The Origin of Water's Anomalous Properties Captured by X-ray Experiments

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Water is the most important liquid for our existence on Earth and it plays an essential role in physics, chemistry, biology and geoscience. What makes water unique is not only its importance but also the anomalous behavior of many of its macroscopic properties. For example, density, specific heat, viscosity and compressibility of water behave in ways opposite to other liquids that we know. If we look at a glass of ice water, everything is, in a sense, upside down. Strangely enough for the liquid state, water is the densest at 4 °C, and therefore it stays on the bottom. This is why life can exist at the bottom of a lake and an ocean during winter, even when the surface is frozen. The origin of this strange behavior, unique to water among the important liquids, is one of the most essential questions in physics and chemistry.

There has been an intense debate about the origin of the strange properties of water for over a century. Many speculations and different theories have been proposed to explain these remarkable properties. One major hypothesis, that has strong indirect support from theoretical work, is that there could exist two different liquid states, as a high density liquid (HDL) and a low density liquid (LDL) with a coexistence line in the P-T diagram deep in the supercooled regime at elevated pressure. This liquid-liquid transition (LLT) line is proposed to end with decreasing pressure and increasing temperature in a liquid-liquid critical point (LLCP) and its extension into the one-phase region corresponds to the Widom line. Liquid water fluctuates between two different states (HDL and LDL) when it is cooled and these fluctuations reach a maximum level at the Widom line.

The challenge has been that water crystallization has prevented measurements of the bulk liquid phase below the homogeneous nucleation temperature of ~232 K and above ~160 K, leading to a 'no-man's land' devoid of experimental results regarding the structure. A new

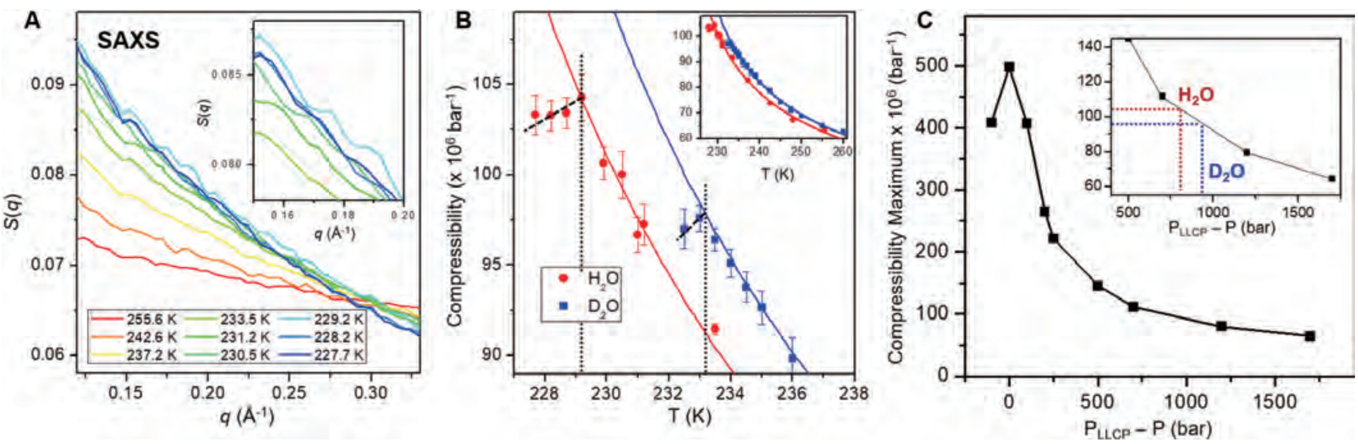

Fig. 1: Summary of the results reported in [1]. (A) Temperature dependent scattering structure factor, *S(q)* of H_2O at the SAXS region. The SAXS intensity is initially increasing upon cooling, then reaches the maximum at around 229 K, and subsequently decreases for lower temperatures. The inset shows the magnified view from q=0.15 to 0.2 Å^{-1}. (B) Temperature dependent isothermal compressibility, κ_T of H_2O (red) and D_2O (blue) obtained from the extrapolation to the zero momentum transfer ($S(0)$). A power law fit (solid line) was used to guide the eye up to the maxima and followed by dashed line to indicate the change in direction of the slope. (C) The maximum of the compressibility as a function of the pressure difference compared to the LLCP estimated by MD simulations performed with the iAMOEBA water model.

technique using ultrafast single-shot X-ray diffraction probing with free-electron lasers (FELs) and fast cooling of micron-sized droplets in a vacuum showed the existence of metastable bulk liquid water down to temperatures of 227 K and allowed us to venture into previously unexplored ranges [1]. The measurements on deeply supercooled liquid water were performed at the nanocrystallography and coherent imaging (NCI) beamline of PAL-XFEL (Pohang Accelerator Laboratory - X-ray Free-Electron Laser) in South Korea as a first user experiment.

The results reported in [1] is summarized in Figure 1. The small angle X-ray scattering (SAXS) intensity initially increases upon cooling, then reaches the maximum at around 229 K, and subsequently decreases for lower temperatures. Isothermal compressibility and correlation length can be derived from the SAXS intensities and it was found that they also reach a peak at 229 K. From the wide angle X-ray scattering (WAXS) measurement, it was also found that the continuous increase of structures with local tetrahedral coordination became more enhanced upon deep supercooling, which shows an accelerated transition towards a LDL dominated structure. It is fully consistent with the picture drawn from the SAXS measurement. This is the first experimental evidence of the existence of the Widom line and the LLCP, which can explain the origin of water's anomalous properties. Another remarkable finding of the study is that the unusual properties were different between normal and heavy water, and was more enhanced for the lighter water, thus showing the importance of nuclear quantum effects. A big challenge awaiting researchers in the next few years will be the direct search of the LLCP.

References

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