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Advancing into Water's "No Man's Land": Two Liquid States?

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Dedicated to Professor Alfons Geiger on the occasion of his 70th birthday

glass transition · metastable liquids · phase transitions · water · X-ray diffraction

Water is the most abundant liquid on the surface of the earth and is known for its anomalous physical liquid properties.[1,2] The most famous anomaly is the density maximum at 277 K and 1 atm, defining the border to a region of negative expansivity at lower temperatures.[3] Many anomalous properties become significantly pronounced on supercooling below the freezing point. Over the course of the past thirty years a number of scenarios have been proposed for describing the behavior of water in the supercooled region: 1) The stability limit/critical point free scenario (SL/CPF),[4,5] 2) the singularity-free scenario (SF),[6] 3) and the liquid–liquid critical point scenario (LLPC).[7] At the center of these scenarios is the hypothesis that in the low-temperature regime bulk water is composed of a mixture of two structurally distinct liquids: The low-density liquid(LDL) and the high-density liquid (HDL). Computer simulations suggest that the LDL form exhibits a high degree of local tetrahedral order, reminiscent of ice I,[8,9] whereas the HDL form has been experimentally characterized as having a disordered local environment and a higher coordination number[10] (see Figure 1). The proposed two liquid forms of water have experimentally well-characterized counterparts in the amorphous, glassy state.[11] The low-density amorphous (LDA) form can be produced by either hyperquenching liquid water or by vapor deposition on a cold substrate followed by subsequent annealing. By applying high pressure, LDA can be transformed reversibly into a high-density form (HDA) via a first-order-like transition. Upon increasing the temperature above water's glass transition temperature at $T_g = 136$ K, however, crystallization occurs very rapidly at about $T_X = 150$ K, making it very hard to study the liquid or amorphous state beyond this point.[11]

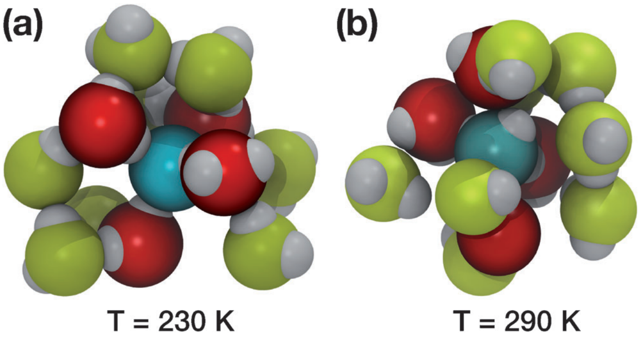

Figure 1. Typical local environment of a water molecule at the indicated temperatures. At low temperature water approaches a four-coordinate state with high tetrahedral order. Clusters were selected from MD simulations of the TIP4P/2005 model at 1 bar.

The LLCP scenario, introduced by Gene Stanley and coworkers in 1992,[7] is a conceptual extension of the first-order-like transition observed between the two amorphous states of water. It hypothesized the existence of a first-order phase transition between two metastable liquids that ends in a critical point and is based entirely on results of molecular dynamics simulations. Experimental evidence is hampered by the very fast crystallization occurring above $T_X = 150$ K and below the so-called "homogenous nucleation limit" of about $T_H = 232$ K at normal pressure.[1] Unfortunately, the entire HDL/LDL equilibrium line is placed in this region, which has been known as water's "no man's land" (see Figure 2). Recently, even the simulation results forming the basis for the LLCP scenario have been challenged.[12,13] By sampling the configurational space of model water using "umbrella sampling" Monte Carlo simulations in the temperature range of the proposed HDL/LDL transition, Limmer and Chandler could not identify the LDL form as a distinct thermodynamic state, but rather as a highly distorted form of ice Ic, with no free energy barrier separating the two. The earlier simulation results were deemed to be caused by insufficient sampling due to very slow relaxation processes.

In a very recent turn of events, however, the LLCP scenario has made a strong resurgence. By using a variety of different sampling techniques, Palmer et al.[14] could now unambiguously establish the existence of a first-order liquid–liquid phase transition between a HDL and a LDL form of the "ST2" water model originally used by Stanley and coworkers.[7] They could identify the Gibbs free energies of the two phases of liquid water in relation to the ice state and could

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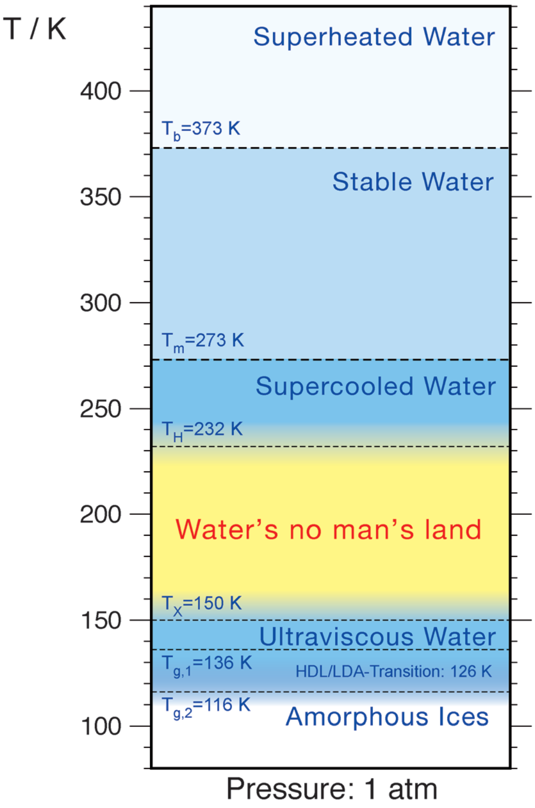

Figure 2. Characteristic temperatures observed for the stable and metastable forms of liquid and amorphous water under normal pressure conditions.

demonstrate their thermodynamic consistency. In addition, the height of the free energy barriers separating the different phases obeys well-known scaling relations with respect to the system size.

With the LLCP scenario back in the ring, is there hope that liquid water's puzzling phase behavior could be backed up by experimental evidence? Well, experimental progress has been made very recently. Two groups report results attacking the "no man's land" from both sides.

A large international collaboration headed by Anders Nilsson[15] recently reported data obtained at the Linac coherent light source at the SLAC National Accelerator Laboratory on the structure of liquid water well below the homogeneous nucleation temperature. By probing thousands of well-defined supercooled micrometer-sized (9, 12, 34, or 37 μm) water droplets produced via a Rayleigh jet with ultrafast X-ray laser pulses, they were able to conduct X-ray scattering experiments for every droplet separately. Due to the high intensity of the available X-ray beam, a complete diffraction pattern could be determined for each droplet by sampling about 100 X-ray shots of only 50 fs duration. Frozen droplets could be sorted out due to the presence of Bragg peaks. At the lowest temperature of 227 K about 3 % of the total number of droplets could still be identified as belonging to the liquid state, even after 5 ms. This suggests that liquid water can exist transiently on the millisecond timescale at a temperature well below the "homogenous nucleation temperature". These experiments represent a significant breakthrough, since they lower the temperature limit for available liquid structure data by 23 K from the previous record[16,17] and, for the first time, represent significant experimental penetration of water's "no man's land".

At a temperature of 227 K, the structure of liquid water is found to be very different from the structure of water at ambient conditions. Water has almost been completely transformed into a tetrahedrally structured liquid (as indicated in Figure 1 a), very similar to the structure of LDA. Sellberg et al. report that the experimentally determined structural transformation of water follows rather closely to what has been predicted by molecular dynamics simulations of the TIP4P/2005 model for water.[15] This might be of some significance for the question whether the LLCP scenario might be real, since the TIP4P/2005 model has been reported to exhibit a metastable liquid–liquid critical point.[18]

A second study recently investigated the properties of liquid water on the low-temperature side of the "no man's land". The two research groups led by Thomas Loerting from Innsbruck and Roland Böhmer from Dortmund discovered a hitherto unreported second glass transition of water at temperatures well below the "no man's land".[19] The starting point of their study was the high-density form of amorphous water (HDA), which has been annealed and is stable at normal pressure under liquid-nitrogen conditions. When the material is slowly heated, HDA is found to undergo a calorimetric glass transition at $T_{g,2} = 116$ K, producing a strong endothermic DSC signal, which is about five times stronger than the signal of the earlier documented glass transition of water at $T_{g,1} = 136$ K. By using broad-band dielectric spectroscopy, the relaxation times were determined to be lower than 100 s, indicating a transition to a liquid-like, albeit highly viscous dynamics. The authors point out that pressure annealing is the key to the preparation of the initial HAD phase and the reason that the second glass transition went unnoticed so far. Upon further heating, the high-density liquid (HDL) transforms into the low-density amorphous phase LDA around 126 K, which then undergoes the previously reported glass transition to LDL at 136 K. Dielectric loss spectra recorded for the HDL and LDA forms during the HDL/LDA transition at 126 K indicate that the relaxation in LDA is significantly slower than that in HDL. Further heating up to 151 K finally leads to a transformation of LDL to cubic ice. For both HDL and LDL there is a roughly 10–14 K wide window where the ultraviscous liquids can be studied. The relaxation times determined by temperature-dependent dielectric loss spectroscopy indicate an Arrhenius-like thermal activation with an activation energy of 34 kJ mol^{-1} observed for both liquids. HDL and LDL can be classified on the fragility scale as "strong" and "superstrong" glass formers, respectively. The fact that two distinct liquid forms of water exist and can be studied certainly does not prove the existence of a LDL/HDL phase transition, but represents a promising step towards an ultimate understanding of the unique behavior of liquid water.

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