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Glass transition dynamics in water and other tetrahedral liquids: ‘order–disorder’ transitions versus ‘normal’ glass transitions

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Abstract

We review some aspects of the confusion concerning the glass transition in water, and then show that it must be of a quite different character from that in other molecular liquids, and in fact is the kinetically controlled part of a classical order–disorder transition. (This is the conclusion reached in a review of the low temperature phenomenology of amorphous water currently being published in *Science* by the present author. Material that would normally appear in the present abbreviated paper will appear in the *Science* article to which the interested reader is referred.) We do this using a combination of (i) thermodynamic reasoning for ‘bulk’ water (based on known properties of supercooled water and nearly glassy water), and (ii) direct measurements on nanoscopic (non-crystallizing) water. Both require the heat capacity to be sharply peaked near 220 K and thus to imply the existence of a ‘strong-to-fragile’ transition during heating. Both require the excess heat capacity to drop to near-vanishing values in the vicinity of 130–150 K. The similarity to order–disorder transitions in crystalline solids is noted, the relation to the second critical point scenario for water is discussed, and the modelling of the anomaly by current theories is considered. Finally we argue that water, with its fragile-to-strong liquid transition below the melting point, links (lies in between) the extremes of classical network liquids (where this transition occurs only above the experimentally accessible range) and fragile molecular liquids, where the fragile-to-strong transition is pushed beneath the glass temperature.

There has been much confusion in the literature about the glass transition in water [1]. Some argue that it may never have been observed [2–4] while others argue, on a variety of grounds, that it lies at about 136 K [5–8]. The strongest argument for it not occurring at 136 K would seem to lie in the great difference between the behaviour of its dielectric loss, observed at 10 kHz [9], during steady heating over the temperature range 120 K– T_{crist} , and the

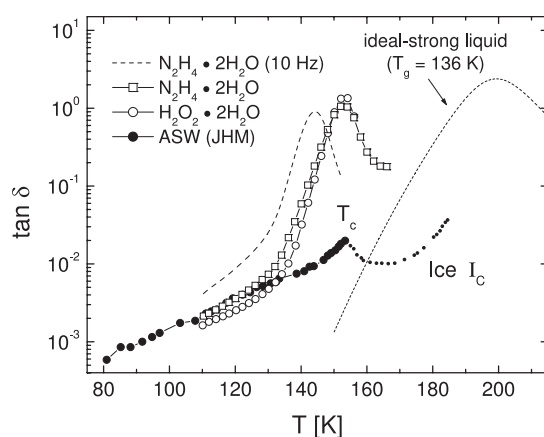


Figure 1. Dielectric loss curves for amorphous water from [9] compared with the same for liquid-cooled hydrogen peroxide and hydrazine solutions which have ‘normal’ glass transitions in the range 136–140 K. Also shown is the loss curve predicted for a liquid with similar dielectric strength and glass temperature, but with Arrhenius relaxation times and exponential relaxation function (ideal ‘strong’ liquid). (From [10] by permission of the American Institute of Physics.)

dielectric loss (under identical conditions) of aqueous H_2O_2 or N_2H_4 solutions [10] that have unambiguous glass transitions at the same temperature, 140 K. The key diagram comparing the respective dielectric losses is reproduced in figure 1. The aqueous solutions begin to show loss at around 130 K, but the water shows no comparable loss before it crystallizes suddenly at 155 K.

However, reference [10] pointed out one way in which water could be so different and still have a glass transition near 136 K. It is that water, rather than being a fragile liquid in this temperature range [11, 12] or even an intermediate liquid, like the solutions of figure 1, is actually an ideally strong liquid with Arrhenius temperature dependence of the relaxation time, and exponential relaxation function. In this case, as shown by the dotted curve in figure 1 [10], the dielectric loss at 10 kHz could remain very small down to 155 K even when the relaxation time is 100 s at 136 K.

But in this case, knowing the highly fragile nature of water near its freezing point, there must have been a fragile-to-strong liquid state transition in the temperature range around 220 K, as has been argued in a number of papers dating from 1993 [13–17]. We return to this question shortly.

1. Strong water

An ideally strong liquid behaviour for water is what is required to explain the absence of a glass transition in sensitive studies of the heat capacity of water by normal differential scanning calorimetry (DSC) methods during heating at the rate usually used in the study of glass transitions of molecular liquids [2]. Finally it provides a way of understanding why there has been such difficulty in deciding whether or not amorphous water has a glass transition (see the review in [1]).

It is possible, by various extended annealing procedures (e.g. 90 min annealing at 130 K before scanning), to produce a heat capacity jump at 136 K, and it is legitimate to call this a glass transition, as has been the custom since the well-known studies of Johari and co-workers [5, 7], because it does indeed reflect a return to some ergodic state during temperature

scanning. However, it is a little dangerous to call it *'the'* glass transition for water because the ergodicity-breaking temperatures in strong liquids (and hence glass transition temperature in strong liquids) depend greatly on the scan rates used to detect them. This can be seen from the long known but rarely tested relationship for ergodicity breaking (called, by Cooper [18], the Lillie number), which is currently under study in our laboratory [19, 20]. The relation is

$$Q d\tau/dT = 1 \quad (1)$$

at the ergodicity-breaking temperature, where Q is the cooling rate, and τ is the relaxation time. The ergodicity-breaking temperature, by analogy with the dielectric relaxation loss peak phenomenon, can be identified with the hysteresis peak temperature for extensive properties when studied through the glass transformation range using the same cool/heat rates [19, 20]. It is close in value to the glass temperature in the case of normal glass-formers.

Equation (1) can be used, along with the activation energy for diffusion in water (45 kJ mol^{-1}) taken from the studies recently reported by Kay and co-workers [21] or from other structural relaxation studies on glassy water [22] ($45\text{--}50 \text{ kJ mol}^{-1}$), to deduce from equation (1) the ergodicity-breaking temperatures in water during cooling at different Q values (or ergodicity-restoring temperatures during reheating at different Q values). And they, and hence also T_g , can vary from 120 to 220 K. A recent demonstration where T_g must rise above 200 K is that of Sadtschenko and co-workers [23], using very fast scans.

So the true situation with respect to the T_g of water remains ambiguous. What is clear, though, is that it should be very feeble and unlike any other yet studied, with the possible exception of that of BeF_2 which was also thought until recently to not have a 'glass transition' because the calorimetric signal was so weak [24]. BeF_2 is indeed analogous to water in important ways, but we reserve comment on this similarity for our final point of discussion.

2. Complete C_p function for water

Let us return to considering what the full heat capacity–temperature function for water would look like if crystallization were not to intervene to prevent its observation. This may be achieved in at least two ways. One is to use thermodynamic data from highly supercooled water (down to 235 K), and from amorphous water (crystallization enthalpy [8], and vapour pressure based entropies [25]), to deduce by thermodynamic constraint arguments [26] how the heat capacity could vary between 150 and 235 K without violating thermodynamic laws. The other is to measure the heat capacity of water in nanoconfinement where crystallization does not occur. The state of the water in such confinement is a matter for discussion which we will not enter into here. The interesting observation, though, is that by both routes [27] a form of heat capacity is obtained that is quite unlike that seen in any other common molecular glass-former. It is a function that is sharply peaked in the vicinity of 220 K and then drops off to vanishing values in the vicinity of 140 K, consistent with the extreme weakness, or absence, of the thermal effect observed by authors through the decades. (The most recent values [28], when measured at scan rates of 5 K min^{-1} , are only 30% of those reported earlier [8], and are $0.7 \pm 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$. These are to be compared with $30\text{--}35 \text{ J K}^{-1} \text{ mol}^{-1}$ for $\text{H}_2\text{O}\text{--}\text{N}_2\text{H}_4$ solutions [29], a factor of 50 difference!)

The sharp peak at 220 K is sufficient to explain the existence of the strong-to-fragile transition during heating, simply by invoking the Adam–Gibbs equation for the relaxation time [30]. The relation is

$$\tau = \tau_0 \exp(C/TS_c) \quad (2)$$

where τ_0 and C are constants and S_c is the configurational entropy, usually taken as the excess entropy. The departure from Arrhenius behaviour is due, in the Adam–Gibbs theory, to the

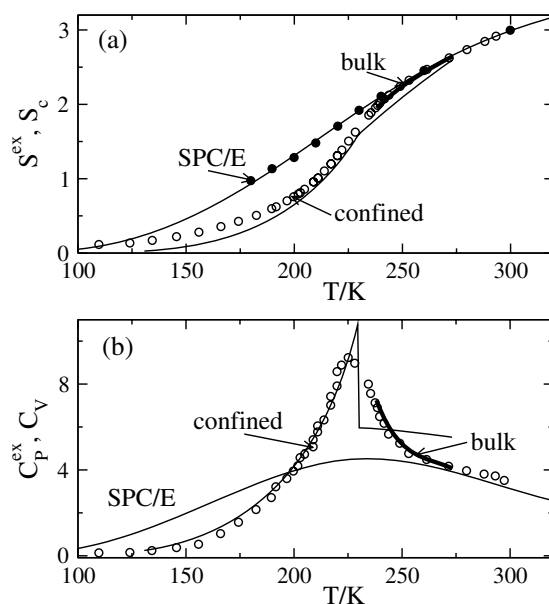


Figure 2. Fit of 1 G model of [31] to entropy and heat capacity data of water confined in 3 nm silica pores [28] and SPC-E simulations. The fit of low temperature data is very good but the model predicts a weak first order transition at 225 K between low density and high density liquids at this pressure (ambient). Axis units are k_B . SPC-E model data were obtained at constant volume (From [31] by permission of the American Institute of Physics.)

finite temperature dependence of S_c , which is determined by the heat capacity. If the excess heat capacity makes a dramatic turn, as seen in figure 2, then clearly the departure from Arrhenius behaviour (i.e. the fragility) must also change suddenly (from fragile above the transition to strong below it). This is also required by the new dynamical model of Matyushov [31]. We note that while the strong–fragile transition manifested by dynamic studies of nanoconfined water has been attributed to finite size effects [32, 33], these cannot be the reason for the matching transition deduced from thermodynamic data available above and below the transition [26].

The form of the heat capacity versus T function is that of an order–disorder transition. These have been much studied in the crystalline state, but are more or less unknown in liquids far from their critical points, except for the famous case of the lambda transition in liquid helium, and to a lesser extent the μ – λ transition in sulfur. In the former case the transition temperature is a critical point. In many crystals it is uncertain whether the lambda transition is a true critical point or whether, alternatively, it has some first order character near the peak temperature. In either case, the interesting aspect is the source of the cooperativity of the disordering process and its generally fast kinetics. The kinetics of the elementary ordering process is fast enough that the structure ‘freezes’ only when there is very little configurational entropy remaining. Water is like this. The residual entropy in glassy water is very small compared with that for other glass-formers [25, 34]. An energy landscape like that for folding proteins is suggested [35]—i.e., a ‘funnel’, such that a state close to the ground state is achieved.

The order–disorder description of the water transition is quite compatible with the ‘second critical point scenario’ developed by Stanley and co-workers since 1991 [36–38], but emphasizes its low temperature characteristics. The second critical point after all is an order–disorder transition. Accordingly, the low temperature heat capacity can be modelled by theories

that have cooperative excitations as their basis. The recently developed ‘Gaussian excitations’ model of Matyushov and the author [31, 39] derives the cooperativity of its excitations from the stabilization of excitations by the disorder already present. The theoretical equations produce a very satisfactory account of the low temperature heat capacity of water in nanoporous hard confinement [40], as can be seen from figure 2, taken from [31]. The fitting implies that, at ambient pressure, the transition still has a weak first order character to it, implying that the critical point is at negative pressure, rather than at about 100 MPa [37], or at about 27 MPa [41]. However, this is not a strong conclusion, other parametrizations being possible with slightly different outcomes.

3. ‘Big picture’ aspects

Finally we want to show that the scenario developed here for water has implications beyond water. Indeed, water can be seen as a sort of Rosetta stone pointing to the relation between classical network strong liquids and the fragile molecular liquids whose heat capacities have until recently resisted a simple theoretical description.

When inorganic liquids have tetrahedral network character, the ‘strong’ liquid extreme of SiO₂ and GeO₂ is obtained. Both have small but measurable glass transition endotherms, though the small heat capacity jumps make it impossible to assess their Kauzmann temperatures with any reliability. Information on behaviour of SiO₂ above 2500 K can only be obtained by computer simulation. BeF₂ is a more accessible network liquid whose behaviour was puzzling until a strong-to-fragile transition in the liquid state at temperatures far *above* the melting point was identified, with the aid of simulations [42]. A heat capacity spike was also revealed by the simulations at the temperature of the strong-to-fragile dynamic transition, matching up well with the experimental data from lower temperatures, and suggesting behaviour like that of water in figure 2 but shifted up in temperature. This implies that the excitations are similar to, but somehow less cooperative in this case than, those for water.

Looking in the opposite direction to *less* structured liquids, the Gaussian widths of the spectrum of excitations become broader and the excitations accordingly more cooperative. This converts the higher order transitions to first order transitions occurring at low temperatures, now below T_g in most cases [31]. When the substance lacks a good low energy crystal structure, the high disorder of the liquid state above the liquid–liquid transition temperature stabilizes the liquid sufficiently that the substance becomes a recognizable ‘glass-former’. It is implied that there may be a number of fragile glass-formers with liquid–liquid transitions just below the glass temperature. Tri-phenyl phosphite may be an unexpected example of this effect pushed out into the region of observability [43]. It is possible that the phenomena currently being reported by Ediger and co-workers [44] (in which vapour deposition routes provide means of accessing low entropy states, normally lying well below the normal glass temperatures), may be related to this.

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