# Several glasses of water but one dense liquid

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Depending on the external temperature and pressure, pure substances can assume different phases, two of them (gas and liquid) lacking long-range order. The crystal phase, especially in molecular systems, can assume a multiplicity of distinct ordered structures, differing in the relative position and orientation of the molecules. In the case of water, the ubiquitous liquid that covers our Earth, 17 ordered polymorphs (1) are experimentally known to date, an indisputable signal of the existence of a plethora of distinct stable local molecular environments. While we are all accustomed to the idea of multiple crystal structures, not everybody knows that theoretical work suggests that some pure substances, including water (2, 3), could possibly exist in more than one liquid state. The liquids are expected to differ in local structure and density. Such a counterintuitive but stimulating idea, up to now verified only by numerical simulations (2, 4), has fostered a significant experimental effort in the last 20 y (see, e.g., refs. 5–10)—an effort that is finally beginning to bear tasty and ripe fruits. In PNAS, Stern et al. (11) report evidence suggesting that a high-density form of liquid water, distinct from the low-density one observed at ambient pressure, indeed exists (and can be experimentally investigated) between 1,000 and 3,000 atm near 150 K.

The search for distinct liquids in water is far from being a trivial hunt. Simulation studies predict that the two liquid forms emerge under deep supercooling at positive pressures (2). Both the low- and the high-density liquid should exist only in metastable equilibrium, converting into the stable crystalline ice immediately after being generated. How immediate is "immediately" is the central question. All pure liquids can exist in metastable equilibrium below the melting line for a limited amount of time, until a fluctuation which locally creates a sufficiently stable crystalline nucleus appears, progressively transforming the liquid into an ordered structure. The probability that such a fluctuation appears increases on cooling. At the temperature where the high-density liquid is expected to
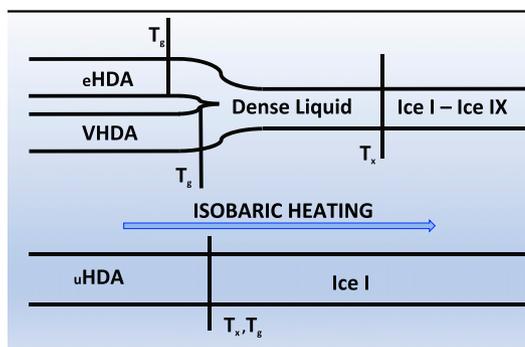
Fig. 1. Cartoon of the transformations explored by Stern et al. (11) at pressures between 1,000 and 3,000 atm. Glasses very different in their preparation and final densities, like the eHDA and VHDA, on isobaric heating first transform into a liquid at the calorimetric glass transition T_g and then crystallize at T_x on further heating. Despite their original differences, T_x is the same for both materials. In addition, the crystal above T_x contains the same relative concentration of ice I and ice IX, a clear indication of identical nucleation pathways. These findings strongly suggest that the precursor state, before crystal nucleation, is the same liquid in metastable equilibrium in both samples. In contrast, the unrelaxed uHDA sample, which is known to contain ice seeds (17), crystallizes at a lower T_x and results in a sample with no ice IX component.

form, nucleation would possibly take place within a few milliseconds, making the experimental observation of the high-density liquid extremely difficult.

Stern et al. (11) take a different approach to the problem. Instead of cooling the liquid in the no-man's-land—the name given to the range of temperatures and pressures where nucleation prevents the experimental observation of the metastable liquid (12)—they warm up dense amorphous solid water, searching for optimal conditions in which the glass turns into a liquid first (at the calorimetric transition temperature T_g) and into a crystal (at the crystallization transition T_x) on further heating.

Indeed, water, like several other substances, can exist also as a nonequilibrium history-dependent disordered

solid. Amorphous states of water can be prepared in several distinct forms and via different preparation routes (13): by hyperquenching droplets of water (14), by vapor depositing water on cold substrates (15), and by pressure-driven amorphization of ice (16). Dissimilarly from most of the other substances, distinct preparation procedures result in materials with significantly different properties, an evidence of water's polyAmorphic behavior. Nowadays we distinguish between a low-density amorphous ice (LDA), which can be directly produced by hyperquenching or vapor deposition, a high-density amorphous ice (HDA) further subdivided into expanded (eHDA) and unrelaxed (uHDA), depending on the amount of frozen-in crystal nuclei (17), and a very-high-density amorphous ice (VHDA). These high-density forms are all produced by pressure-driven amorphization. Neutron scattering diffraction measurements show the details of the structure of LDA, HDA, and VHDA (18). While in LDA a water molecule participates on average in four hydrogen bonds, in HDA a fifth molecule enters the first coordination shell, and more than one enters the shell for VHDA. The possible interrelations between these different forms have been discussed in a recent review (13). Here we note that in the two-liquids hypothesis the sharp transition which converts LDA to HDA and back on changing pressure (19) is interpreted as the out-of-equilibrium analog of the transition between the low- and the high-density liquid.

Heating amorphous water to detect the calorimetric glass transition temperature T_g and the crystallization temperature T_x aiming to access the metastable liquid surviving between T_g and T_x is not a new idea. It has been successfully used to detect the conversion of LDA and eHDA to a low-density form of water before crystallization at ambient pressure (6, 20, 21). It has also been shown that at ambient pressure T_g for LDA and eHDA clearly differ, another piece of evidence suggesting that LDA and eHDA are the glasses associated with the low-density and high-density liquid, respectively (21). Scarcer, and sometimes indirect, attempts have also been made to detect T_g for HDA under applied external pressure, where the high-density liquid should be metastable only with respect to crystallization. Still, the out-of-equilibrium nature of the amorphous ices, the intrinsic dependence of the results on experimental protocols (heating and compression rates, for example), and the difficulty in clearly identifying the unfreezing of the translational and orientational degrees of freedom have often cast doubts on the possibility of extrapolating information on the liquid from studies of the glass.

What makes the work of Stern et al. (11) special is a combination of state-of-the-art methods with a simple but deep and effective idea. Stern et al. (11) argue that if different glasses share the same T_x then all samples just before crystallization must be in the same thermodynamic state. Simply, sample preparation history no longer matters. This strongly suggests that all samples have turned into the same liquid after their T_g. As a further check they argue that if all samples are in the same liquid state just before crystallization, then they should crystallize following identical nucleation pathways, hence generating identical amounts of crystalline ices. Stern et al. (11) show that for pressures between 1,000 and 3,000 atm, relaxed HDA and VHDA (prepared at 19,000 atm) despite their structural and density difference melt on heating into a dense liquid and then crystallize at the same T_x (Fig. 1). The observed T_x is higher than in all previous studies, signaling, besides a shrinkage of no-man's land, the high quality of the prepared samples, carefully annealed to suppress, to the best of today's experimental abilities, crystalline seeds. More importantly, Stern et al. (11) show that the crystals resulting from heating eHDA and VHDA contain comparable relative amount of ice I and ice IX, confirming the observation, in a quite wide range of pressures, of a truly metastable dense liquid.

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The experiments by Stern et al. (11) open the door to a study of the structural and dynamic properties of the high-density liquid in a reasonably wide range of temperatures and pressures. Developments in sample preparation and in experimental methodologies are thus penetrating the no-man's land from below, offering the possibility to investigate both the high-density and the low-density liquid forms, paving the way to future exploration of their interconversion. It will be important to further investigate how long these ultraviscous liquids can survive without crystallizing, what the corresponding structural relaxation times are (a definitive proof of their ergodic behavior), and how these times connect to the one observed on the high-temperature side of no-man's land. To start with, now that eHDA and VHDA preparation protocols have been established, investigating the heating rate dependence of T_g and T_x could help in establishing how long the dense liquid can survive. Establishing precise calorimetric and crystallization temperatures for different pressures, as well as characteristic relaxation times of ultraviscous water, is of pivotal importance also in many other fields: in environmental science where molecular clouds can have both crystalline and amorphous forms of ice; in solar and extrasolar system science where icy moons, circumstellar disks, and other outer-space bodies also contain both ice and amorphous ice; and in cryobiology, where biomaterials must be kept at low temperatures and crystallization must absolutely be avoided to prevent irreversible damages due to ice growth.

To summarize, the work of Stern et al. (11) reports another important piece of evidence—and a strong one—that water is indeed able to form two different liquids at low temperature and positive pressures, in full agreement with numerical studies suggesting the existence of a liquid–liquid critical temperature (2, 4), located in the no-man's land. Ultrafast probing techniques, like the one recently applied to follow the evaporation-driven cooling of falling water droplets (7), will hopefully allow measurements of equilibrium bulk properties in the time interval preceding crystallization. The stage has been set for the full characterization of these two different liquids emerging from nonergodic glass states and—why not?—for the direct observation of their interconversion. The idea that water can form more than one liquid phase would then be definitively proven.

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