

COMMENTARY

Which way to low-density liquid water?

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When rapidly cooled, a liquid undergoes dynamic arrest, forming an amorphous solid commonly called glass. Amorphous solids can also be created by different routes, for example by destabilizing the crystal structure at low temperature by applying pressure or intense radiation, or by depositing gas molecules on very cold substrates. Even though the resulting materials encode information about the preparation route in their frozen structure, they are usually considered members of the same family. This is not the case when the liquid is water. Back in 1985, Mishima et al. (1) and Mishima (2) reported that water forms two distinct amorphous ices, differing in their density and in local structure (the relative position and orientation of nearby molecules in the glass). In low-density glass [with a density of $0.94 \text{ g}\cdot\text{cm}^{-3}$ (3), not very different from that of crystalline ice] each molecule is surrounded by, and hydrogen-bonded to, four neighbors, a realization of a random tetrahedral network. In high-density glass [with a density at ambient pressure of about $1.15 \text{ g}\cdot\text{cm}^{-3}$ (4)] each molecule also has four hydrogen bonds on average, but a fifth molecule has entered the first coordination shell. By measuring the density as a function of pressure, Mishima et al. (1) and Mishima (2) showed that the transition between the two amorphous ices is rather sharp and characterized by hysteresis, features that are typically encountered in first-order thermodynamic transitions. These experiments have been seminal, seeding within the scientific community two related but still controversial ideas: the possible existence of more than one glass, a phenomenon nowadays indicated with the word “polyamorphism” (5) and, perhaps more importantly, the possibility that the two glasses are the out-of-equilibrium manifestation of two distinct liquid phases (6).

Years after the original experiments of Mishima et al. (1), Perakis et al. (7) show in PNAS that it is nowadays possible—exploiting state-of-the-art X-ray spectroscopy—to observe step-by-step the transformation process leading from properly annealed high-density amorphous ice [eHDA (8)] to low-density amorphous ice (LDA), this time at ambient pressure on increasing temperature. With the simultaneous

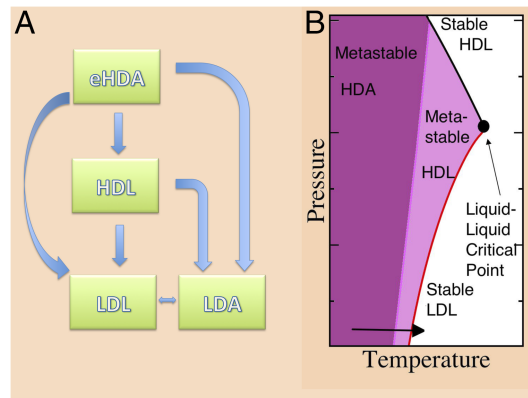


Fig. 1. (A) Cartoon of the possible paths connecting the relaxed high-density amorphous ice (eHDA) to the low-density forms via the cascade of transformations possibly involving the high-density ultraviscous liquid (HDL), the low-density ultraviscous liquid (LDL), and/or the low-density amorphous ice (LDA). (B) Cartoon of the low-temperature phase diagram of metastable water based on the hypothesis of a liquid-liquid transition. The black line ending in a black circle indicates the coexistence line between low-density and high-density forms. Emphasis is on the regions of stability and metastability of the high-density form. The red line indicates the limit of stability (spinodal) of the HDL. The corresponding spinodal for the LDL is not shown. The region of metastability of the high-density form (metastable with respect to the low-density form) is separated in two parts by the glass transition line, separating the HDA and HDL fields. The arrow at the bottom indicates the path followed in the experiment of Perakis et al. (7). This path crosses first the glass transition line of HDA and then the HDL spinodal, so that the system progresses from eHDA to HDL and finally to LDL.

measurement of the evolution of the sample structure (via wide-angle X-ray scattering) and sample dynamics (via small-angle X-photon correlation spectroscopy, XPCS) it becomes possible to reveal the real nature of the transition and attempt to answer a long list of unsettled questions. Are we really entitled to speak about polyamorphism in out-of-equilibrium systems? Are the two glasses really different phases (albeit dynamically arrested)? Is the observed steep change of the density first reported by Mishima a

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proper first-order transition? Do these amorphous ices convert to a (metastable) ultraviscous liquid before crystallizing, or is the crystallization perhaps mediated by the unfreezing of the orientational degrees of freedom (9–11) (i.e., an orientational glass transition)? If they convert, on crossing the glass transition temperature, to an ultraviscous liquid, is it possible to observe in a limited temperature window the metastable liquid(s) and to characterize its (their) structural and dynamic properties?

By finding out precisely how the two glasses interconvert Perakis et al. (7) help to discriminate between different hypotheses and guide us toward a deeper understanding of metastable and glassy water. The authors suggest that the transformation proceeds via a cascade of phase changes (Fig. 1A): First, eHDA goes to ultraviscous high-density liquid (HDL), which then transforms to ultraviscous low-density liquid (LDL). This cascade of transformations allows them to observe both ultraviscous forms of liquid water (the low- and the high-density liquids).

The strength of the experiment by Perakis et al. (7) lies in the temperature-resolved measurement of the amorphous ice structure, which indisputably shows the cross-over from the typical spectral shape of eHDA to that of LDA in the investigated temperature window. The crucial simultaneous measurement of the dynamic structure factor shows in addition that a collective fast process starts to be detectable around 115 K (when the sample is clearly eHDA). This relaxation process becomes faster and faster on heating. At 130 K the sample, which has fully converted to the low-density structure, still retains the collective fast process. Supported by previous calorimetric and dielectric relaxation experiments on samples with a similar thermal history (12), the diffusive nature of the collective fast process is interpreted as evidence of liquid behavior. If the authors are correct, what they have observed is the existence of both (doubly metastable) HDL and (singly metastable) LDL.

This astonishing result is consistent with the liquid–liquid critical point (6) hypothesis, the thermodynamic scenario predicting that water—despite being a one-component system—exists in two distinct liquid forms, differing in density and local structure, below the liquid–liquid critical temperature. According to this hypothesis (13, 14), on cooling the low-density liquid dynamically arrests into LDA, whereas on cooling under pressure the high-density liquid dynamically arrests into HDA. Interestingly, whereas the stability field of HDA is limited to large pressures, the region where the high-density phase is metastable with respect to the low-density one extends down to ambient pressure (Fig. 1B), consistent with the observation that HDA can be recovered at ambient pressure. However, on raising temperature at ambient pressure the limit of stability of the metastable high-density phase is encountered and the system has to convert to the low-density one. Because the hypothesized liquid–liquid critical point (6) is located in the region where the stable phase is

the crystal, at ambient pressure HDL is doubly metastable, both with respect to crystallization and with respect to the LDL form.

Does eHDA transform to HDL, and then to LDL, as the authors suggest, or does the transformation take place via any of the possible shortcuts shown in Fig. 1A? The work of Perakis et al. (7) will undoubtedly prompt additional experiments and interpretations. An accurate model of the decay of the density fluctuations in eHDA, HDL, LDL, and LDA in the experimentally probed wave vector q region could be very valuable to assess whether the measured collective diffusion is really associated with molecular

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diffusion on the 100-nm scale. Density fluctuations arising from thermal diffusion, a phenomenon observed also in disordered solids, could also show diffusive character at small wave vector. It is also important to clarify the nature of the reported q -independent slow mode, which apparently completely decorrelates the density fluctuations, and which seems to be insensitive to the cross-over from glass to liquid. Does it originate from viscoelastic relaxation, possibly of the same type as the q^0 mode recently observed in soft networks (15)? It will also be important to assess how long the system can be kept in the ultraviscous liquid state without crystallizing, and how the measured relaxation times connect with the available data in supercooled states, a comparison that could also shed light on the hypothesized fragile-to-strong cross-over of the ambient pressure liquid water viscosity (16–19). Finally, further experiments will be needed to convince the scientific community that irradiation damage, often present in XPCS experiments, does not affect the reported results.

To conclude, Perakis et al. (7) provide strong evidence that water is indeed able to sustain two different liquid structures, a result that would rule out all proposed thermodynamic scenarios that do not predict the existence of a liquid–liquid critical point in the “no-man’s land,” the region lying between the crystallization temperatures encountered when heating the glass and cooling the liquid. The fact that both liquid structures can be observed at ambient pressure (Fig. 1B) despite their metastability with respect to crystalline ice or with respect to both LDL and crystalline ice is indeed striking. Heating eHDA unexpectedly provides access both to low- and high-density ultraviscous liquids.

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