

EXPERIMENTAL EVIDENCE OF A LIQUID-LIQUID TRANSITION AT 240 K IN INTERFACIAL WATER

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The scope of this highlight 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].

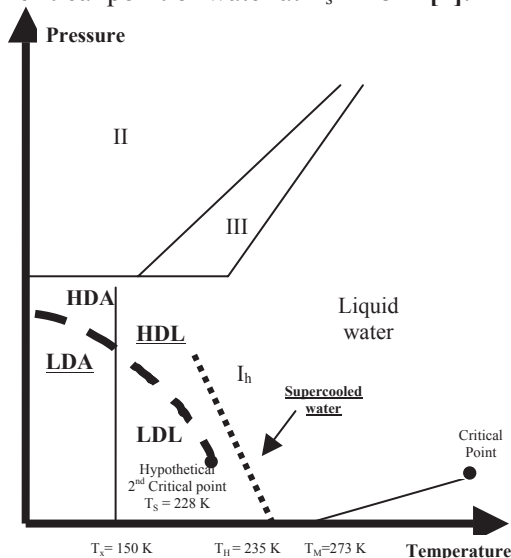


Figure 1. Simplified phase diagram of water, showing the hypothetical 2nd critical point and the related transition line (thick dash line) between a high density liquid (HDL) and a low density liquid (LDL). Here, using interfacial water as a model system, we show that such a first order liquid-liquid transition between a low and a high density form of liquid water is possible.

A condition for the existence of this critical point is the presence of a first order transition between a High (HDL) and a Low Density Liquid (LDL), see dashed line in Fig.1. 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), crystallise 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 the liquids: High Density Amorphous ice and Low Density Amorphous Ice.

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.

As shown by DSC (Fig.2) this system experiences a significant phase transition at 240K. Density change of the interfacial water above and below the transition has been inferred from diffraction data (not shown, 7C2, LLB). High resolution incoherent quasi-elastic neutron scattering (IN16, ILL) has then been used to probe local long time rotational and translational dynamics (see Fig.3) of the interfacial water as sensed by the water molecules hydrogen atoms.

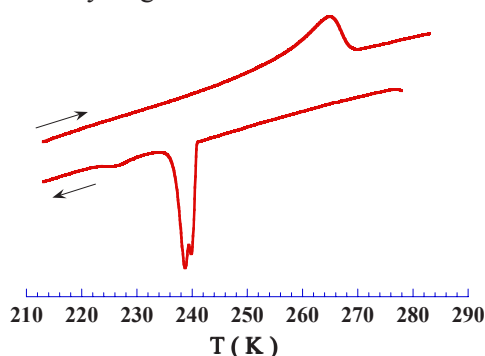


Figure 2. Thermograms (5 K / mn) of a monolayer of water at the Vycor hydrophilic surface. Cooling and heating are indicated by arrows.

We show that on a timescale of 1 nanosecond, (i) $\langle u^2 \rangle_{\text{Rot}}$ significantly increases above 150 K (Fig.4a). This is the onset of rotational dynamics of the water molecules (glass transition for rotational dynamics to be related to T_x Fig.1).

(ii) Below 165 K, interfacial water is a low density amorphous material ($Q_0=Q_0^{\text{LDA}}=1.71 \text{ \AA}^{-1}$, Q_0 is the first peak in $S(Q)$) showing no long range translational dynamics ($\langle u^2 \rangle_{\text{Trans}} \approx 0$, Fig.4b). Above 165 K, no change is observed in water density ($Q_0=Q_0^{\text{LDA}}=1.71 \text{ \AA}^{-1}$, not shown) but translational dynamics becomes possible on a 1 nanosecond 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** (Fig.4b).

(iii) At 240 K, this Low Density Liquid (LDL) experiences a first order transition (Fig. 2) to transform to a High Density Liquid, HDL ($Q_0=1.86 \text{ \AA}^{-1}$) [2] 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 (Fig.4). An experiment at lower

resolution (Inset Fig.4) i.e. shorter time (QENS, ANL/IPNS) confirms this point.

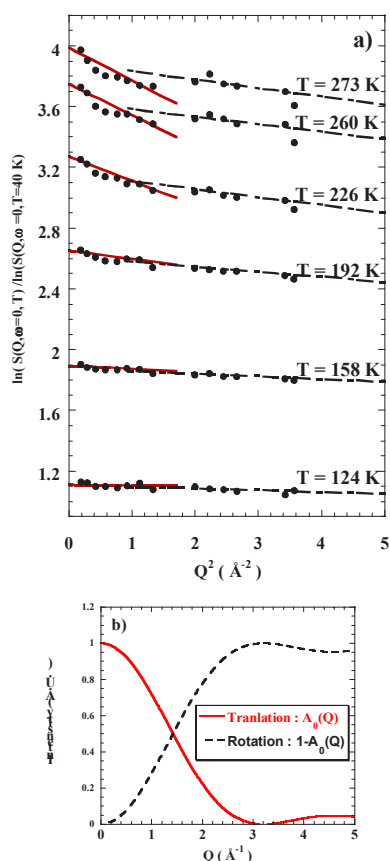


Figure 3. a) Normalized $\ln S(Q, \omega=0)$ vs Q^2 at selected temperatures in the range 77 K, 280 K (IN16, ILL). At high temperature, two distinct linear regions may clearly be defined. b) The translational and rotational contributions to the scattered intensity are strongly Q dependent, making it possible to discriminate between them. From the data in the low Q range [0.1\AA^{-1} - 1.0\AA^{-1}] of Fig. 3a, we extract a first characteristic mean square displacement, $\langle u^2 \rangle_{\text{Trans}}$, related to the water molecule long range diffusion. From the data in the higher Q range [1.1\AA^{-1} - 1.9\AA^{-1}] we define $\langle u^2 \rangle_{\text{Rot}}$, a mean square displacement related to the local molecular reorientations.

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 $T_g = 165 \text{ K}$ [3]) 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 evidences 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 material science (cement technology, nuclear waste confining materials, geology) and biology (dynamics of hydration water).

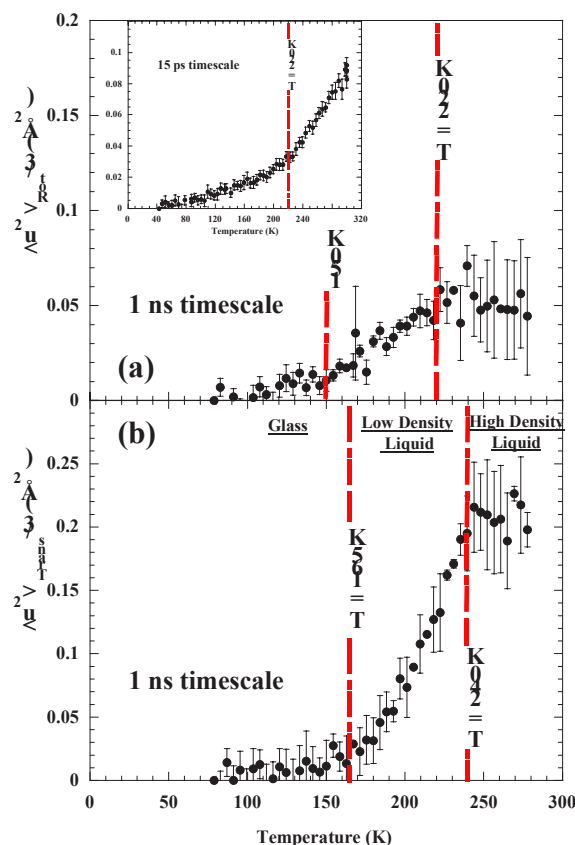


Figure 4. Temperature dependence of rotational and translational mean-square displacements of interfacial water $\langle u^2 \rangle_{\text{Rot}}$ (a) and $\langle u^2 \rangle_{\text{Trans}}$ (b) have been extracted from the two Q ranges defined in Fig. 3. Inset: lower resolution (shorter times) experiment (QENS, ANL/IPNS) confirming the saturation effect observed on IN16 due to the “high density” water fast dynamics above 240 K. The different transitions (see text) detected in water rotational (a) and translational (b) behaviours are noted by red dash lines. As expected in water, where translational dynamics is driven by hydrogen bond life time (i.e. rotational behaviour), any transition in the long range translational behaviour is preceded by a transition in the water molecules rotational behaviour.

References:

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