* 2000, Russina *et al.* 2000), in polymers (Frick and Richter 1995) and in the hydration water of some proteins (Paciaroni *et al.* 1998, 1999, Tarek and Douglas 2000), it is important to stress that the appearance of the BP in the liquid phase is generally considered as a precursor sign of the glass transition. In this study, owing to the strong hydrophilicity of the inner surfaces of the Vycor glass pores and to the low levels of hydration that were considered, we can assume that the water molecules are already in a glass-like state at relatively high temperatures (Gallo *et al.* 1999, 2000a,b,c, Gallo 2000). Therefore, if we consider the observed deviations from MCT in the β region as signs of an imminent liquid-to-glass transition, it is not surprising that such anomalies are already visible not far from ambient temperature. Finally, the fact that the exponent a increases as T decreases favours the recent hypothesis according to which confined water undergoes a fragile-to-strong transition with decreasing temperature (Bergman and Svenson 2000).

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