The origin of water's anomalous properties revealed by X-ray lasers

Water, both common and necessary for life on earth, behaves very strangely in comparison with other substances. How water's density, specific heat, viscosity and compressibility respond to changes in pressure and temperature is completely opposite to other liquids that we know. We all are aware that all matter shrinks when it is cooled resulting in an increase in the density. We would therefore expect that water would have high density at the freezing point. However, if we look at a glass of ice water (Fig. 1), everything is upside down, since we expect that water at 0°C being surrounded by ice should be at the bottom of the glass, but of course as we know ice cubes float. Strangely enough for the liquid state, water is the densest at 4 degrees C, and therefore it stays on the bottom whether it's in a glass or in an ocean. This is why life can exist at the bottom of a lake and an ocean during winter even when the surface is frozen. If we cool water below 4 degrees, it starts to expand again. If we continue to cool pure water (where the rate of crystallization is low) to below 0, it continues to expand – the expansion even speeds up when it gets colder. Many more properties such as compressibility and heat capacity become increasingly strange as water is cooled. As we know it so far there is no life without water.

The microscopic origin of the anomalous properties of water has been elusive and there has been an intense debate for over a century. One major hypothesis, that has strong indirect support from theoretical work, is that there could exist two different liquid states, high-density liquid (HDL) and low-density liquid (LDL). The phase boundary between the two phases would be at high pressures. 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 [1,2]. At the Widom line, the density fluctuations would reach a maximum (see Fig. 2). 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 technique using ultrafast single-shot X-ray diffraction probing with free-electron lasers 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 a 'no-man's land' [3,4]. The measurements were performed at SACLA **BL3** beamline and the NCI beamline of PAL-XFEL [5]. The results obtained from the experiment is summarized in Fig. 3. 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 maximum at 229 K. From the wide angle X-ray scattering (WAXS) measurement, it was also seen 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. The derivative with respect to the temperature of the position of the structure factor also shows maxima at 229 K. 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 this is fully consistent with the LLCP hypothesis, which can explain the origin of water's anomalous properties [5]. There are fluctuations that extend from the LLCP all the way up to ambient pressures and temperature causing water behave in a strange way. We can call the Widom line the smoke from the fire being the LLCP. This is the strongest experimental evidence of the LLCP. Another remarkable finding of the study is that the unusual properties were different between

Fig. 1. A glass of ice water with a thermometer measuring 4 degrees C at the bottom.

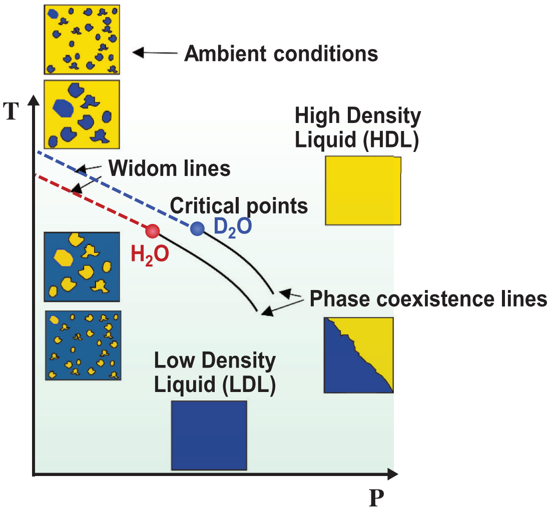

Fig. 2. Schematic picture of a hypothetical phase diagram of liquid water, showing the Widom lines, liquid-liquid critical points, and phase separation lines of H_2O and D_2O.

normal and heavy water, and was more enhanced for the lighter water, thus showing the importance of nuclear quantum effects [4].

With the help of ultra-short X-ray pulses, we were able to X-ray unimaginably fast before the ice froze and could observe how it fluctuated between the two states. For decades there have been speculations and different theories to explain these remarkable properties and why they got stronger when water becomes colder. Now we have found such a maximum, which means that there should also be a critical point at higher pressures.

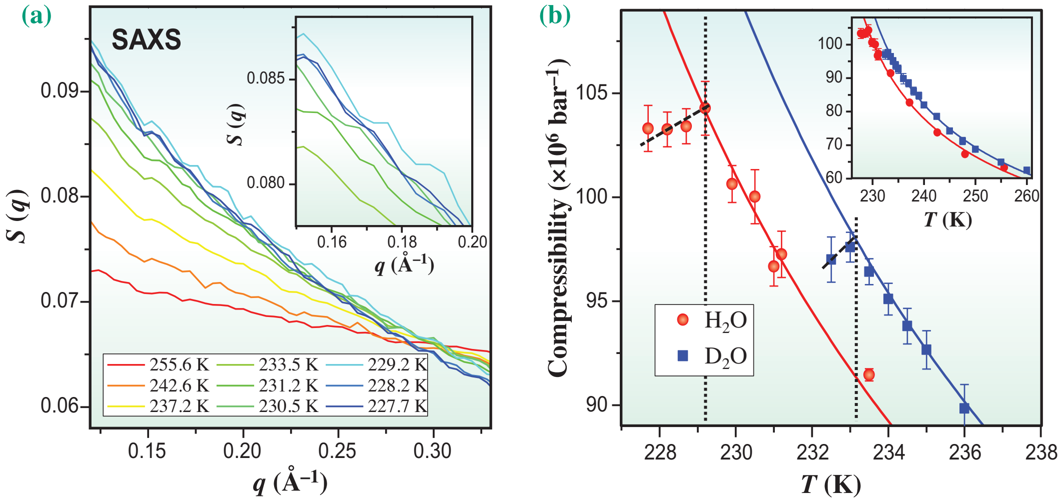

Fig. 3. **(a)** Temperature dependent scattering structure factor, $S(q)$ of H_2O at the SAXS region. The inset shows the magnified view from $q = 0.15$ to 0.2 Å^{-1}. **(b)** Temperature dependent isothermal compressibility of H_2O (red) and D_2O (blue).

Kyung Hwan Kim[a], Alexander Späh[b] and Anders Nilsson[b,*]

[a] Department of Chemistry, POSTECH, Korea
[b] Dept. of Physics, AlbaNova University Center, Stockholm University, Sweden

*Email: andersn@fysik.su.se

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