Experimental report

10/07/2017

Proposal: 9-13-572 **Council:** 10/2014

Title: Pressure dependence of MSD in deeply cooled confined water: a new wayof testing the Liquid-Liquid Transition hypothesis

Research area: Soft condensed matter

This proposal is a resubmission of 9-13-522

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Samples: silica xerogel

Instrument	Requested days	Allocated days	From	To
IN5	6	5	29/07/2015	03/08/2015

Abstract:

Aim of this proposal is to verify the Liquid-Liquid Transition hypothesis in deeply cooled confined water. The LLT hypothesis has been recently proposed in the literature and has given rise to passionate debate; it has been suggested to be present in the hydration water of proteins and to trigger the so called protein dynamical transition. The novelty of our approach is in the use of Elastic Incoherent Neutron Scattering (EINS)to measure the pressure dependence of mean square displacements (MSD)at constant temperature across the putative LLT. Moreover, we investigate water confined in the pores of a hydrophylic disordered silica matrix obtained from the alcoxide precursor TMOS via the sol-gel method. In this new matrix the confinement conditions experienced by water in biological systems are closely mimicked and the hydration level can be easily varied.

Experimental Report 6-02-556 (IN6) - 9-13-572 (IN5)

Pressure dependence on quasi-elastic broadening in deeply cooled confined water

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The aim of the project was to study the pressure dependence on the local dynamics of deeply cooled confined water molecules, to possibly give evidences of its putative Liquid-Liquid Phase Transition (LLPT) [1 - 4]. The temperature and pressure ranges explored were $(20 < p < 3000)bar$ and $(180 < T < 255)K$.

The sample used was a silica confining matrix prepared via sol-gel method, at two hydrations $h = 0.10$ and $h = 0.40$ ($h = \frac{[gH_2O]}{[gSiO_2(dry)]}$). The experiment was performed using the high pressure cylindrical sample holder designed and tested by Prof. Judith Peters and coworkers at ILL [5]. The liquid transmitting pressure was the Fluorinert [6]. For the experiments, no separation between the powder sample and the fluorinert was used, to let it flow through the sample grains and to transmit the pressure homogeneously within the matrix. The Fluorinert's high average molecular mass ($\approx 416\,$g/mol) ensured that it could hardly go inside the matrix pores and that its dynamics was slow enough to be totally negligible.

Quasi-elastic spectra were acquired using different incident wavelengths. In particular:
- For IN5, the incident wavelength was $\lambda = 8\,$Å, giving an energy resolution of 0.022 meV FWHM, and an observable Q range of $(0.1 < Q < 1.4)$Å^{-1};
- For IN6, the incident wavelength was $\lambda = 5.1\,$Å, providing a resolution for E of 0.070 meV FWHM, and an observable Q range of $(0.3 < Q < 2.0)$Å^{-1}.

Figure 1 shows a first informative result about the effects of Fluorinert contribution on the total signal, by summing the $S(Q, \Delta E)$ spectra over all the energies.

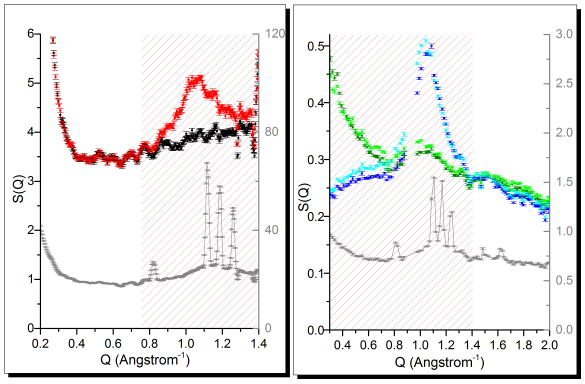

Figure 1: Appearance of coherent signal from Fluorinert. Left panel: IN5 data of empty cell without (black) and with Fluorinert (red); right panel: IN6 data of the sample $h = 0.10$, without (olive 180 K, light green 225 K) and with Fluorinert (blue curve 180 K, cyan curve 225 K). The grey datasets (right side scale) are examples of Bragg peaks appearance due to the Fluorinert crystallization.

Indeed, the presence of a coherent contribution is visible in the Q range [0.7,1.3]Å^{-1}, which made an analysis of the system under investigation impossible in that region. On the other hand, the presence of this signal allowed to detect whether the pressure and temperature reached

were causing a freezing of the Fluorinert, so that there was neither a control nor a measure of the actual pressure applied to the sample anymore. However, the remaining IN6 Q interval was useful to check for every P-T point that no water ice was formed, because it would have caused an appearance of 3 typical ice Bragg peaks. This confirmed that no freezable water was present in the sample.

Therefore for the QENS analysis, IN5 spectra were cut up at values of $Q \leq 0.7\,\text{Å}^{-1}$, while the IN6 data were considered only for $Q \geq 1.3\,\text{Å}^{-1}$, thus no satisfactory quantitative analysis of the Q dependence for all the pressure and temperature points investigated was done. For all the fitting procedures, 2 Lorentzians + 1 delta function (each convoluted with the instrumental resolution) were needed.

The following results were then obtained with IN5 data by averaging, for each spectrum, the HWHM fitting results of the highest 3 Q points, and by studying the T and P dependence for the 2 hydrations. Figure 2 shows the resulting plots.

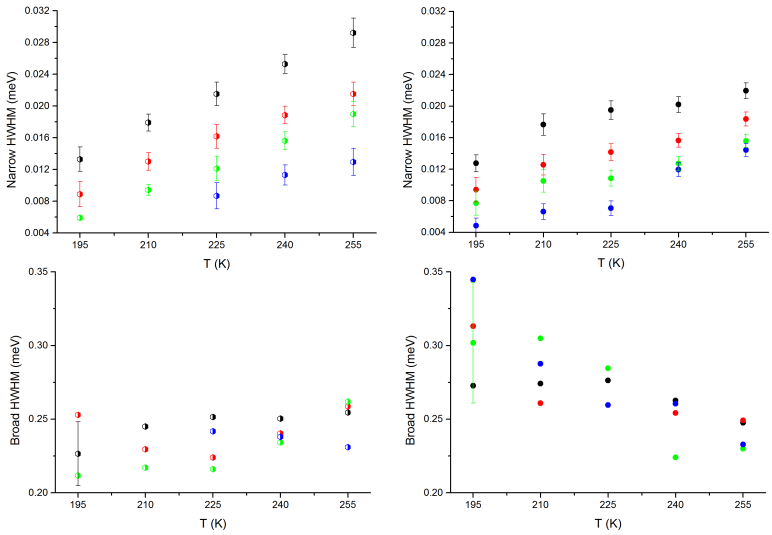

Figure 2: HWHM VS T, for 4 pressures: 20 bar (black), 500 bar (red), 1000 bar (green), 2000 bar (blue). Left panels: $h = 0.10$ sample; right: $h = 0.40$.

The "broad" (fast) relaxation dynamics shows no easily visible trend or remarkable difference with T/P/hydration, but only a general descending trend of HWHM with temperature increasing for the $h = 0.40$ sample, not detected for the other one. Regarding the slow dynamics, the behaviour is visibly different: the $h = 0.10$ curves have all a linear trend as function of T and, as expected, the curves are shifted to lower values of HWHM with pressure increasing; $h = 0.4$ curves have a similar trend for the first points, then the slope tends to decrease, until it increases again at the highest T.

[1] Poole, P.H. et al.; *Phase behaviour of metastable water.* Nature, (**1992**) 360, 324-328.

[2] Palmer, J.C. et al.; *Metastable liquid-liquid transition in a molecular model of water* Nature, (**2014**) 510, 385-388.

[3] Liu, L. et al.; *Pressure dependence of Fragile-to-Strong Transition and a possible second critical point in supercooled confined water.* Phys. Rev. Lett., (**2005**) 95, 117802.

[5] Peters, J. et al.; *High hydrostatic pressure equipment for neutron scattering studies of samples in solutions.* High Pressure Research, (**2011**) iFirst, 1–6.

[6] Sidorov, V. A. et al.; *Hydrostatic limits of Fluorinert liquids used for neutron and transport studies at high pressure.* J. Phys.: Condens. Matter, (**2005**) 17, pp. 3005–3008.