Direct observation of liquid-liquid transitions in aqueous solutions

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We investigate structural changes during liquid-liquid transitions in supercooled aqueous solutions. In glycerol solution the transition involves nanoscopic phase separation, but in N_2H_5TFA solution both liquid states are homogeneous at the molecular level. The implied existence of two liquid phases in supercooled water provides a unified explanation for its anomalies.

There is evidence (mostly from simulations) that supercooled water can undergo a phase transition between two different liquid states at a temperature far below the homogeneous-nucleation temperature $T_{hom} \sim 230$ K [1]. Since at room temperature only one liquid-water phase is known to exist, the phase boundary between the two liquid states must terminate at a temperature below T_{hom}; the critical point at the end of the phase boundary would cause diverging susceptibilities and so explain the anomalies at higher temperatures.

Here, we investigate aqueous liquid-liquid transitions using the (isotopically diluted) OH-stretch mode of water as a structural probe. Freezing is prevented by adding different solutes. We find (Fig. 1) that the liquid-liquid transition in glycerol solution [2] involves a metastable low-temperature liquid, which rapidly converts into a suspension of nanoscopic ice crystals [3]. In (thermodynamically ideal) N_2H_5TFA solution however [4], we observe two liquid phases that both appear to be homogeneous at the molecular level, and that are reversibly inter-convertible [5]. We find that the low-temperature liquid has a hydrogen-bond structure similar to (but more disordered than) low-density amorphous water. This structural similarity suggests a direct connection between the observed liquid-liquid transition and the to date unproven HDA-LDA transition in water predicted at higher pressure and lower temperature; and based on the equivalence of high ionic concentrations with the application of high pressure [4] this connection implies that a liquid-liquid transition also exists in neat water, providing a unified explanation for many of its well-known anomalous properties.

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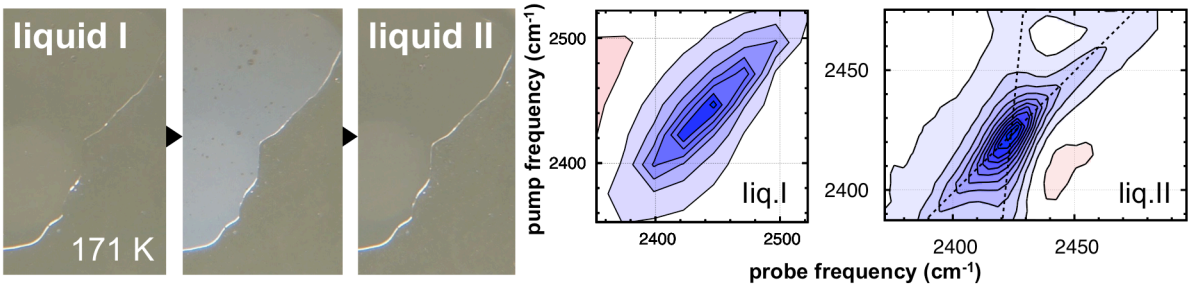

Fig. 1. Liquid-liquid transition in aqueous glycerol solution at 171 K [2,3]. Left: during the transition, micrometer-sized droplets of the low-temperature liquid phase immersed in the high-temperature liquid phase cause the sample to scatter visible light. Right: 2DIR spectra show that whereas liquid I has a single-Gaussian distribution of hydrogen-bond strengths, the hydrogen-bond distribution of liquid II is the sum of a broad and a narrow distribution, the latter being very similar to that of ice I.