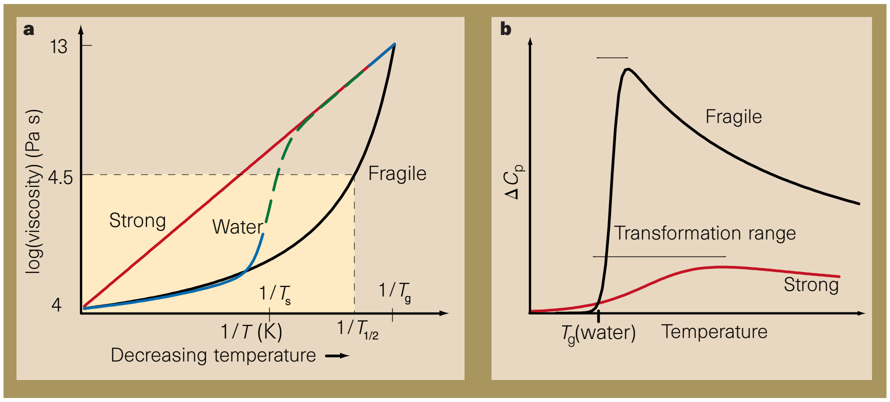

Figure 2 **Kinetic fragility.** a, **The fragility plot. In this representation, the viscosity, $\eta(T)$, of 'strong' liquids shows a uniform increase, whereas for fragile liquids, the viscosity increases faster as the temperature gets lower. On the basis of available evidence, water changes from fragile to strong behaviour before the glass transition is reached, as shown schematically here. T_s marks the temperature where various properties of water appear to diverge with a power-law singularity. T_g is the glass transition temperature. $T_{1/2}$ is defined such that $\log(\eta(T)) = ½ \log(\eta(T))$. The kinetic fragility, $F_{1/2} = 2(T_g/T_{1/2}) - 1$, is closer to one the more fragile the liquid is.** b, **The excess specific heat of the liquid ΔC_p near the glass transition temperature T_g. Fragile liquids show a sharper drop than strong liquids because their viscosity increases more rapidly (over a narrower interval of temperature) to the value at T_g. The transformation range is the interval ΔT_g over which the specific heat drops to glass values, as indicated. Water exhibits behaviour illustrated here for strong liquids, but only up to 150 K where it crystallizes.**

(log(viscosity) versus $1/T$; Fig. 2a), some liquids show a steady increase, but for others, the viscosity rises faster as temperature gets lower. The former are termed strong liquids, whereas the latter are fragile.

Fragility can be quantified in various ways; Ito *et al.*[3] consider two kinetic measures, and demonstrate consistency between them. One measure of the kinetic fragility, $F_{1/2}$, relates to the temperature, $T_{1/2}$, at which log(viscosity) reaches half its value at the glass-transition temperature T_g (Fig. 2a). The other is the normalized width of the 'transformation range' over which glass formation occurs, $\Delta T_g/T_g$ (Fig. 2b). The specific heat drops from a high value for liquid to a low value for glass in this range, and corresponds to a rise in viscosity by two to three orders of magnitude (Fig. 2b). Ito *et al.* go on to show that these kinetic measures of fragility are also consistent with a thermodynamic measure they propose, which is based on how rapidly the entropy of the liquid drops below its value at the melting temperature, T_m. The more fragile liquids show a more rapid fall in entropy (Fig. 3). This is very gratifying, because the notion of fragility, and indeed the name, harks back to the Adam–Gibbs theory[4] of the glass transition, according to which the increasingly rapid rise of viscosity on cooling is due to a progressive reduction in the liquid's entropy. It appears that all around, there is much consistency.

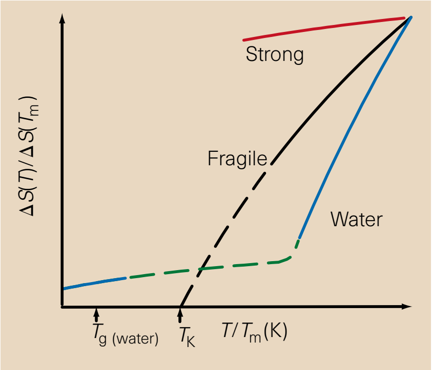

Figure 3 **Thermodynamic fragility measured by Ito *et al.*[3]. The entropy difference between the liquid and the solid, $\Delta S = S(\text{liquid}) - S(\text{solid})$ normalized by its value ($\Delta S(T_m)$) at the melting temperature T_m, shows a stronger drop with temperature (T/T_m) for fragile liquids than strong liquids. Water, in this representation, is seen to be an extremely fragile liquid at high temperatures. The extension (dashed line) illustrates the expected behaviour of water's entropy in the range of 150 K to 236 K where it cannot be measured. T_K is the 'Kauzmann temperature' (illustrated for a fragile liquid) where, by extrapolation, ΔS goes to zero.**

Water spoils this tidy picture. The transformation range for water proves to be quite large, and implies that near T_g water is a very strong liquid, much like silicon dioxide, a liquid that shares many similarities with water. On the basis of how rapidly its entropy changes near the melting temperature, however, water emerges as the most fragile of all liquids considered (Fig. 3).

Although puzzling at first sight, this observation is consistent with the striking behaviour of water near 228 K (T_s in Fig. 2a), first noted by Speedy and Angell[5]. They showed that many dynamic quantities (such as viscosity and relaxation times) and also thermodynamic ones (for instance, isother-

100 YEARS AGO

After a visit to Egypt in 1894, Miss Benson tells us she first entertained the idea of undertaking some excavation, and in the following year she obtained permission to clear away some of the earth that still covered the ruins of the temple of Mut. For three seasons Miss Benson and her friend, Miss Gourlay, have occupied themselves in removing débris and, though they have made no very startling discoveries, they have succeeded in correcting Mariette's plan of the temple in several details … . It will be seen, therefore, that Miss Benson and Miss Gourlay have had some reward for their three seasons' work; and, although surface-excavation at Karnak is not a very arduous or difficult undertaking, it is not unreasonable that they should be proud of having obtained the first permission to excavate given to women in Egypt. Whether their example will be followed by other ladies remains to be seen, though we think on the whole such work is perhaps better left to the male professional digger, who can camp on the spot, and having knowledge of Arabic is naturally better able to control his men, and check to some extent the thefts of the smaller antiquities.

From *Nature* 6 April 1899.

50 YEARS AGO

A new 16-mm. sound and colour film, "The Nature of Plastics", which has been sponsored by Bakelite, Ltd., was shown for the first time at the British Council Theatre in London on April 5. The film, which runs for about 20 minutes, is a scientific documentary and is designed to explain to the intelligent layman the broad principles of the structural characteristics of plastics and their associated physical properties. The molecular chain structure is particularly emphasized and is illustrated by large-scale molecular models. Then, with the aid of mechanical analogies, the packing of the chains is related to the physical properties, tight-, medium- and loose-packing corresponding to fibres, heat-softening plastics and rubbers respectively. In the case of the rubber structures, the chains can be locked by means of cross-connecting atoms, and this produces a heat- and chemical-resistant material which is called a heat-hardening or thermosetting plastic.

From *Nature* 9 April 1949.