591f Relationship between Supercooled Water's Phase Behavior and That of Its Binary Mixtures with Non-Polar Solutes

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We probe the metastable phase behavior of supercooled water by calculating phase diagrams of binary mixtures of non-polar solutes in water. We use a statistical mechanical model of mixtures of water with van der Waals solutes that captures the basic thermodynamic signatures of hydrophobic hydration [1]. We find that the presence (or absence) of a second critical point in pure water has a profound effect on the global phase behavior of its binary mixtures. We show calculations for several different solutes and present general trends on the effects of solute size and interaction energy upon the global phase behavior of mixtures. We argue that this line of inquiry offers rich possbilities, both for understanding the properties of pure water under extreme conditions, and for enriching our knowledge of fluid-phase equilibria phenomenology to encompass systems in which one component possesss more than one critical point.

[1] Ashbaugh, H.S., Truskett, T.M., and Debenedetti, P.G., J. Chem. Phys., 116, 2907, 2002.