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Entropy-driven liquid-liquid transitions in supercooled water[1]

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Twenty years ago it was suggested that the anomalous properties of supercooled water may be caused by a critical point that terminates a line of metastable liquid-liquid separation of lower-density and higher-density water. I describe a phenomenological model in which liquid water at low temperatures is viewed as an athermal solution of two hydrogen-bond network structures with different entropies and densities. Alternatively to the lattice-gas/regular solution model, in which fluid phase separation is driven by energy, the phase transition in the athermal two-state water is driven by entropy upon increasing the pressure, while the critical temperature is defined by the reaction equilibrium constant. The order parameter is associated with the entropy, while the ordering field is a combination of temperature and pressure. The model predicts the location of density maxima at the locus of a near-constant fraction of the lower-density structure. Another example of entropy-driven liquid polyamorphism is the transition between the structurally ordered "Blue Phase III" and disordered liquid in some chiral materials; this transition is experimentally accessible. I also discuss the application of the two-state model to binary solutions of supercooled water in which liquid-liquid transition may also become accessible to direct observation. Some atomistic "water-like" models such as mW, do not show liquid-liquid separation in the metastable liquid domain. However, even without actual liquid-liquid separation, the anomalies observed in MD simulations of mW can be accurately described by the entropy-driven nonideality of two molecular configurations, the same physics that presumably drives the liquid-liquid transition in real water.

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