

WATER BEHAVIOUR

Glass transition in hyperquenched water?

Arising from: Y.-Z. Yue & C. A. Angell *Nature* 427, 717–720 (2004)

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 Angell¹ 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 transition². Our findings are consistent with a glass-to-liquid transition-onset temperature (T_g) in the

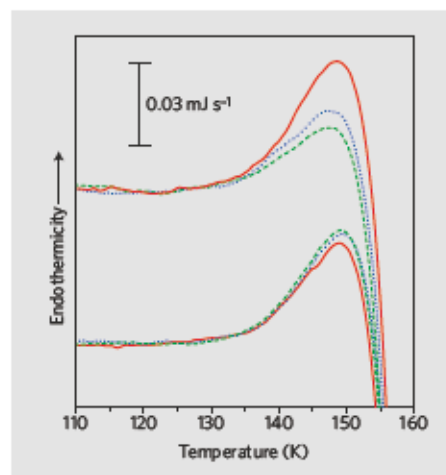


Figure 1 | Liquid-like relaxation in hyperquenched water at or below 140 K. Top curves: effect of cooling rate of unannealed hyperquenched water samples, after deposition at 140 K for 16 min, on differential-scanning calorimetry (DSC) measurements recorded on subsequent heating at 30 K min⁻¹; the cooling 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 impurity⁵. The ordinate scale is for 1 mg sample weight. The scans are superimposed at low temperatures.

region of 136 K (refs 3,4), and they indicate that measurements of the liquid's properties may clarify the anomalous properties of supercooled 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 rate². Decreasing T_f is experimentally observable by DSC on subsequent reheating, and is evident mainly as an increasingly pronounced overshoot² (Fig. 1); an overshoot can also develop upon annealing below T_g (ref. 6).

The ΔC_p increase of annealed samples⁴ (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).

Ingrid Kohl*, Luis Bachmann†, Erwin Mayer*, Andreas Hallbrucker*, Thomas Loerting*†

*Institute of General, Inorganic and Theoretical Chemistry, and †Institute of Physical Chemistry, University of Innsbruck, 6020 Innsbruck, Austria
e-mail: ingrid.kohl@uibk.ac.at

1. Yue, Y.-Z. & Angell, C. A. *Nature* 427, 717–720 (2004).
2. Moynihan, C. T., Eastaig, A. J., DeBolt, M. A. & Tucker, J. *J. Am. Ceram. Soc.* 59, 12–16 (1976).
3. Johari, G. P., Hallbrucker, A. & Mayer, E. *Nature* 330, 552–553 (1987).
4. Hallbrucker, A., Mayer, E. & Johari, G. P. *Phil. Mag. B* 60, 179–187 (1989).
5. Kohl, I., Mayer, E. & Hallbrucker, A. *Phys. Chem. Chem. Phys.* 2, 1579–1586 (2000).
6. Hodge, I. M. & Berens, A. R. *Macromolecules* 15, 762–770 (1982).
7. Angell, C. A. *J. Non-Cryst. Solids* 102, 205–221 (1988).
8. Ito, K., Moynihan, C. T. & Angell, C. A. *Nature* 398, 492–495 (1999).
9. Debenedetti, P. G. *Metastable Liquids* (Princeton Univ., New Jersey, 1996).
10. Starr, F. W., Angell, C. A. & Stanley, H. E. *Physica A* 323, 51–66 (2003).

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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 interpretation¹ 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 water², is a primary (glass-like) relaxation, then it is even weaker than previously supposed³ — only 3% above vibrational background and just a quarter the strength of the phenomenon that occurs in silica (SiO₂; the ‘strongest’ liquid known⁵). 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 hyperquench, a fragile-to-strong transition⁶, for