

Success of the Moynihan cooperative two-state model for water, order-disorder transitions, and the big picture for glasses.

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Abstract.

We review the confusion concerning the glass transition in water and show how it can be understood in the light of the polyamorphic transition exhibited by water, which was the subject of a theoretical paper by C. T. Moynihan in 1997. We show how the behavior of water at low temperatures is consistent with expectations from this model and that it must therefore be of a quite different character from the glass transition in other molecular liquids. It is, in fact, the kinetically controlled part of a classical order-disorder transition. We show 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 220K and thus to imply the existence of a “strong-to-fragile” transition in the dynamics during heating. Both require the excess heat capacity to drop to near-vanishing values in the vicinity of 130-150K where the “glass transition for water” is supposed to lie. The similarity of the phenomenology to that of order-disorder transitions in crystalline solids is noted, and the relation to the second critical point scenario for water is discussed. Finally the modeling of the anomaly by the Moynihan model, and by a new Gaussian excitations model which has mathematical features in common with the Moynihan model, is considered. Agreement with the low temperature heat capacity behavior is very good, but a weak first order transition near 225K, rather than a “Widom line” crossing is implied. According to this finding the critical point of the polymorphic transition would lie at negative pressure as in the case of liquid silicon in the related Aptekar model (supported by MD simulations using the Stillinger-Weber potential). Finally we argue that water, with its fragile-to-strong liquid transition below the melting point, serves as a Rosetta stone, linking the extremes of classical network liquids (such as SiO_2 and BeF_2 where this transition occurs only above the experimentally accessible range) to fragile molecular liquids. In the latter, the fragile-to-strong transition is pushed, by increasing cooperativity, down beneath the glass temperature where it morphs into a first order transition that resolves the Kauzmann paradox in two complimentary ways, one of them involving crystallization.