WATER BEHAVIOUR

Glass transition in hyperquenched water?

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It has been unclear whether amorphous glassy water heated to around 140–150 K remains glassy until it crystallizes or whether instead it turns into a supercooled and very viscous liquid. Yue and Angell[1] compare the behaviour of glassy water under these conditions to that of hyperquenched inorganic glasses, and claim that water stays glassy as it heats up to its crystallization point; they also find a 'hidden' glass-to-liquid transition at about 169 K. Here we use differential scanning calorimetry (DSC) heating to show that hyperquenched water deposited at 140 K behaves as an ultraviscous liquid, the limiting structure of which depends on the cooling rate — as predicted by theoretical analysis of the liquid-to-glass transition[2]. Our findings are consistent with a glass-to-liquid transition-onset temperature (T_g) in the

region of 136 K (refs 3,4), and they indicate that measurements of the liquid's properties may clarify the anomalous properties of super-cooled water.

We hyperquenched micrometre-sized water droplets on a substrate held at 140 K (ref. 5) and immediately cooled it to 77 K at rates of 0.2, 2.0 and 5.0 K min^{-1}. DSC scans recorded subsequently (Fig. 1) show that the height of the endothermic peak (ΔC_p) decreases with increasing cooling rate. This effect disappears in DSC scans of samples that were prepared and cooled in the same manner but which were also annealed at 130 K (Fig. 1).

The mean ΔC_p (T_g) values of unannealed samples after cooling are: at 0.2 K min^{-1}, 1.7 ± 0.3 J K^{-1} mol^{-1} (135 ± 1 K) (from 18 samples); at 2.0 K min^{-1}, 1.1 ± 0.2 J K^{-1} mol^{-1} (136 ± 2 K) (from 9 samples); and at 5.0 K min^{-1}, 0.7 ± 0.1 J K^{-1} mol^{-1} (135 ± 1 K) (from 9 samples). For $T_g \approx 136$ K, water relaxes during deposition at 140 K for 16 min, moving towards metastable equilibrium.

The limiting structure obtained on subsequent cooling may be characterized in terms of a limiting 'fictive' temperature (T'_f), which decreases with decreasing cooling rate[2]. Decreasing T'_f is experimentally observable by DSC on subsequent reheating, and is evident mainly as an increasingly pronounced overshoot[2] (Fig. 1); an overshoot can also develop upon annealing below T_g (ref. 6).

The ΔC_p increase of annealed samples[4] (Fig. 1) contains an overshoot contribution, and water's 'true' ΔC_p increase at T_g must be lower, approaching the value of about 0.7 J K^{-1}

mol^{-1} obtained on cooling at 5.0 K min^{-1}. A lower ΔC_p value seems consistent with increasingly 'strong' behaviour of supercooled water[7-10]. Our findings therefore support the postulated fragile-to-strong transition of liquid water on cooling from ambient temperature into the supercooled and glassy state[8,10].

Our results are not consistent with the sub-T_g or "shadow" peak postulated by Yue and Angell, because their criterion is that the onset temperature of the peak is the same as the annealing temperature (see Fig. 3b in ref. 1). This is not observed here because T_g does not vary with annealing temperature (Fig. 1).

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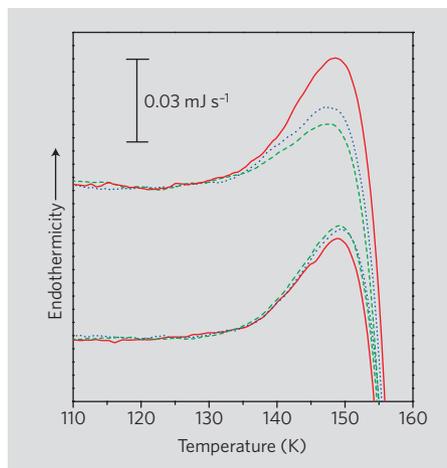10. Starr, F. W., Angell, C. A. & Stanley, H. E. *Physica A* **323,** 51–66 (2003).

Figure 1 | Liquid-like relaxation in hyperquenched water at or below 140 K. Top curves: effect of cooling rate of unannealed hyperquenched water samples, after deposition at 140 K for 16 min, on differential-scanning calorimetry (DSC) measurements recorded on subsequent heating at 30 K min^{-1}; the cooling rate was increased from 0.2 K min^{-1} to 2.0 K min^{-1} and to 5.0 K min^{-1}, and the corresponding scans are indicated by solid, dotted and dashed lines, respectively. Note the decrease in the height of the endothermic step with increasing cooling rate. Bottom curves: effect of annealing at 130 K for 90 min on hyperquenched water samples, after deposition at 140 K for 16 min and cooling at 0.2, 2.0 and 5.0 K min^{-1}, on DSC scans recorded on subsequent heating at 30 K min^{-1} (line designations as in top curves). Note the disappearance of the effect of cooling rate for unannealed samples. Scans are normalized with respect to the weights and ice impurity of the samples and are drawn on the same scale. The ΔC_p values are corrected for 22% ice impurity[5]. The ordinate scale is for 1 mg sample weight. The scans are superimposed at low temperatures.

WATER BEHAVIOUR

Yue & Angell reply

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The alternating support for and denial of a glass transition for amorphous water at 136 K has resumed after a hiatus of 20 years, during which it seemed secure. We revived the alternative interpretation[1] by looking again at the calorimetric signal that previously provided the most direct evidence for the glass transition[2,3] — and now Kohl *et al.*[4] present new data to support the original interpretation. We show here that their results are also consistent with our conclusions.

The new data of Kohl *et al.* show that if the exceedingly weak endothermic step (or peak),

originally reported as being the glass-to-liquid transition (T_g) of water[2], is a primary (glass-like) relaxation, then it is even weaker than previously supposed[3] — only 3% above vibrational background and just a quarter the strength of the phenomenon that occurs in silica (SiO_2; the 'strongest' liquid known[5]). If it is a glass transition, then it is the broadest on record for a single-component system, with $\Delta T_g / T_g = 0.11$ (refs 3,5). As Kohl *et al.* observe, these characteristics would support the idea that water has undergone, during the hyper-quench, a fragile-to-strong transition[5], for
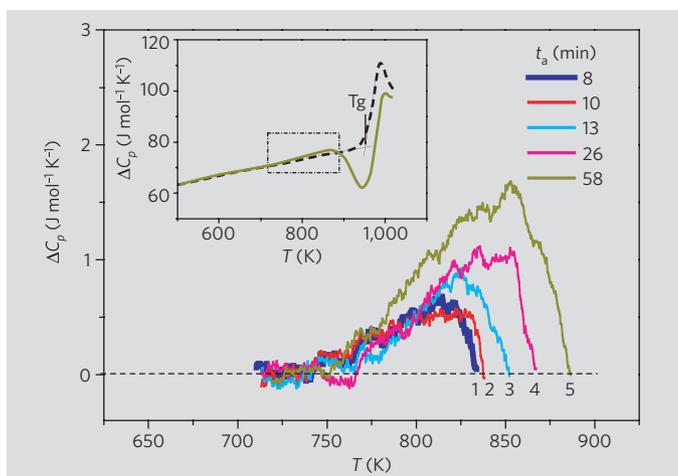
Figure 1 | **Results analogous to those in Fig. 1 (top curves) of Kohl et al.[4], but for non-crystallizing basaltic hyperquenched glass.** Excess heat capacities over those of 'standard glass' (inset: standard glass, dashed line; annealed hyperquenched glass, solid line; boxed area, pre-peak) are shown. The temperature (T_g) of the glass-to-liquid transition for standard glass is 941 K. To demonstrate the analogy, we chose 823 K as the equivalent of the 140-K quench temperature of Kohl et al. for water (823/941 = 140/160). A sample was annealed at temperature T_a of 823 K for time t_a of 8 min to simulate the integral annealing of their sample over the 16-min deposition time, and then cooled to low temperature at 5 K min^{-1}, as in their fastest cool. Curves from the differential scanning calorimetry upscans: 1, curve from simulation described above; 2, curve obtained after 2 min of further annealing at 823 K, then fast cooling before the 30 K min^{-1} upscan, which yields the same upscan as does the protocol of Kohl et al.; 3–5, curves generated by simulating the slower cool-downs of Kohl et al. from 140 K and increasing anneal times at 823 K. If our measurements were curtailed by crystallization (at 850 K here), as for water, the diagram would look the same as that of Kohl et al.[4].

which there is striking evidence[6–8].

However, we have to point out that the enhancement of the endothermic peak on slow cooling from 140 K, used by Kohl et al. to support the primary-relaxation scenario, is also the behaviour expected for an annealing pre-peak (our Fig. 1, inset), which was how we interpreted the weak endotherm[1]. After all, the simplest way of understanding the existence of annealing pre-peaks (or "shadow" glass transitions) is to regard them as the annealing-enhanced glass transitions of the short-relaxation-time components ("microglasses"[9]) of the non-exponentially relaxing macroglass.

Our analogous scans are shown in our Fig. 1. If these were cut off by crystallization at a temperature of 830 K, in the same way as those for hyperquenched glassy water are cut off by crystallization at 155 K, then our Fig. 1 would have the appearance of Fig. 1 of ref. 4. The maximum ΔC_p (0.6 J K^{-1} mol^{-1}) for curve 1 is close to that (0.7 J K^{-1} mol^{-1}) for the 5-K min^{-1} scanned hyperquenched water of Kohl et al.[4]. The inset to Fig. 1 shows how weak these pre-peaks are relative to the real glass transition.

The scans in Fig. 1 suggest that the 'T_g' for our system is 760 K, which is 20% below the real T_g of 941 K (see our Fig. 1, inset) and well below the annealing temperature of 823 K. We do not regard the identity of T_g with the annealing temperature as a central criterion, as Kohl et al. assert: neither our Fig. 1 here, nor Figs 2 and 3 in ref. 1, show this behaviour

(although others[10] use this criterion). Furthermore, if we anneal for 55 days (rather than for minutes) at the lower temperature of 773 K before scanning, the pre-peak onset moves up to 920 K (Y.-Z. Y. et al., unpublished results) and approaches the strength of the standard glass transition. The pre-peak onset temperature can evidently occur anywhere, depending on the fraction of the quenched-in energy that is left unrelaxed by the anneal.

In an earlier study[11], it was the magnitude of the unrelaxed enthalpy remaining when crystallization occurred that showed that T_g for water had been wrongly assigned. When there is no unrelaxed enthalpy in a substance undergoing vitrification, then annealing, or slow cooling, should result in T_g being raised[12] (an extreme being the case of silver-salt glasses after 5 years' annealing[13]). In Fig. 1 of Kohl et al., we see no increase in T_g resulting from the slower cooling of the hyperquenched glassy water collected at 140 K.

We conclude that the new measurements of Kohl et al. leave unresolved the problem of water's post-annealing endothermic step (peak) at 136 K. It is possible that this conundrum could be solved by using their cool-and-anneal procedures[3,4] on samples of water in nanoporous supports[8] in which crystallization can be suppressed. We would expect the results to show that both of the above scenarios contribute to the effect.

An ironic twist to this problem is contained in findings[14] that show that the T_g of the high-density polyamorph of water must be

135–140 K at ambient pressure, and that the transition (only partly seen) is strongly endothermic (large ΔC_p), as for our glass. On appropriate thermal treatment, this polyamorph should presumably show an interesting annealing pre-peak.

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