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# Further evidence of a liquid–liquid transition in interfacial water

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## Abstract

In a previous paper we combined calorimetric, diffraction and high-resolution quasi-elastic neutron scattering data to show that after exhibiting a glass transition at 165 K, interfacial water experiences a first order liquid–liquid transition at 240 K from a low-density to a high-density liquid. Here we present further evidence of these transitions obtained by high-energy inelastic neutron scattering.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

This study is related to the tremendously active field of water dynamics and the debate on the hypothetical low-temperature critical point of water at  $T_S = 228$  K [1].

A condition for the existence of this critical point is the presence of a first order transition between a high-density liquid (HDL) and a low-density liquid (LDL). At normal pressure, supercooled water spontaneously freezes below the homogeneous nucleation temperature,  $T_H = 235$  K. Upon heating, the two forms of amorphous solid water, LDA (low-density amorphous ice) and HDA (high-density amorphous ice), crystallize above  $T_X = 150$  K. As a consequence, up to now no experiment has been able to explore the properties of liquid water in this very interesting temperature range between 150 and 235 K. The coexistence line has actually only been studied using the low-temperature amorphous forms of water: high-density amorphous ice and low-density amorphous ice [2, 3].

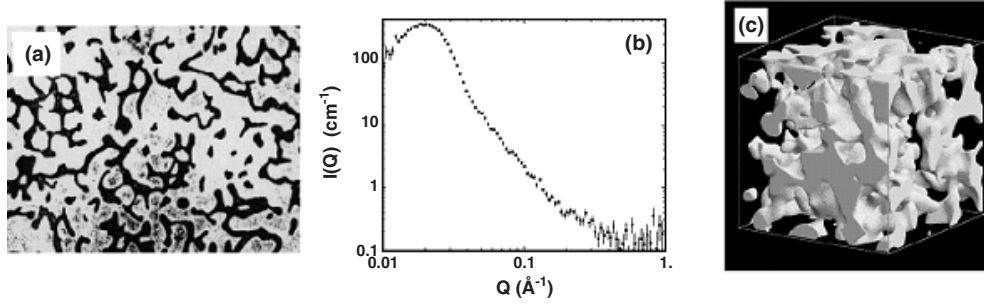
We have been able to measure for the first time the dynamics of non-crystalline water from 77 to 280 K and have accessed orientational and translational nanosecond dynamics of water on the surface of a porous Vycor silica glass.

## 2. Experiment and discussions

### 2.1. Sample preparation

In our study water is adsorbed as a monolayer on Vycor<sup>4</sup>, a porous hydrophilic silica glass. It is important to stress that since confinement effects are not at play in the present study, the

<sup>4</sup> Vycor brand porous glass no. 7930 is a product of Corning Glass Works.



**Figure 1.** Vycor (see footnote 4) is obtained by spinodal decomposition of a  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  mixture. Leaching out the  $\text{B}_2\text{O}_3$  rich phase by acid leaves a  $\text{SiO}_2$  open porous network. (a) Transmission electron micrograph of Vycor (reproduced from [4]). The pore size distribution of Vycor obtained from the Brunauer–Emmett–Teller (BET) measurements shows an average pore radius of 35 Å. The specific surface area of the material is  $130 \text{ m}^2 \text{ g}^{-1}$ . (b) Small angle neutron scattering (SANS) spectrum of Vycor. The broad peak centred at  $Q_M = 0.02 \text{ \AA}^{-1}$  is characteristic of spinodal decomposition. From a statistical point of view, the Vycor structure can be described by a characteristic size of  $1/Q_M = 50 \text{ \AA}$ . (c) 3D view of Vycor. (Reproduced from [5].)

Vycor pore size (figure 1) is not a relevant parameter. Instead, what is taken advantage of from an experimental point of view is the high specific surface area ( $130 \text{ m}^2 \text{ g}^{-1}$ ) resulting from the porous structure.

A partially hydrated sample was prepared by absorption of water in the vapour phase, until a level of hydration corresponding to a monolayer coverage was obtained (25% hydration).

## 2.2. Previous results

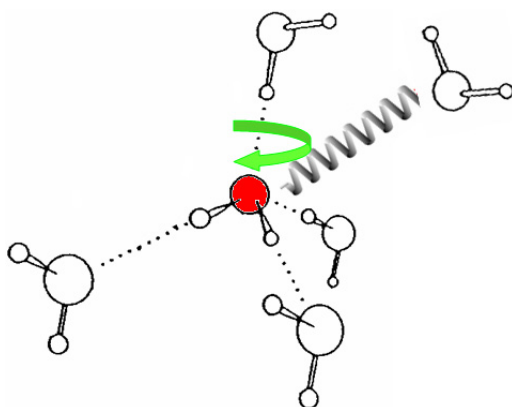
In a previous paper [6], we have shown by differential scanning calorimetry (DSC) that interfacial water in a monolayer at the surface of Vycor experiences a significant phase transition at 240 K. Change in density of the interfacial water above and below the transition (high and low density, respectively) has been inferred from neutron diffraction data.

Concurrently, incoherent quasi-elastic neutron scattering has been used to probe rotational and translational dynamics of the interfacial water as sensed by the hydrogen atoms of the water molecules. Measurements in the nanosecond (ns) time range have been performed on the ILL IN16 backscattering spectrometer, while measurements in the 15 picosecond (ps) timescale have been performed on the quasi-elastic neutron scattering (QENS) time-of-flight inelastic neutron spectrometer at ANL/IPNS.

Based on incoherent neutron scattering data and subsequent computer molecular dynamics simulations [7], a picture of local bulk water dynamics at a short ps timescale can be accounted for by the model given in [8] shown in figure 2. With this model the rotational dynamic structure factor can be given by

$$S_{\text{Rot}}(Q, \omega) = A_0(Q)\delta(\omega) + (1 - A_0(Q))L_{\text{Rot}}(Q, \omega) \quad \text{with } L_{\text{Rot}}(Q, \omega) = \frac{1}{\pi} \frac{\tau_1^{-1}}{\tau_1^{-2} + \omega^2}, \quad (1)$$

where  $A_0(Q) = j_0(Qr_{\text{OH}})^2$  is the elastic incoherent structure factor of a hydrogen atom experiencing a rotation over the intramolecular O–H distance,  $r_{\text{OH}}$  (0.98 Å), with a correlation time  $\tau_1$ , and  $j_0(x)$  is the spherical Bessel function. If a molecule is not H-bonded to any other molecule, it diffuses freely with a translational diffusion coefficient  $D_t$  and the corresponding



**Figure 2.** In bulk water, a water molecule is H-bonded on average to four or fewer neighbouring molecules. If due to thermal energy, one H-bond OH–O moves apart from linearity by more than  $25^\circ$  the bond breaks. When three of the four H-bonds engaged by a molecule are simultaneously broken, the molecule follows a rotational diffusive movement, characterized by a correlation time  $\tau_1$ , associated with the lifetime of the H-bond. In interfacial water where we are dealing with a monolayer of water molecules, on average the number of H-bonds is supposed to be reduced to three.

dynamic structure factor is

$$S_{\text{trans}}(Q, \omega) = \frac{1}{\pi} \frac{f(Q)}{f(Q)^2 + \omega^2} \quad \text{where } f(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0}. \quad (2)$$

This is obeyed until one or more H-bonds are formed again. The molecule will remain on this ‘site’ for a residence time  $\tau_0$  (of the order of 1 ps at room temperature), before experiencing this cycle again.

A key point is to keep in mind that any transition related to the translational behaviour of water has to be preceded by a transition related to the rotational behaviour of water.

If these rotational and translational dynamics are uncorrelated, the global dynamics of a single water molecule is described by the convolution of equations (1) and (2):

$$S_{\text{inc}}(Q, \omega) = A_0(Q) \cdot S_{\text{trans}}(Q, \omega) + (1 - A_0(Q)) S_{\text{Trans}}(Q, \omega) \otimes L_{\text{Rot}}(Q, \omega). \quad (3)$$

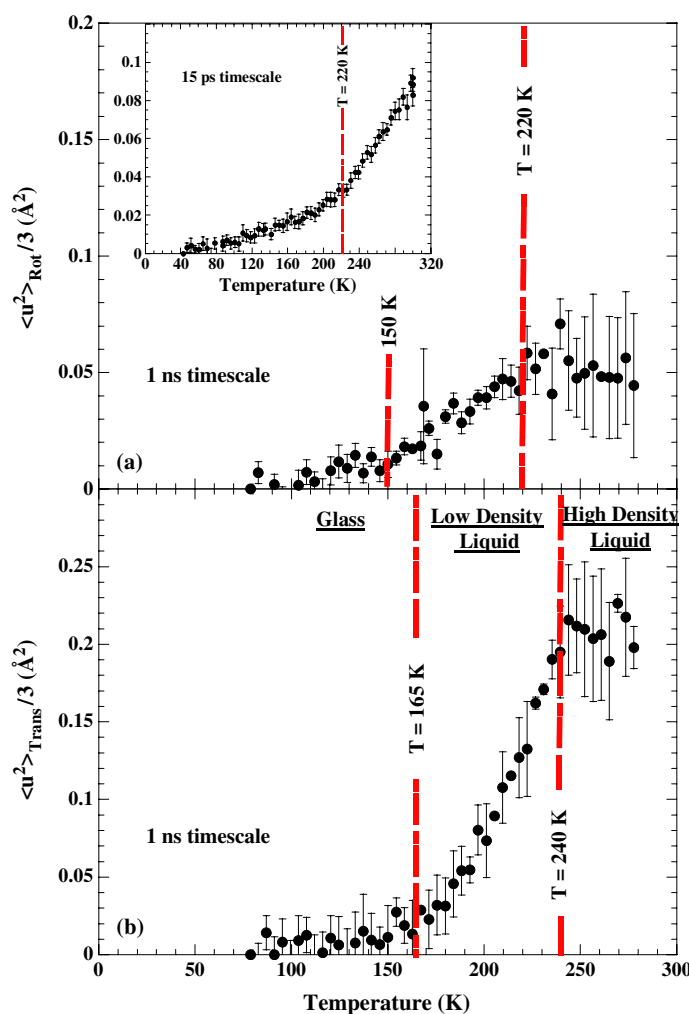
While a detailed line-shape analysis makes it possible to extract all the parameters of the above equation, due to the limited neutron flux on such a high-resolution instrument as IN16, such a detailed analysis can only be made at a few temperatures.

An Elastic scan<sup>5</sup> has shown two distinct regions from which the mean square displacements deduced from the low- $Q$  ( $0.1$ – $1.0 \text{ \AA}^{-1}$ ) and high- $Q$  ( $1.1$ – $1.9 \text{ \AA}^{-1}$ ) ranges, denoted  $\langle u^2 \rangle_{\text{Trans}}$  and  $\langle u^2 \rangle_{\text{Rot}}$ , have been extracted [6]. According to equation (3), they are associated with the long-range translational diffusion and local rotational dynamics, respectively. All together, the obtained QENS data demonstrate that on a timescale of 1 ns:

(i)  $\langle u^2 \rangle_{\text{Rot}}$  significantly increases above 150 K (figure 3(a)). This is the onset of rotational dynamics of the water molecules.

(ii) Below 165 K, interfacial water is a low-density amorphous ice (with  $Q_0 = Q_0^{\text{LDA}} = 1.71 \text{ \AA}^{-1}$ ,  $Q_0$  is the first peak in  $S(Q)$  structure factor [6]) showing no long-range translational

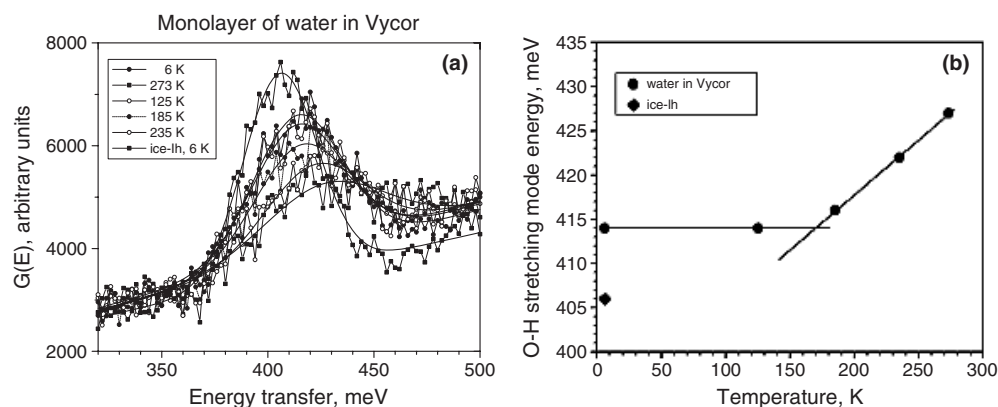
<sup>5</sup> This means recording for few minutes the  $Q$  dependence of the elastic intensity (with high energy resolution). In a way similar to the famous x-ray Debye–Waller effect, the  $Q$ -dependent Gaussian intensity loss  $\exp(-Q^2 \cdot \langle u^2 \rangle)$  can be related to the spatial extension ( $\langle u^2 \rangle$ ) of atoms around their equilibrium position.



**Figure 3.** Temperature dependence of rotational and translational mean-square displacements of interfacial water  $\langle u^2 \rangle_{\text{Rot}}$  (a) and  $\langle u^2 \rangle_{\text{Trans}}$  (b) have been extracted from the two  $Q$  ranges defined in [6]. Inset: lower-resolution (shorter times) experiment (QENS, ANL/IPNS) confirming the saturation effect observed on IN16 due to the fast dynamics of ‘high-density’ water above 240 K. The different transitions (see text) detected in water rotational (a) and translational (b) behaviours are noted by black dashed lines. As expected in water, where translational dynamics is driven by H-bond life-time (i.e. rotational behaviour, see figure 2), any transition in the long-range translational behaviour is preceded by a transition in the rotational behaviour of the water molecules [6].

dynamics ( $\langle u^2 \rangle_{\text{Trans}} \approx 0$ ; figure 3(b)). Above 165 K, no change is observed in water density (not shown) but translational dynamics becomes possible on a 1 ns timescale, as shown by the  $\langle u^2 \rangle_{\text{Trans}}$  non-null value. This is a clear signature of a glass transition at 165 K (figure 3(b)).

(iii) At 240 K, this LDL experiences a transition to HDL, ( $Q_0 = 1.86 \text{ \AA}^{-1}$ ) [6] and rotational and translational correlation times related to  $\langle u^2 \rangle_{\text{Trans}}$  and  $\langle u^2 \rangle_{\text{Rot}}$  significantly decrease leading to a ‘saturation’ of the signal on IN16 (figure 3). An experiment at lower resolution, i.e. a shorter timescale (QENS, ANL/IPNS), actually shows that  $\langle u^2 \rangle_{\text{Rot}}$  increases (inset figure 3) above 220 K, therefore confirming this ‘saturation’ effect.



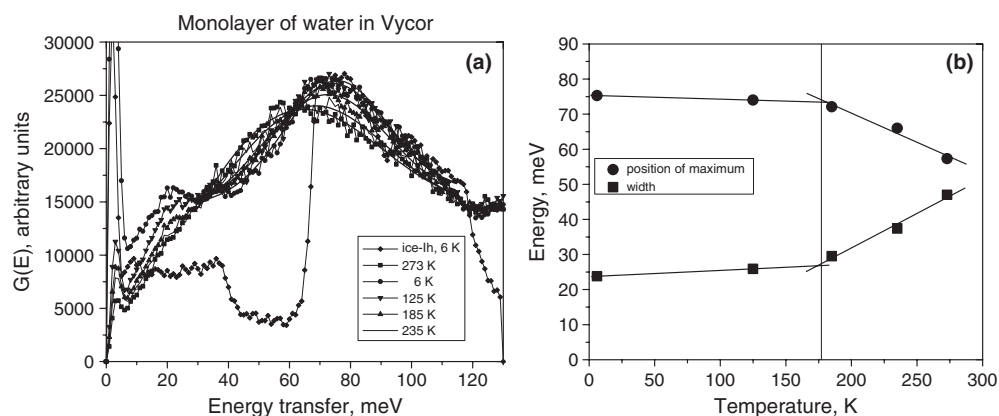
**Figure 4.** (a) Vibrational density of states measured with an incident neutron energy  $E_i = 600$  meV (lines with points) and the Gaussian fit (curves without points) of a water monolayer on Vycor in the range of O–H stretching modes as a function of temperature from 6 to 273 K; the dry Vycor spectrum was subtracted. Ice-Ih signal is given for comparison. (b) Temperature dependence of O–H stretching modes (midpoints of the Gaussians) from the spectra in (a).

### 2.3. Inelastic neutron scattering

Using the inelastic neutron scattering spectrometer HRMECS (ANL/IPNS) with incident neutron energies  $E_i = 600$  and 150 meV we were able to access a very broad energy transfer, ranging from 20 to 500 meV. This range covers the intermolecular librational band of water molecules (30–120 meV) and the intramolecular O–H stretching modes of water. Water has a large mean-squared displacement of hydrogen atoms,  $\langle u^2 \rangle$ , and to reduce the effect of the Debye–Waller factor,  $\exp(-Q^2 \langle u^2 \rangle)$ , all neutron scattering data were collected at small scattering angles.

The obtained intramolecular O–H stretching modes of interfacial water (see figure 4) compared to ice-Ih at the same temperature (6 K) exhibit a strong shift towards higher energy (406 meV in bulk ice and 414 meV in interfacial water). This energy stays about unchanged at  $T = 125$  K and it increases about linearly with temperature at  $T > 170$  K, as clearly seen in figure 4(b). As shown by an IR study of ice-VII under pressure [9], a shift of the intramolecular O–H stretching modes towards higher energy is expected to be associated with a decrease of the H-bond strength. Thus, the high-energy HRMECS experiment leads to the conclusion that H-bonds in interfacial water at temperatures below 125 K are already weaker than in bulk ice, and at 235 K and above are significantly weaker, being similar to those in bulk liquid water. There is a crossover in the maximum of the peak position of  $G(E)$  (figure 4(b)) which suggests a phase transition in water at  $T \sim 170$  K.

The intermolecular librational band of water molecules is strongly correlated to the level of strength and disorder in the H-bond network. The weaker the H-bond the softer the librational band, and the more disorder in the H-bond network the broader the librational band. As compared to the steep rise of the librational band observed in bulk ice-Ih (at  $\sim 67$  meV), the shape of this excitation observed in interfacial water (figure 5) suggests weakening and a high degree of disorder of the H-bond structure. As suggested by previous diffraction data, interfacial water is to be described as a glassy like material [6]. For quantitative comparison the librational band of interfacial water was fitted by a Gaussian function and the temperature dependence of the midpoint of the Gaussian and its relative width (see figure 5(b)) show a crossover around  $T = 177$  K, which is supposed to be related to a glass transition in water. This is also in agreement with the results of the stretching modes study.



**Figure 5.** (a) Same as figure 4(a) but with an incident neutron energy  $E_i = 150$  meV, so as to accurately measure the intermolecular librational band of water around the 70 meV range. Curves with points represent the experimental data (the dry Vycor signal was not subtracted), curves without points show a Gaussian fit of the librational bands. The ice-Ih signal is given for comparison. (b) Temperature dependence of midpoint of the librational band (middles of the Gaussians, from the spectra in (a)) and their relative width,  $\Delta = \text{HWHM}/\sqrt{\ln 2}$  (HWHM, half-width at half-maximum).

To summarize, the inelastic neutron scattering spectra exhibit a strong softening and a high degree of disorder of the H-bond structure in interfacial water.

The existence of a liquid–liquid transition is a key element in discriminating between the different scenarios proposed for the peculiar properties of liquid water. In spite of strong similarities between interfacial water and bulk water (structure, calorimetric  $T_g = 165$  K) the extrapolation of the interfacial water 240 K liquid–liquid transition to the existence of a liquid–liquid transition in bulk liquid water would be speculative. Nevertheless, the evidence presented here of a liquid–liquid transition involving water is a real breakthrough and is of general interest. Beyond the fundamental interest above, the finding of liquid water at temperatures as low as 165 K is relevant to fields as different as materials science (cement technology, nuclear waste confining materials, geology) and biology (dynamics of hydration water).

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