Solidity-induced crystallization of ultraviscous water

Jeppe C. Dyre

DNRF Centre "Glass and Time," IMFUFA (Building 27), Department of Sciences,
Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark
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Pure water is a surprisingly poor glass former at ambient pressure; crystallization is so fast that it is impossible to study the supercooled ultraviscous liquid phase. It is argued that this is a consequence of the further unusual property of water that the crystalline phase is markedly less dense than the liquid phase. This implies an effective instability of the ultraviscous liquid, where regions of high negative pressure induce crystallization via a thermodynamic driving force that is stronger than the opposite force arising from the large positive pressure regions. This effect is significantly enhanced by kinetic factors.

[Preliminary note without references]

All liquids form glasses if they are cooled rapidly enough to avoid crystallization. Glass is the amorphous state created when molecules essentially freeze at their liquid positions as the system falls out of equilibrium at the glass transition temperature T_g. A poor glass former needs rapid cooling to avoid crystallization, whereas a good glass former is characterized by low crystallization rates at all temperatures. Examples of good glass formers include the classical silicate and borate glasses, numerous organic liquids, several binary ionic salts and, nowadays, also a few metallic alloys. Most metals and alloys are poor glass formers, though, and crystallize within milliseconds in the deeply supercooled phase. This is not surprising, given the spherical nature of the metal-atom interactions which implies that the nucleation barrier is small.

Water has been studied extensively from many perspectives, including its properties below the freezing point. There is a "no-mans land" between 150 K and 230 K where supercooled water crystallizes so rapidly that its physical properties cannot be studied. This process is so fast, in fact, that some groups have suggested that there is no calorimetric T_g in the ordinary sense. In any case, deeply supercooled water is characterized by an extremely high crystallization rate. Although the water molecule is very simple, its interactions with neighboring molecules have little in common with metal-like spherical interactions, so this cannot explain why water is such a poor glass former. Rather, the strong hydrogen bonds promote network formation, and in this respect water is more like silicates or borates. Also like these high-temperature network forming liquids water has several crystal forms, a property that usually impedes crystallization. Thus by analogy water should not be an exceptionally poor glass former, but a good one. The question is why that is not the case.

Ultraviscous water must have the characteristics common to all highly viscous liquids. These liquids are characterized by relaxation times that are very long compared to typical microscopic times ($\sim 10^{-13}$s). If η is the viscosity and G_∞ the instantaneous shear modulus, the relaxation time τ is roughly given by Maxwell's relation $\tau = \eta/G_\infty$. Close to the calorimetric glass transition the viscosity approaches 10^{12} Pa s and the relaxation time becomes 100-1,000 seconds (typical values of G_∞ are in the $10^9 - 10^{10}$ Pa range). These long relaxation times are evident from measurements of, e.g., dielectric relaxation (probing molecular rotations), measurements of the frequency-dependent shear modulus (probing shear stress relaxation) or bulk modulus (probing pressure relaxation). Thus ultraviscous water has slowly relaxing stresses. As argued by Kauzmann, Goldstein, and others, any ultraviscous liquid is like a disordered solid with sudden, rare "flow events" (molecular rearrangements) taking the system from one "solid" state – potential energy minimum – to another. We shall refer to the stresses of these solid states as "frozen-in," although they are really only frozen on the short time scale and do relax on the time scale of τ. The "solid-like-ness" of ultraviscous liquids has been referred to as their solidity.

The solidity of ultraviscous liquids implies that the stress tensor is not diagonal, but has slowly relaxing off-diagonal elements of the same order of magnitude as the diagonal elements. Nevertheless, one can define the pressure p at any point via $p \equiv -\mathrm{tr}(\sigma)/3$. How large are the frozen-in pressures of ultraviscous water? We can estimate the magnitude of the pressure fluctuations from the isothermal instantaneous bulk modulus K_∞. According to the fluctuation-dissipation theorem, if the average pressure is zero, one has $K_\infty = 1/(k_B T) \int \langle p(\mathbf{0})p(\mathbf{r})\rangle d\mathbf{r}$. If the pressure correlation length is denoted by ξ, we find $K_\infty \sim \langle p^2 \rangle \xi^3/(k_B T)$. By analogy with granular media where the stresses due to the strongly anharmonic forces vary wildly from grain to grain, we expect the correlation length to be of order the average intermolecular distance a, perhaps slightly larger; thus $\langle p^2 \rangle \sim K_\infty(k_B T)/a^3$. Substituting $K_\infty \sim 3$ GPa, $a \sim 3$Å, and $T \sim 200$ K into this gives $|p| \sim 0.5$ GPa.

Water is peculiar in many respects, the most famous one being that its crystalline form is considerably less dense than the liquid phase ($\sim 10\%$). The free energy cost of creating a crystallite is $\Delta G = \Delta E + p\Delta V - T\Delta S$. At ambient pressure one usually ignores the $p\Delta V$ term because $p \sim 0$ compared to the kinetic pressure (the pressure of an ideal gas of same density). Now, the solidity of ultraviscous liquids implies that there are very large frozen-in pressures.

The fact that these average to zero at ambient laboratory pressure does not imply, however, that $\langle p\Delta V\rangle = 0$: At these large frozen-in pressures ΔV is not constant. Thus at large negative pressure $\Delta V > 0$ is significantly larger than at equally large positive pressure. The result is that $\langle p\Delta V\rangle < 0$, providing a bulk extra thermodynamic force promoting crystallization. The fact that the pressure was assumed to vary randomly in space does not affect this argument.

How large is this extra thermodynamic force? Taking the frozen-in pressure fluctuations to be of order 10^9 Pa and $\Delta V/V \sim 10\%$, the extra free energy contribution is of order $k_B T_0$ per water molecule where $T_0 \sim 100$ K. This is of the same order of magnitude as the bulk free energy difference between the liquid and crystalline phases at 200 K. This significant extra term strongly enhances the crystallization tendency by reducing the critical radius of crystal formation (beyond which growth is automatic) and by lowering the barrier at this radius.

What are the effects of this extra effective free energy term, will water spontaneously crystallize? The answer to this question we recall the well-known fact that the relaxation time of an ultraviscous liquid is always strongly pressure dependent. At large pressure the relaxation time becomes much larger; at negative pressure relaxations are much faster. At Gigapascal pressures this effect is huge. We conclude that at large negative pressure in the ultraviscous liquid phase of water the above identified extra strong thermodynamic driving force promoting crystallization is strongly enhanced.

Finally, we briefly contemplate the consequences of the above idea. The extra term is reduced as pressure increases and will be virtually absent at high pressure. Thus ultraviscous water should not crystallize spontaneously at high pressure. Indeed, this is the case (as trivially expected, of course, from the standard $p\Delta V$ term). A further consequence is that just a few percent of another chemical compound significantly stabilizes the ultraviscous phase, because the entropy of mixing of the liquid phase reduces the free energy gain by crystallizing. This is also the case experimentally (also not too surprising). – More speculatively, one might ask whether the LDA form of water is actually microcrystalline, consisting of ultra-small crystallites [cond-mat/0612671]. These would be deformed by the frozen-in pressures, making their observation by neutron or X-ray scattering difficult.

In conclusion, one unusual property of water implies another – the fact that water expands upon freezing implies that it is a much poorer glass former than expected from its network structure and several complex crystal forms.