Theory of amorphous ices

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We derive a phase diagram for amorphous solids and liquid supercooled water and explain why the amorphous solids of water exist in several different forms. Application of large-deviation theory allows us to prepare such phases in computer simulations. Along with nonequilibrium transitions between the ergodic liquid and two distinct amorphous solids, we establish coexistence between these two amorphous solids. The phase diagram we predict includes a nonequilibrium triple point where two amorphous phases and the liquid coexist. Whereas the amorphous solids are long-lived and slowly aging glasses, their melting can lead quickly to the formation of crystalline ice. Further, melting of the higher density amorphous solid at low pressures takes place in steps, transitioning to the lower-density glass before accessing a nonequilibrium liquid from which ice coarsens.

Phenomenology

Amorphous ices are nonequilibrium, low-temperature phases of water (1-3). These phases lack long-range order and their properties are fundamentally dependent on the protocols by which they are prepared (4, 5). They are molecular glasses that exhibit a variety of reproducible behaviors, including transitions between different amorphous states. This paper provides quantitative analysis and numerical simulation of this polymorphism and predicts a nonequilibrium phase diagram, offering explanations of previous experimental observations (1, 3, 6-9) and possibly guiding future experiments on supercooled water.

Our treatment can be applied generally in many cases where there is interest in comparing phase behaviors of nonequilibrium glasses with those of equilibrium liquids and crystals. For water in particular, however, our results bear on whether observed nonequilibrium polymorphism can be interpreted as evidence of more than one distinct liquid phase of water. It is a topic of current interest and controversy. There are no direct measurements of two-liquid behavior in water, but the low-temperature critical point that would accompany such behavior has been offered as an explanation for unusual properties of liquid water, such as maxima in various response functions (4, 10), and molecular simulation results are often cited as supporting this theoretical idea, e.g., refs. 11-14. However, water anomalies can be explained with models for which there is demonstrably only one liquid phase (15), and seemingly rigorous equilibrium analysis of various simulation models argues against cold water exhibiting the existence of two distinct liquids (16, 17). Rather, it seems that an illusion of two-liquid behavior in simulation coincides with coarsening of ice, and this paper shows how arresting those fluctuations yields a multitude of nonequilibrium amorphous solids.

Significance

Glassy water is abundant, occurring in such varied circumstances as thin films condensed on interstellar dust particles and as hosts to hyperquenched protein crystals. Yet quantitative understanding of this class of materials is limited, hampered by lack of formalism needed to systematically treat long time scales and far-from-equilibrium behaviors. Here, we describe a theory to overcome some of this difficulty and apply the theory with simulation to establish the existence of distinct amorphous ices and coexistence between them. This advance allows systematic treatment of dynamics interconverting and melting these non-equilibrium solids, and thereby provides principled explanations of experiments that have probed these processes.
transitions observed in experiments (1, 8, 9) and in nonequilibrium relaxation simulations of the mW model. (b) The mean reduced density ($\rho_\ell$) as a function of nonequilibrium control parameters computed for the mW model with the s ensemble near the nonequilibrium triple point. (c) Van Hove self-correlation functions for the three phases at the liquid's principal wave vector $k$, all computed for the mW model at conditions near the nonequilibrium triple point. (D–F) Snapshots from simulations, where a bond connecting molecular centers $i$ and $j$ is colored according to the value of $\eta_{ijk}$ averaged over a second neighbor $k$ (the quantity $\eta_{ijk}$ being defined below in Distinct Phases and Coexistence). The bond is red if this value is less than 0.1; otherwise, it is blue. A typical configuration of LDA ice is pictured in D, that of a domain of LDA ice in coexistence with HDA ice is in E, and that of HDA is in F.

transition (“excitations” are defined precisely in the next section). Aging or structural relaxation occurs through coupling excitations; the closer the excitations the more frequent the coupling. In the liquid, $T > T_p$, the distribution of lengths between excitations is exponential, like that of an uncorrelated gas of particles. Dynamics in that case takes place hierarchically, with the fastest and slowest time scales dictated by the domains with smallest and largest $\ell$, respectively. By contrast, in the glass, $T < T_g$, the distribution of $\ell$ is nonexponential and has a pair correlation function $c(\ell)$ that is most probable at a domain length $\ell_m$, and there is a single activation energy associated with that domain length. As $T_g$ decreases with decreasing cooling rate, $\ell_m$ grows, and a larger length implies a greater stability of the glass. In particular, the glass formed with a specific $\ell_m$ can be cooled far below its $T_g$, and when it is then heated slowly, it loses its stability at an apparent glass transition temperature $T_m$, where $T_m < T_g$. The difference $T_g - T_m$ grows as $\ell_m$ decreases (or equivalently, as $\nu$ increases) (23).

The distinction between $T_g$ and $T_m$ is important for water precisely because rapid cooling is required to avoid crystallization of that material. We illustrate the behavior for water in Fig. 1A. The cooling rate required to produce $\ell_m \approx 1.5$ nm would require an even slower $\nu \approx 0.1$ K/s. A procedure other than straightforward cooling would be needed to produce amorphous solids of water with $\ell_m \approx 5$ or 10 nm.

The dependence of $T_g$ and $T_m$ upon $\nu$ emphasizes that these temperatures are nonequilibrium properties, and their projections onto a $p$–$T$ plane depend implicitly upon the protocol by which the system is driven from nonequilibrium. The distinction between $T_g$ and $T_m$ has been noted by Yue and Angell (24), but without the connection to $\ell_m$. Formulas with this connection predict the dashed and dotted lines in Fig. 1A. They are derived elsewhere (22, 23) and summarized in SI Text. The formulas allow us to interpret phenomena that have been observed experimentally, and they allow us to anticipate phenomena examined later in this paper.

To begin, notice that $T_g$ and $T_m$ are nonmonotonic functions of pressure. This variation reflects the nonmonotonic variation of the onset temperature, which in turn reflects a well-known fact about water: at low pressures, transformations of liquid water to more ordered states (whether to ice or to supercooled liquid) occur with decreases in density, whereas at high pressures they occur with increases in density. A line passing through the locus of minima in $T_g$ partitions the high- and low-pressure regimes in Fig. 1A. As the local structure of the high-density amorphous (HDA) region is necessarily distinct from that of the low-density amorphous (LDA) region, there is a possibility of a nonequilibrium transition between the two. This transition occurs in the vicinity of the line separating LDA and HDA regions in Fig. 1A. Indeed, as noted by the circles in that figure, an HDA–LDA transition is observed experimentally close to that line. The transition cannot persist into the liquid because fluctuations in the liquid remove long-lived distinction between the two (17, 25). Determining the nature of the transition and its end point requires further analysis, which we will get to soon.

Also notice in Fig. 1A that HDA glass with rather small $\ell_m$ has been produced experimentally. Through cycles of changing $T$ and $p$, or by other means (6, 9, 26), the stability of that material can be enhanced, possibly producing a material with $\ell_m \approx 1.5$ or 2 nm. In that case $T_m < 130$ K. Such a material could be cooled to a very low temperature and depressurized, but still with the high-density structure and nonequilibrium length locked in. From Fig. 1A we see that subsequent warming would then cause a transition at a temperature close to $T_m$, at which point, given its pressure and temperature, the destabilized HDA will transform to LDA in cases where $T_m$ of LDA is higher than that of HDA. Further warming will then melt LDA followed by rapid crystallization. Indeed, a version of this predictable multistep process has been observed experimentally (9). SI Text illustrates this behavior with simulation trajectories made possible from our numerical preparation of HDA and LDA, and it further discusses this interpretation of the experiments.

**Preparations of Amorphous Ices with the s Ensemble**

As noted, amorphous ices (or any other glass) have structures distinct from those of an equilibrium liquid, distinct in the way excitations are distributed (22). Preparation of amorphous ices in the laboratory can take microseconds to minutes to even hours. This range of time scales required by experiment is inaccessible by straightforward molecular simulation. Nevertheless, it is possible...
to produce robust immobile amorphous states in a computer simulation. It is done through an importance sampling that focuses on relevant parts of trajectory space. The procedure is a non-equilibrium version of large-deviation formalism (28). Such an approach has been successful in simulating stable glasses of simple-liquid mixtures (29–32). We adapt that approach here with one additional feature: while using a dynamical order parameter to highlight noncrystalline amorphous states, as has been done before, we use a second-order parameter that distinguishes nonequilibrium amorphous states of different densities. Both order parameters are functions of path, as required to characterize nonequilibrium phases.

The order parameter we use to measure mobility is the total number of enduring displacements (EDs) occurring in an N-particle system during a trajectory of length $t_{obs}$ (30). Other functions of system history could also be used (29, 31, 32). An ED occurs when a particle jumps from one position to another, and it sticks for a significant period in the new position (33). Such motions manifest the elementary excitations in a structural glass former (34). They occur intermittently, and when one such event occurs, it takes on average $\Delta t$ to complete. This instanton time, $\Delta t$, is much smaller than the structural relaxation time of a glass-forming melt. Structural relaxation follows from coordinated motions of a large number of elementary excitations (34).

The number of EDs per particle per unit time is

$$\dot{c}[t] = \frac{\Delta t}{N t_{obs}} \sum_{i=1}^N \sum_{\Delta \tau = \Delta t} \Theta\left[\hat{\mathbf{r}}_i(t) - \mathbf{r}_i(t - \Delta t) - \sigma \right],$$

where $\mathbf{x}(t)$ stands for the trajectory of the system, $\sigma$ is the displacement length (a fraction of a molecular diameter), $\Theta(x)$ is the unit Heaviside function, and $\hat{\mathbf{r}}_i(t)$ is the position of molecule $i$, averaged over the time interval $t - \Delta t/2$ to $t + \Delta t/2$. The averages over $\Delta t$ coarse-grains out nonenduring vibrations. Applying the prescriptions of ref. 34 to models of water gives $\Delta t$ as approximately the structural relaxation time at normal liquid conditions, and $\Delta t$ an order of magnitude smaller. For the calculations illustrated below, we use $\Delta t = 1$ ps and $\Delta t = 0.1$ ps. Other choices for $\Delta t$ and $\Delta t$ yield consistent results.

The second-order parameter we use is a dimensionless measure of density history. For constant pressure and fixed $N$, it can be expressed in terms of the system’s instantaneous density, $\rho(t)$:

$$\hat{\rho}[t] = \frac{\Delta t}{N t_{obs}} \max_{\rho(t)} \sum_{\Delta \tau = \Delta t} \rho(t - \Delta t) - \rho_{\text{ini}}$$

where $\rho_{\text{ini}}$ and $\rho_{\text{ini}}$ are the average densities of the equilibrium liquid and crystal, respectively, at a particular thermodynamic state.

These order parameters have associated fields, which render the spatial patterns associated with distinct phases and interfaces. The interexcitation lengths $t$ and $t_{obs}$ characterize the patterns of the excitation field in the liquid and glass, respectively.

The relevant equilibrium probability distribution function is

$$P(c, \rho) = \langle \delta(c - c[\mathbf{x}]) \delta(\rho - \rho[\mathbf{x}]) \rangle_{\lambda},$$

where $\delta(x)$ is Dirac’s delta function and the subscripts angle brackets $\langle \rangle_{\lambda}$ denote equilibrium average over trajectories that include amorphous microstates only. Such microstates have small values of the Steinhardt–Nelson–Ronchetti $Q_6$ parameter (35). This parameter is finite for crystalline ice states and vanishes as $O(1/\sqrt{N})$ for amorphous states. It is therefore possible to identify reasonable ranges of $Q_6$ values that discriminate between amorphous and crystalline states of water. The amorphous equilibrium distribution functional is

$$P(c[\mathbf{x}]) \propto p_{\text{eq}}[\mathbf{x}] \prod_{i} \Theta\left[Q_{6i} - Q_{6c}(c_i)\right]$$

where $p_{\text{eq}}[\mathbf{x}]$ is the unconstrained trajectory distribution, and $Q_{6c}$ is the crystalline order parameter for the system configuration at the $r$th time interval. We have checked that in the region of the equilibrium phase diagram where our calculations are performed that our results are insensitive to a cutoff $Q_6$, to the extent that it is large enough to encompass typical liquid fluctuations and small enough to exclude crystal formation (i.e., for an $N = 216$ particle system, the acceptable range is $0.1 < Q_6 < 0.18$). See ref. 16.

Conditioned as it is to sample only amorphous states, $P(c, \rho)$ is unimodal, with the most probable region near the average values of $c$ and $\rho$ for the liquid. The distribution, however, exhibits fat tails at the low values of $c$ typical of glass. These tails (i.e., large deviations) can be stabilized with nonequilibrium fields that couple to $c[\mathbf{x}(t)]$ and $\rho[\mathbf{x}(t)]$. Specifically, with the fields $s$ and $\lambda$, the equilibrium distribution of trajectories $P(t)$ is reweighted to

$$P_{s,\lambda}[t] \propto P(t) e^{-[(\delta(c - \delta(c_0))]_{\lambda}}$$

for which the nonequilibrium order-parameter distribution is

$$P_{s,\lambda}(c, \rho) \propto P(c, \rho) e^{-[(\delta(c - \delta(c_0))]_{\lambda}}$$

Positive values of $s$ favor low-mobility (i.e., glassy) states, and positive values of $\lambda$ favor high-density states.

We have applied these equations to the mW model of water (36). The reference temperature and pressure of the mW model are $T_0 = 250$ K and $p_0 = 1$ bar, respectively. The mW model is the simplest of atomistic models to exhibit reversible thermodynamics, freezing, and relaxation of water (16, 18, 19, 36, 37). That it also faithfully exhibits transitions to and from glass, as we detail, is evidence that the model contains essential features underlying the physical properties of water both in and out of equilibrium.

Our trajectories fix the number of molecules, $N$, the pressure, $p$, and the temperature $T$. The system is evolved over a time $\Delta t$ with a Nosé–Hoover barostat (38). At every $\Delta t$, all $N$-particle momenta are randomized, and this process is repeated up to a trajectory of length $t_{obs}$. We typically use $N = 216$ and $t_{obs}$ to be 10 to 400 times the structural relaxation time of the reversible melt. The nonequilibrium distribution for these trajectories, Eq. 4, is then sampled using transition path sampling (39). Ref. 30 provides an illustration of such a calculation for a supercooled simple-liquid mixture, but without the extra field $s$. The field $\lambda$ has a thermodynamic meaning, like a chemical potential, but affecting a time-averaged density rather than an instantaneous density. In contrast, $s$ has a dynamical meaning, essentially the rate at which EDs are suppressed (40).

Although this protocol overcomes huge time scales associated with glass transitions (41), the calculations are nevertheless time-consuming. As such, we have considered limited size systems, large enough to exhibit clear signatures of glass transitions but not larger. The side length of a simulation box with $N = 216$ is slightly larger than $6\sigma$, where $\sigma$ is a molecular diameter. That side length is large compared with the equilibrium correlation length of the homogeneous liquid, which is about $s$ or smaller. However, $6\sigma$ can be small compared with nonequilibrium lengths that characterize robust glasses. Prior work (29, 30) has found that anomalous responses of glass transitions begin to disappear from simulations when system sizes are decreased below 200 particles. With $N \approx 200$, the stability of glasses we produce is limited to $r_{obs} \approx 6\sigma = 1.5$ nm (41).

**Distinct Phases and Coexistence**

The nonequilibrium phase behavior we find in this way is illustrated in Figs. 1 and 2. We find three distinct amorphous phases: one ergodic liquid and two glasses. For a finite $t_{obs}$ with fixed $p$ and $T$, anomalous responses consistent with first-order transitions occur at specific values of $s$ and $\lambda$, which we label as $s^*$ and $\lambda^*$, respectively. Glasses formed at the higher temperatures require higher $s$ and are thus intrinsically less stable than those formed at lower $T$ with lower $s$. The amorphous solid regions end where no value of $s$ can stabilize a glass distinct from the liquid. That region cannot extend above $T_c$.
The first-order characters of the glass transitions are manifested by precipitous changes in density and mobility that tend to discontinuities as $N_{\text{coh}} \to \infty$. Transitions between the two amorphous solids are illustrated in Fig. 1B, and transitions between the amorphous solids and the liquid in Fig. 2B. Consistent with experiments on salty water (42), our coexistence line between the amorphous solids and the liquid in Fig. 2, and transitions between LDA and HDA (3). The predicted density differences between LDA, HDA, and liquid are also consistent with experiments for the alternative solid. (22, 45). Notice from the plateau values of $F(k,t)$ that fluctuations in molecular positions in HDA are larger than those in LDA. This juxtaposition predicted from our simulations is consistent with experiment (46).

The structure of the LDA glass is locally tetrahedral, as illustrated by the typical configuration shown in Fig. 1D. The LDA basin has the same density as the crystalline phase, ordinary ice Ih, consistent with experimentally prepared LDA ices (4). The local order is quantified with $\eta_{ij} = (u_{ij} \cdot u_{ijk} + 1/3)^2$, where $u_{ij}$ and $u_{ijk}$ are the unit vectors pointing between a tagged molecule $i$ to a pair of nearest neighbors $j$ and $k$, respectively. For the LDA phase we have stabilized with the $s$ ensemble, $(\eta_{ij})_{\lambda} \approx 0.05$. In comparison, for the liquid and the HDA phase, $(\eta_{ij})_{\lambda} \approx 0.2$.

HDA ice rendered in Fig. 1F has an average structure similar to that of high-pressure liquid water (44). Our computed radial distribution functions for these phases are shown in Fig. 3. The structures of the liquid and glass phases differ in the fluctuations from the average. Spatial arrangements of excitations are uncorrelated in the liquid, but are anticorrelated with a large correlation length in a glass (22). This difference is most evident in the dynamics, Fig. 1C, because the anticorrelation arrests mobility (22, 45). Notice from the plateau values of $F(k,t)$ that fluctuations in molecular positions in HDA are larger than those in LDA. This juxtaposition predicted from our simulations is consistent with experiment (46).

Fig. 2. Nonequilibrium distributions for mobility $c$, reduced density $\rho$, and the susceptibility $\chi(s)$ for cold water. (A) $-\ln P_{\lambda}(c,\rho)$ calculated with the mW model for $t_{\text{obs}} = 300\Delta t$, $s = s^*$, and $\lambda = 0$ at the state point $T/T_0 = 0.8$, $p/p_o = 1$. (B) Mean mobility and susceptibility calculated at the state point in A for different trajectory lengths, $t_{\text{obs}}$, illustrating scaling consistent with a first-order phase transition in trajectory space. The susceptibility peaks at nonequilibrium coexistence, $s = s^*$, and $\lambda = \lambda^*$, and $t_{\text{obs}} = 200\Delta t$ at the state point $T/T_0 = 0.75$, $p/p_o = 10^4$. (D) Marginal distribution functions of $\rho$ calculated for LDA–HDA coexistence at the state point in C. Shading indicates error estimates of 1 SD. Contours are spaced by unity, and the coloring is a guide to the eye.

Fig. 3. Relaxation behavior of amorphous ices produced with the $s$ ensemble. (A, Left) Average potential energy per particle, in units of $T_0$, as a function of time for the mW model prepared in an ensemble at $s > s^*$, $T/T_0 = 0.8$, $p/p_o = 0$, and $t_{\text{obs}} = 200\Delta t$ and evolved with $s = 0$, $T/T_0 = 0.76$, $p/p_o = 0$. The dashed black line is an exponential function with characteristic time, $200\Delta t$. (A, Right) Average pair distribution functions at two indicated points in time. Faint lines show the $g(r)$ for the alternative solid. (B, Left) Average reduced density as a function of time for the mW model prepared in an ensemble at $s > s^*$, $T/T_0 = 0.76$, $p/p_o = 2 \times 10^4$, and $t_{\text{obs}} = 200\Delta t$ and evolved with $s = 0$, $T/T_0 = 0.6$, $p/p_o = 5 \times 10^4$. (B, Right) Average pair distribution functions at two indicated points in time. Faint lines show the $g(r)$ for the alternative solid.
The marginal distribution of $c$, $\int d\rho P_\rho(c,\rho)$, has mean value $\langle c \rangle$, and its variance gives the susceptibility, $\chi(s) = -(\partial^2 \langle c \rangle / \partial s^2) = N_{\text{obs}} \left( \langle c - \langle \rangle \rangle^2 \right)$. In the thermodynamic limit, $\langle c \rangle$ and $\chi(s)$ are singular functions at the point of a glass transition, $s = s^*$. In simulations, the development of this singular behavior can be detected from system-size dependence. Specifically, for a first-order transition, the width of the change in $\langle c \rangle$ around $s = s^*$ should decrease proportionally to $1/N_{\text{obs}}$ and the height of $\chi(s)$ at $s = s^*$ should grow proportionally to $N_{\text{obs}}$. This scaling with respect to space–time volume is exhibited by the functions graphed in Fig. 2B. Similarly, at coexistence, the free-energy barrier between the two stable basins should grow proportionally to space–time surface area, $(N_{\text{obs}})^{3/4}$. This scaling is consistent with the growth exhibited in Fig. 2D, although a compelling demonstration is beyond the scope of the small system size and statistics we are able to treat. Also, as space and time obey different symmetries, finite size scaling may depend on other combinations of $N$ and $t_{\text{obs}}$. See, for example, analogous issues in theory of quantum phase transitions (47).

**Melting and Transitioning Between Amorphous Solids**

Having prepared glassy configurations with the $s$ ensemble, we can now study two experimental observations. The first is the nonmonotonic thermal responses found when heating LDA. The material first takes on heat, then it precipitously releases heat and crystallizes (1, 6). The experimental LDA coincides with the LDA that is first prepared with the $s$ ensemble at some temperature $T < T_c$ and then cooled to a lower temperature where it remains stable for essentially all time. Melting LDA occurs when that low temperature is increased, a process that can be simulated by simply turning off $s$ at the initial preparation temperature.

Results of such simulations are shown in Fig. 3A. The non-equilibrium average potential energy per molecule in units of $T_{\text{eq}}$ $\pi(t)$, is computed by averaging over 1,000 independent trajectories initiated from configurations taken from the ensemble of inactive states. With $s = 0$, these amorphous solid states are thermodynamically unstable. The stable basin is the crystal, but that basin cannot be accessed without reorganization, and reorganization requires access to ergodic liquid states. The inactive glassy states are at a low potential energy state relative to the supercooled liquid. Upon instantaneously turning off the $s$ field, the system remains immobile for a relatively long time, on average about $t = 20\lambda t_0$. This waiting time corresponds to the time for a rare fluctuation to produce an excitation. Once this reorganization begins, the system immediately begins to crystallize, and by $t = 1,000\Delta t$ on average the system has begun releasing energy as long-ranged order builds up. Fig. 3A (Right) shows the average radial distribution functions $g(r)$ for the beginning and end of the trajectory. Initially, the radial distribution function shows the local order characteristic of LDA, indicated by the separation between the first and second solvation shell (48). At the end of the trajectory, this local ordering has developed into a long-ranged ordered crystal, as indicated by the splitting of the second solvation shell and the persistent correlations at large separations.

The second experimental observation we consider is the finding of an abrupt transition from HDA to LDA when HDA is quenched to lower pressures keeping temperature low (3). This process can be simulated by initiating trajectories at configurations from an immobile HDA basin, prepared with $s > s^*$ and $p/p_{\text{eq}} > 10^4$, and running these trajectories with $s = 0$ and $p/p_{\text{eq}} < 10^4$. Fig. 3B shows the result from averaging over 1,000 such trajectories. The average waiting time to transition across the HDA–LDA boundary is only $10\Delta t$, reflecting that only relatively small reorganization is required for transitioning between these two amorphous phases. The excess free energy due to the change in pressure is dissipated through an average concentration of mobility $c$ that is only $0.02$. After the initial burst of excitation, the system monotonically relaxes into the LDA state. Initially, the structure reflects the HDA configurations where the dynamics were initialized, whereas at later times the structure adopts the open local order of LDA. Other illustrations of behaviors deduced from our preparations of amorphous ices are given in SI Text. For example, reversal and hysteresis of the process illustrated in Fig. 3B is shown, demonstrating that the glassy states prepared in our simulations are robust. To our knowledge, no prior simulations of low-temperature water have achieved this quality.

**Conclusions**

The most important and general results of this work are twofold: the demonstration that it is possible with molecular simulation to systematically prepare and predict properties and transitions of experimentally realizable amorphous solids, and the demonstration of analytical theory that can predict and interpret various behaviors of these materials. We illustrate here for water predictions and simulations of LDA–HDA transitions at conditions consistent with experimental observations; we also present the predictions of density differences between LDA, HDA, and ergodic liquid phases in accord with experimental observations; and finally, we present predictions of pathways by which HDA and LDA phases melt, again in accord with experimental observations.

Much has been written suggesting that the HDA–LDA transition might reflect a transition between two distinct phases of liquid water, e.g., refs. 2–5, 10, 49. This extrapolation from glass to liquid seems difficult to justify in light of the singularity that separates the nonequilibrium amorphous solids from the ergodic liquid. Occurring as they do through driving a material out of equilibrium over a finite period, the space–time transition is precipitous but not discontinuous. Nevertheless, a singularity underlies the phenomena. This fact about glass physics may have its first experimental demonstration in ref. 42, where coexistence lines for reversible transitions between different glasses of salty water are established and shown not to extend above the line of glass transition temperatures.

That particular experimental work finds more than one coexistence line separating distinct amorphous phases. Our discussion of phenomenology emphasizes that any one material can exhibit a range of glass behaviors reflecting a range of values of $t_{\text{eq}}$. How this variability can translate in general into distinct nonequilibrium phases is not yet known, and the answer is likely system dependent. For example, distinct amorphous phases seem generally possible in cases of a poor glass-forming liquid, as it is for water, because coarsening of crystal phases of one density can compete with vitrification of the liquid of another density. Whether other competing effects can be imagined and realized experimentally is an open question.

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Super-Arrhenius relaxation is associated with underlying hierarchical dynamics, where relaxation depends upon the size of relaxing domains. This dependence is responsible for a glass transition when the material is cooled at a rate \( \nu \). Specifically, the system transitions from ergodic to nonergodic behavior at a temperature \( T_g \), where

\[
1/\nu = |d\tau/dT|_{T_g},
\]

below which \( \tau(T) \) is locked at its nonequilibrium value \( \tau_{\text{eq}} = \tau(T_g) \). Therefore

\[
1 = 2 \nu \tau_{\text{MF}} \frac{\beta_g}{d_i} \exp\left(\frac{\gamma \sigma}{d_i}\right),
\]

where

\[
\beta_g = J_o(p) \left[ \frac{1}{T_g(p)} - 1/T_o(p) \right] = d_i \ln(\tau_{\text{eq}}/\sigma),
\]

or

\[
\frac{1}{T_g(p)} = \frac{1}{T_o(p)} + \frac{d_i}{J_o(p)} \ln(\tau_{\text{eq}}/\sigma).\]

Eq. S6 gives the dashed lines in Fig. 1A.

An approximate solution to the transcendental Eq. S4 is useful when \( T_o \) and \( T_g \) are of the same order and \( \beta_g / d_i \gg \ln(\beta_g / d_i) \). In that case

\[
\ln(\tau_{\text{eq}}/\sigma) \approx \sqrt{-\ln\left[2 \nu \tau_{\text{MF}} \gamma J_o(p) / T_o(p) \right] / d_i \gamma}. \tag{S7}
\]

This solution can serve as the first guess to the numerical solution, the first guess differing from the numerical solution for water by a few percent.

Because \( \tau(T) = \tau_{\text{eq}} \) for all \( T < T_g \), the relaxation time \( \tau \), Eq. S2, is Arrhenius for that regime. If the glass with its fixed \( \tau_{\text{eq}} \) is cooled to a very low temperature, and then warmed on a time scale of \( \tau_w \), it will undergo a transition at an apparent glass transition temperature \( T_{ag} \), where \( \tau_w = \tau_{\text{MF}} \exp(\beta_{ag} \gamma / \sigma) \).

Accordingly,

\[
\frac{1}{T_{ag}(p)} = \frac{1}{T_o(p)} + \frac{\ln(\tau_w / \tau_{\text{MF}})}{J_o(p) \ln(\tau_{\text{eq}} / \sigma)}. \tag{S8}
\]

Eq. S8 yields the dotted lines in Fig. 1A, with \( T_{ag}(p) \) evaluated for a warming-time scale of minutes, i.e., \( \tau_w \approx 10^2 \text{ s} \approx 10^{14} \tau_{\text{MF}} \).

Application of these formulas requires \( T_o(p), J_o(p), \) and \( \tau_{\text{MF}} \). The low-pressure forms have been determined previously (5). High-pressure behaviors have been determined similarly. Fig. 1A shows the behavior of \( T_o(p) \), and its form is well approximated by a spline,

\[
T_o(p)/T_o = -0.015 \log(p/p_o) + 0.976, \quad 0 < p/p_o < 5 \times 10^3
\]

\[= 0.199 \log^2(p/p_o) - 1.344 \log(p/p_o), \quad 5 \times 10^3 < p/p_o < 2 \times 10^3\]

\[= 0.173(\log^2(p/p_o) - 1.078 \log(p/p_o) + 2.521, \quad 2 \times 10^3 < p/p_o < 8 \times 10^4. \tag{S9}
\]

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**Fig. S1.** Reduced energy scale \( J_o(p) / T_o(p) \) as a function of pressure. Circles are results computed with the mW model following methods detailed in refs. 1 and 2. Corresponding states analysis (3) indicates that these results should hold for all reasonable models of water as well as for the actual substance. The solid line is the spline fit to the data.
Table S1. Nonequilibrium length, time, and energy scales for LDA ice at ambient pressure

<table>
<thead>
<tr>
<th>$\ell_{eq}$/nm</th>
<th>$v$/K s$^{-1}$</th>
<th>$\tau_\sigma$/s</th>
<th>$T_\sigma/T_0$</th>
<th>$T_{ag}/T_0$</th>
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<tr>
<td>10.0</td>
<td>0.1</td>
<td>$10^2$</td>
<td>0.65</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Fig. S1 shows the behavior of $J_0(p)/T_0(p)$, and its form is well approximated by a spline,

$$
J_0(p)/T_0(p) = 22.5, \quad 0 < p/p_0 < 2 \times 10^2
$$

$$
= -3.9 \log(p/p_0) - 2.7 \times 10^2 + 1.8 \log(p/p_0),
$$

$$
+ 18.1, \quad 2 \times 10^2 < p/p_0 < 1.2 \times 10^4
$$

$$
= 6.0 \log(p/p_0) - 5.1 \times 10^4 + 0.5 \log(p/p_0)
$$

$$
+ 6.8, \quad 1.2 \times 10^4 < p/p_0 < 8 \times 10^5. \quad [S10]
$$

Table S1 illustrates predictions of these formulas applied to water at ambient conditions, computing $T_{ag}$ with the warming-time scale of minutes, i.e., $\tau_w = 10^2$ s.

**Dynamics of Transformations of Amorphous Ices.** In this section we provide a few more examples of dynamics that follow from our simulated high-density amorphous (HDA) and low-density amorphous (LDA) phases.

The first example focuses on the reversibility of pressurizing and depressurizing the amorphous ices to transition between HDA and LDA. The nature of these processes is illustrated in Fig. S2. Specifically, configurations taken from the HDA basin prepared and LDA. The nature of these processes is illustrated in Fig. S2. The ability to reverse the HDA to LDA transition demonstrates that the materials produced by the $s$ ensemble are robust solids.

The second example considers the temperature reached at two particular points in time. The time dependence of the potential energy per particle, $\varepsilon(t)$, in good agreement where the low-temperature transition where HDA transforms to LDA, and another apparent glass transition where LDA melts into a nonequilibrium liquid from which crystal ice coarsens.

We observe this behavior, as illustrated in Fig. S3, and the temperatures at which the transitions occur can be understood in terms of the equations presented in the previous section. The figure shows the results obtained from averaging 1,000 independent trajectories initiated from the HDA configurations, with a warming-time scale $\tau_w \approx 10^3 \tau_{MF}$. Eq. S8 then predicts a transition at $T_{ag} \approx 0.44 T_0$, in good agreement where the low-temperature transition is detected in the trajectories. Above that temperature, the radial distribution functions found from our simulation indicate that the resulting amorphous solid is the LDA material. In that case, the activation energy (or equivalently, the value of $J_0$) has changed from that locked in from the higher-pressure HDA material to that of the LDA material. Eq. S8 then gives $T_{ag} \approx 0.80$ for the temperature that LDA will melt, again in good agreement with the results of our trajectories.

Having gained confidence in our theoretical analysis through comparison with simulation, we now turn to the experimental observations of two-step relaxation (7). These recent experiments have found that a stabilized version of HDA brought to low temperatures and pressures exhibits a calorimetric peak at $T \approx 130$ K. By taking this value for $T_{ag}$ and applying Eq. S8 with $\tau_w = 100$ s, we conclude that $\ell_{eq} \approx 5$ nm for this version of HDA. The corresponding $T_{ag}$ for LDA can then be predicted using this.
value for \( \ell_{\text{ne}} \) together with the low-pressure LDA value for \( J_0 \). This evaluation predicts \( T_{\text{ag}} \approx 150 \text{ K} \) for the LDA material that is produced by melting the stabilized HDA. This predicted position for a second calorimetric peak is in harmony with experiment (7).

Notice that, had experimentalists not stabilized the HDA through annealing, the data shown in Fig. 1 suggest that the HDA material would have \( \ell_{\text{ne}} \approx 1.5 \text{ nm} \). In that case, \( T_{\text{ag}} \) computed from Eq. S8 for that HDA material would be \( \approx 85 \text{ K} \). Such a low value for the temperature at which the low pressure form of HDA would become unstable indicates why two-step melting was not detected without first annealing to create a more stable HDA.

Based upon indirect evidence, experimentalists have interpreted two-step melting of amorphous ices as indicative of two distinct liquid phases (7, 8). We find nothing in our simulations to support the idea. The time dependence of the excitation concentration \( \tau(t) \) shows that the material remains solid-like until reaching the apparent glass transition temperature of LDA, which with the warming rate of our simulations occurs near \( 0.8 T_0 \). In other words, some reorganization does occur to allow the transition from HDA to LDA, but the low mobility of a glass remains until ergodic states are accessed at the apparent glass transition temperature for LDA.