Supercooled Water: Anomalous Dynamics on a Background of Peculiar Thermodynamics

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Supercooled water exhibits spectacular anomalies which have been a subject of debates for decades. Twenty years ago Poole *et al.* suggested that the anomalous properties of supercooled water may be caused by a critical point that terminates a line of liquid-liquid separation of lower-density and higher-density water, hidden below the line of homogeneous ice nucleation. This phenomenon can be viewed as "water's polyamorphism". Recent accurate simulations of the ST2 model of water favor the existence of this metastable transition. A phenomenological model, in which liquid water at low temperatures is considered as "solution" of two hydrogen-bond network structures with different entropies and densities explains why supercooled water may unmix and nicely describes the thermodynamic anomalies in supercooled water and in some popular water-like models, such as mW and ST2. The existence of two alternative structures in water may (ST2) or may not (mW) result in liquid-liquid separation, depending on the nonideality of mixing of these two alternative structures. The two-state thermodynamics has been recently generalized to aqueous solutions for describing the liquid-liquid transitions stemming from the hidden liquid-liquid transition in pure water.

In supercooled water, anomalies in dynamics closely follow the thermodynamics anomalies. However, contrarily the vapor-liquid transitions, the dynamic anomalies in supercooled water have been attributed to a structural and viscoelastic relaxation. While the dispersion of sound near the vapor-liquid critical point is solely an effect of the diffusive relaxation of critical density fluctuations, the dispersion of sound in supercooled water is a viscoelastic relaxation phenomenon. Moreover, supercooled water fundamentally differs from water in the vapor-liquid critical region due to a non-conserved nature of the order parameter associated with the orientation of hydrogen bonds in water. Phenomenologically, this order parameter can be viewed as the extent of "reaction" between two alternative structures of water. Rather than obeying the diffusive space-dependent decay, the relaxation of the non-conserved order parameter is independent of the wave number. This would have far-reaching implications for various dynamic properties of supercooled water.