Metastable water: the schism (empiricists vs modelers), and a possible resolution.
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The bizarre behavior of water in its low pressure, supercooled, domain is now well known. Unless confined nanoscopically, response functions and transport properties follow power laws in T that are characteristic of approach to spinodal limits on phase stability. Such behavior has provoked a great deal of computer simulation-based investigation, key results of which turn out to be in stark conflict with the predictions of empirical (engineering) equations of state when extrapolated into the domain of isotropic tension (negative pressure). This domain is the least investigated in all of water research, despite the abundance, in nature, of samples for study (milky quartz, under the microscope). We posit that the secrets of water lurk on the other side of the zero pressure line.

In this talk I compare some of the predictions of currently favored pair potential simulation models with the best available data for real water, in both positive and negative pressure domains. We first apply an approach that is well-tested for models with critical points, to the best available positive pressure equation of state, but fail to find the isochore-crossing "smoking gun" anywhere in the positive pressure domain. Only spinodal divergences are indicated, and the value at ambient pressure coincides with the limit of supercooling from recent short time µdroplet studies. Spinodals without critical points at positive pressure, imply an L-L coexistence line at positive pressures, rather than a LLCP.

Turning to isobaric data, we show how models that are in good accord with experiment at normal temperatures deviate dramatically at large supercooling. While TMDs from certain models agree quite well with experiment at positive pressure, for P < -100 MPa, they vary in opposite directions. However, all leading empirical equations of state, (based on positive pressure (including near Tg) data, and from very fast measurements that postpone crystallization while yielding faster structural relaxation data. We compare them with thermodynamic constructions to argue that a first order transition near 230K provides the most plausible rationalization.

Finally, we introduce new data from non-crystallizing water-rich solutions of a previously unstudied class. Discovered as an offshoot of protein folding studies, these are aqueous solutions of hydrazinium salts that, according to melting point depression data, dissolve to form ideal solutions. At 15 mole% salt they yield cooling thermograms with large endothermic spikes. These mimic the diverging heat capacity of pure water but are not interrupted by crystallization (perhaps due to a sort of wall-free confinement). This allows both sides of the anomaly to be seen before the glass transition intercedes. We will report new TMD data to argue that these spikes are the manifestation of the first order liquid-liquid transition that would occur in water if crystallization did not intercede.

A phase diagram from the H-bond-modified van der Waals thermodynamic model of Peter Poole, provides a simple rationalization for all of these observations.
