Fragility Crossovers in Supercooled Liquid Water

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Abstract:

When pure liquid water is supercooled below its freezing temperature, it exhibits a number of striking anomalies. Most remarkable among these anomalies is the strong temperature dependence of the isobaric heat capacity, C_P, that first exhibits a rise, and then a fall, while lowering temperature substantially below 0 ^oC. In contrast, the isochoric heat capacity, C_V, remains weakly temperature dependent and displays no such anomaly. To understand this and other anomalies of low temperature water, we examine both *wave number and frequency dependent temperature fluctuation* by long molecular dynamics simulations. Significant differences between constant pressure and constant volume conditions appear below 240K in the spatio-temporal correlation of temperature fluctuation. Shell-wise decomposition of relative contribution to the temperature fluctuation reveals an increase in contribution from the distant regions, extending even up to the *fifth hydration shell*, more significant under isobaric than under isochoric conditions. While the temperature fluctuation time correlation function (TFCF) exhibits the expected slow-down with lowering temperature, it shows a rather surprisingly sharp crossover from a markedly fragile to a weakly fragile liquid around 220 K. We establish that this crossover of TFCF (and the related anomalies) arises from a percolation transition in the population of clusters made of liquid-like molecules, defined by coordination number (and consistent with local volumes obtained from Voronoi polyhedra). The disappearance of large liquid-like clusters below 220K displays characteristic features (as reflected in cluster size distribution) that are consistent with theory of percolation. As temperature is further lowered, TFCF exhibits slow power law decay and the relaxation time can be again fitted to Vogel-Fulcher-Tammann law, revealing a dynamic transition around 170 K. Our computed two-dimensional IR and Raman spectra both also carry signatures of a dynamical transition around 160-170 K. However, detailed dynamic studies, including analysis of Stokes-Einstein law and non-linear response function seem to indicate that a dynamical crossover (of the type expected from mode coupling theory) takes place around 190K. We shall explore the inter-relationship between these three temperatures of supercooled water.