



# Multitude of glasses of water

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In this issue of PNAS, the article by de Almeida Ribeiro et al. (1) explores how shear can generate a variety of water-made glasses, including some that are distinct from those currently known and others that are experimentally unattainable by cooling water.

Glasses are out-of-equilibrium disordered structures, often described as liquids that have lost their ability to flow. When a liquid is cooled rapidly enough to prevent crystalline nucleation, its dynamics slow to the point where diffusion over molecular distances can take months, years, or even centuries, resulting in an amorphous solid: a glass (2, 3). However, cooling a liquid is not the only way to form arrested disordered structures. Crystalline materials can also be disordered through neutron bombardment or by applying sufficient external pressure to deform or destroy the crystalline arrangement, particularly if the structure is not densely packed. Similarly, intense shear forces can progressively transform a crystalline material into a disordered structure. When shearing occurs at low temperatures, molecules lack the time to reorganize into a thermodynamically stable structure, resulting in a glassy state when the shear is removed (4).

Liquid water can be vitrified if the cooling rate is sufficiently high to outpace crystal formation (5). At ambient pressure, rapidly cooled water forms a glass with a tetrahedral hydrogen-bonded network known as low-density amorphous ice (LDA), with a density of  $\rho_{LDA} = 0.94 \pm 0.02 \text{ g/cm}^3$ . Under compression, LDA undergoes an abrupt transition to a denser glass called high-density amorphous ice (HDA) (6), with a density of  $\rho_{HDA} = 1.16 \pm 0.02 \text{ g/cm}^3$ , structurally similar to the glass formed by cooling water under high pressure (7). The density gap between LDA and HDA has been interpreted as evidence of the existence of two distinct liquids [generating two distinct glasses (8)], a hypothesis formulated back in 1992 (9). Both simulations (9) and experiments (10) suggest that below a liquid–liquid critical point, located in the metastable region of the phase diagram [recently estimated to be around 200 K and 1,250 bar (11)], water can indeed exist in two liquid phases, despite being composed of identical molecules. Liquids with densities in between the densities of the two coexisting liquid phases are thermodynamically unstable explaining why glasses with the corresponding densities are not observed.

Given that liquid water at ambient temperature spans a wide density range under varying pressures, one might wonder why glasses with densities between  $\rho_{LDA}$  and  $\rho_{HDA}$  cannot be formed if such liquids are suddenly cooled. Indeed, conceptually, glasses can be generated from liquids at arbitrary temperatures and pressures (12). However, practical constraints, such as crystal nucleation times, thermal conductivity, and limitations in experimental techniques, restrict the possible cooling rates and as consequence the

variety of glasses that can be formed in the lab. For water, cooling rates of approximately  $10^6 \text{ K/s}$  are used to bypass crystallization and achieve vitrification. At ambient pressure, cooling with this rate from room temperature to liquid nitrogen temperature (77 K) requires about 200  $\mu\text{s}$ . During the cooling process, the liquid follows the equilibrium density down to the temperature where its relaxation time becomes comparable to the experimental time. Then, it loses equilibrium and it transforms into a glass with a structure resembling, if no further aging takes place, the one of the liquid at this glass-transition temperature. Computer simulations, nowadays capable of achieving such cooling rates (13), suggest that at ambient pressure, the resulting glass corresponds to the supercooled liquid around 190 K, structurally similar to LDA. Current experimental methods can not generate much faster cooling rates, preventing the possibility to generate, by constant-pressure cooling, a water glass with properties corresponding to liquid water at room temperature and  $1 \text{ g/cm}^3$  density.

A groundbreaking 2023 study by Rosu-Finsen et al. (14) demonstrated that ball milling (a method of shearing solids by repeatedly crushing small metallic spheres against a solid sample) can produce a water glass with an intermediate density,  $\rho_{MDA} = 1.07 \text{ g/cm}^3$ , between  $\rho_{LDA}$  and  $\rho_{HDA}$ . Is this glass equivalent to the glass created by cooling liquid water or is it something entirely new? Does it challenge the liquid–liquid critical point hypothesis? De Almeida Ribeiro and colleagues addressed these questions computationally.

First of all, De Almeida Ribeiro and colleagues demonstrated that also in the case of water, shear erases the system's history. When shear is applied to LDA, HDA, or ice  $I_h$ , the initial structure is progressively replaced by a material with well-defined and reproducible properties. Shearing injects energy in the system, forcing the molecules to move (despite the low kinetic energy), exploring different local configurations, and rejuvenating the glass. This finding suggests that shear acts as an additional control variable (at least in the range of shear values explored in the numerical study), enabling in principle an extended equation of state where density depends not only on pressure and temperature (as in thermodynamic equilibrium systems) but

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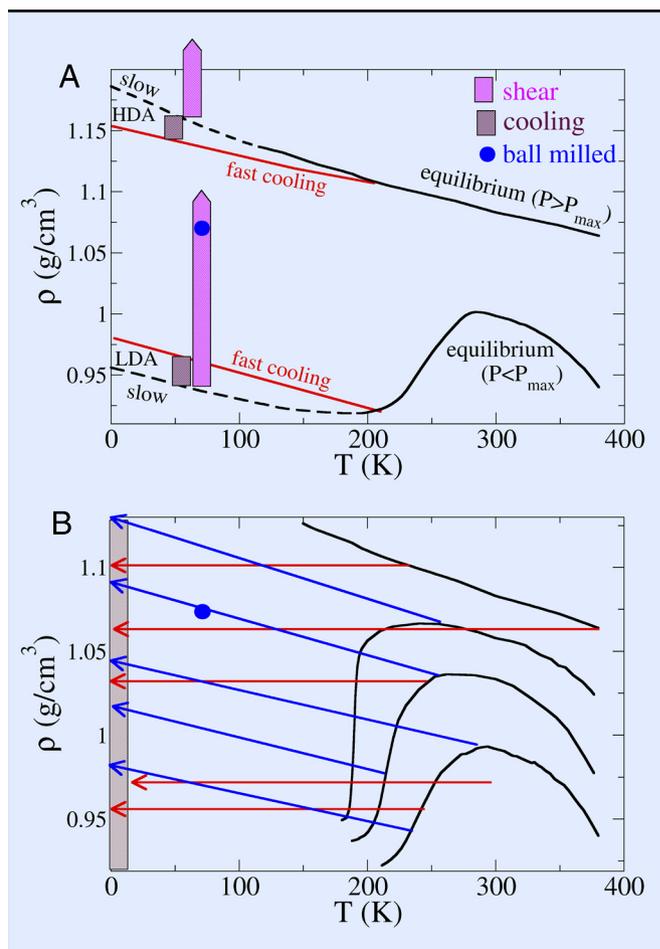
also on shear. This is something quite appealing from a theoretical point of view, and it calls for a theoretical attempt to reproduce the numerical findings.

The authors also demonstrated that at constant temperature (77 K, in the numerical study), the density of the sample increases with shear. At low pressures, where the unsheared sample is in the LDA configuration, shear progressively generates glasses with higher and higher densities, covering the interval between  $\rho_{LDA}$  and  $\rho_{HDA}$ . Also at high pressures, where the unsheared sample is in the HDA configuration, shear increases the density above  $\rho_{HDA}$  (see violet bars in Fig. 1).

Such an increase contrasts with the density changes observed on constant pressure cooling. This ties into one of water's well-known anomalies: its isobaric density maximum (at  $T = 4^\circ\text{C}$  under ambient pressure). This maximum persists at pressures up to  $P_{\text{max}}$  [estimated at  $\approx 150$  MPa (15)]. Fig. 1A shows schematically the temperature dependence of the liquid density for both  $P < P_{\text{max}}$  and  $P > P_{\text{max}}$ . The figure shows the density resulting from a cooling process with the cooling rates achievable in the laboratory, highlighting that experimentally only a limited range of glass densities are accessible (brown bars in Fig. 1A). Interestingly, due to the different behavior of the density with temperature, for  $P < P_{\text{max}}$ , shear generates glasses in a wider density range than those experimentally sampled by cooling. Instead, for  $P > P_{\text{max}}$ , shear and cooling sample different density regions. Consequently, some states in the density-pressure plane can be accessed only through constant-pressure cooling, others only through shearing, and some via both methods (1). Fig. 1A also shows the expected value of the pressurized ball milling density, located in the region of densities accessible only to shear, suggesting that a glass with comparable density can not be generated with present-day experimental techniques via a constant-pressure cooling process.

The study also analyzes glasses formed by shear with those formed by cooling in regions where both methods are viable. At equal pressure, density, and temperature, glasses formed under moderate shear resemble those formed by cooling, sharing structure, aging dynamics, and enthalpy. One may have expected that shearing introduces always some anisotropy in the material, not to mention changes in the local fluctuation of the enthalpy, density, local coordination, and quantities controlling the behavior of response functions. If such effects are relevant, they perhaps show up at higher shear rates, where the correspondence between sheared and cooled glasses breaks down. These important findings suggest that moderate shear could generate glasses equivalent to those produced by cooling at experimentally inaccessible rates. For instance, shear rates of  $10^8 \text{ s}^{-1}$ —possibly achievable with ultrafast acoustic waves (16)—could perhaps produce glasses with structures typical of water at or near room temperature.

The strength of shear lies in its ability to form a reproducible and unique stationary state, regardless of the starting sample. In contrast, glasses formed through cooling are heavily influenced by the cooling protocol and the amount of aging, resulting sometimes in a material which can be unrelated to any liquid state. Only with infinite cooling rates—where the liquid structure remains unchanged during the



**Fig. 1.** (A) Schematic representation of the temperature dependence of the density along a constant pressure path for pressures where a density maximum exists ( $P < P_{\text{max}}$ ) and where it does not ( $P > P_{\text{max}}$ ). The black curves indicate the density dependence measured in equilibrium (continuous line) and the predicted behavior for an experimentally attainable slow cooling rate (dashed-line). The red line indicates the  $T$  dependence of the density for an experimentally attainable fast cooling. While for  $P < P_{\text{max}}$  the density at low  $T$  is larger for faster quenches, the opposite behavior is observed for  $P > P_{\text{max}}$ . Glasses produced by cooling are confined in the region of densities indicated by the brown area. Shear increases always the density with respect to the slow cooling value at the same pressure, offering the possibility to explore the violet-colored range of densities. In the presence of a density maximum, shear expands the range of densities compared to cooling. For  $P > P_{\text{max}}$ , shear and cooling sample different density windows. The blue circle indicates the density of the ball-milled sample, located in the region of densities accessed only by shear. (B) Multitude of glasses generated with infinite cooling rate, in the potential energy (constant volume, red arrows) and in the enthalpy (constant pressure, blue arrows) landscape framework. The black curves indicate the equilibrium equation of state (density vs. temperature) at four different pressures (from *Bottom to Top*: ambient, intermediate, liquid-liquid critical point, large). The dashed brown area indicates that inherent structure glasses with all relevant densities can be generated by an instantaneous quench, providing a connection between the resulting glass and the equilibrium starting state point.

cooling process—can a glass be uniquely associated with its liquid precursor. This concept, first introduced by Frank Stillinger (12), forms the foundation of a thermodynamic framework based on the potential energy landscape (PEL) or its constant-pressure equivalent, the enthalpy landscape (HL). While this theoretical framework has primarily been explored through numerical simulations, recent innovative experimental studies have attempted to implement the landscape ideas revealing a continuity between the liquid

phase and LDA at ambient pressure (17–19). In simulations, infinite cooling rates can be modeled by subjecting an equilibrium liquid configuration to a steepest descent path in the PEL or HL, effectively bringing the liquid to its inherent structure (12, 20). In the constant-volume minimization, the resulting glass retains the same density as the liquid precursor and can exist at any density sampled by the liquid.

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In contrast, in the enthalpy minimization, the glass retains the same pressure as the parent liquid, with its density increasing to compensate primarily for the loss of entropic pressure (the ideal gas contribution, proportional to temperature). Fig. 1B illustrates constant-volume and

constant-pressure instantaneous quenches starting from various equilibrium state points. While these instantaneous quenches are beyond experimental feasibility, they can be generated computationally. This suggests that glasses linked to equilibrium liquid states with densities close to that of ball-milled glass could be conceptually similar to inherent structures calculated with constant-volume and constant-pressure minimization, if starting from temperatures well above the liquid–liquid critical temperature, raising the possibility that the ball-milled glass does belong to the family of liquid-derived glasses (21). Whether this multitude of glasses—generated by infinitely fast cooling—includes the ball-milled amorphous ice (and other sheared glasses) remains an open question. This intriguing possibility is sure to inspire further research.

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