	Experiment title: Inelastic X-ray Scattering of water under pressure	**Experiment number**: HS-1505 +IHR
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Names and affiliations of applicants (* indicates experimentalists):

- *P. Loubeyre, Service PMC, DPTA/SPMC, BP 12, F-91680 Bruyeres-le-Chatel
- *M. Krisch, ESRF, France
- *F. Sette, ESRF, France

Report:

The high frequency dynamics of liquid water have been studied up to 28 Kbar, spanning a density range from 1.0 to 1.37 g/cm^3. For this purpose two distinctly different sample set-ups were utilized: a large volume cell (LVC) providing data from ambient pressure up to P=3.8 Kbar and a diamond anvil cell (DAC) covering the pressure range between P=3.2 and P=27 Kbar. The LVC contained about 1 cm^3 sample volume and was pressurized by a hand pump up to 3.8 Kbar at 277 K. The large sample size allowed to perform the experiment with 1.5 meV (full-width-half-maximum, FWHM) total energy resolution. The DAC contains ≈ $1 \cdot 10^{-5}$ cm^3 sample volume and was pressurized up to 27 Kbar by a steel membrane system driven by a pressurized gas. To avoid crystallization, data from 3.2 to 14 Kbar were taken at T=300 K, while data above 14 Kbar were taken at 410 K. The small sample size required to perform the experiment with a lower energy resolution of 3 meV FWHM. The data quality, however, was not degraded with respect to the LVC data at the same momentum transfer values, Q, as a consequence of the pressure induced increase of the sound velocity and consequent increase in energy transfer. Spectra were recorded for momentum transfers between 3 and 10 nm^{-1}, and typically 2-4 spectra of 5h length were accumulated in order to acquire sufficient statistics. The high-frequency sound velocity, c_∞, was determined by a linear fit to typically 6 to 8 Q-points.

The resulting evolution of c_∞ with density is reported in Fig. 1 for the whole investigated density range in a logarithmic scale (left panel, a), and for a restricted density range in a linear scale (right panel, b). The density dependence of the zero-frequency limit sound velocity, c_0, has been derived from the water equation of state (EOS) [1] and is also reported for T = 277 K and T = 297 K. In Fig.1a it can be observed that c_0 increases by a factor 2.6 in the spanned density region, while c_∞ displays a much weaker density dependence. As a consequence, the two velocities tend to merge together for densities estimated to be about

1.5 g/cm^3. The most striking result of our study is highlighted in Fig. 1b. At densities around 1.1 g/cm^3, the evolution of c_∞ displays a cusp-like behavior, while c_0 shows a smooth behavior. Moreover, we note the excellent agreement between the LVC and DAC results in the overlapping density region.

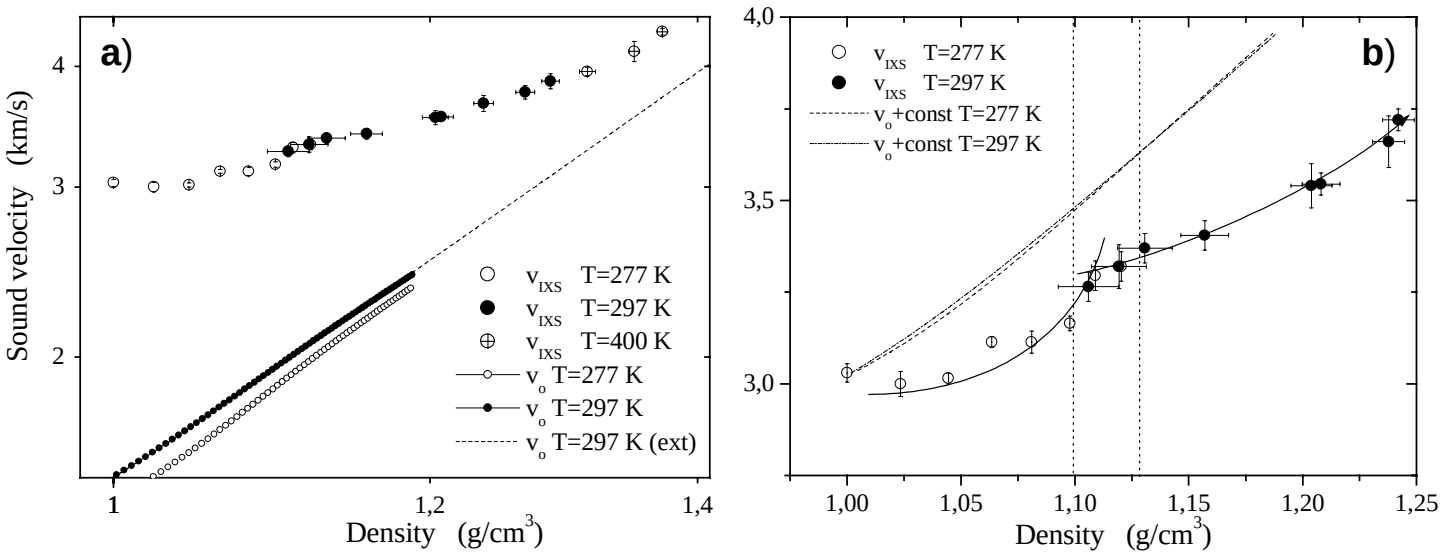

Figure 1: Density dependence of c_∞. **a)** large circles: LVC data and DAC data; small circles: c_0 data obtained from the water EOS [1], dashed line: extrapolation of c_0 to higher densities. **b)** Zoom of figure 1a). c_0 (dashed lines) is offset to the ambient pressure value of c_∞ in order to contrast with the discontinuity in the evolution of c_∞ around ρ=1.11 g/cm^3. The solid lines are guides to the eye.

Previous IXS work on water [2] revealed a "step-like" increase in the sound velocity from its low-frequency value c_0 to its high frequency value c_∞. The transition between the two dynamic regimes is determined by the coupling of the propagating density fluctuations with the dynamics of the structural rearrangements of the particles in the liquid. The complex dynamics of such rearrangements can be summarized by a relaxation process that is successfully described by a relaxation time τ and strength Δ. τ determines the transition frequency below and above which the acoustic dynamics of the system is qualitatively different, and Δ the effectiveness of the coupling between the structural rearrangements and the longitudinal density fluctuations. Within this framework, the large difference between c_0 and c_∞ arises from the coupling of the density fluctuations with the structural rearrangements due to the making and breaking of the hydrogen bond network.

Our present investigation suggests that such coupling is reduced at increased densities. This in turns implies the reduced role of the hydrogen bonding in the intermolecular interaction – an expected result considering the confinement effect due to the externally applied pressure which is balanced by the repulsive part of the intermolecular potential. Consequently, there are no longer relaxation processes capable to considerably affect the density fluctuations spectrum from the Thz regime down to very low frequencies. Furthermore, the results indicate that around densities of 1.11 g/cm^3 there is a basic modification in the properties of the liquid, pointing towards the presence of two liquid phases, respectively existing above and below a critical density value of $\rho_{C'}$. A second critical point in water, located at $T_{C'}$=130±5 K, $P_{C'}$=2.90±0.3 Kbar and $\rho_{C'}$=1.10±0.03 g/cm^3 has indeed been predicted by molecular dynamics studies [3]. It is therefore tempting to interpret the observed anomaly of c_∞ around ρ = 1.11 g/cm^3 as the reminiscence of critical fluctuations between the two liquid forms of water around the critical density $\rho_{C'}$.

References

[1] A. Saul and W. Wagner; J. Phys. Chem. Ref. Data 18, 1989 (1989).

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[3] A. Scala et al.; Phys. Rev. E 62, 8016 (2000).