

VIEWPOINT

Liquid–liquid transitions in one-component systems

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The possibility that more than two disordered equilibrium phases exist in one-component systems is fascinating. When this is the case, the liquid and the gas phase emerging from the fluid phase below the liquid–gas critical temperature are not the only two disordered equilibrium states: the liquid (or the gas) undergoes one further separation in two distinct liquids (or two distinct gases) at lower temperature. First evidence for this possibility was provided in a numerical investigation of the phase diagram of a realistic classic model of water [1], a result which has been revisited and confirmed in several following studies. In the model, at sufficiently high pressure and low temperature, the liquid separates into two distinct liquids, differing in their densities and in their local structures. The novel liquid–liquid critical point arises from two competing different local configurations, one stabilized by an open linear hydrogen-bonded tetrahedral structure, associated with low local energy and low local orientation entropy, and one stabilized by a dense and disordered local molecular arrangement in which distorted hydrogen bonds are found. Consistent with the hypothesis formulated in earlier theoretical work [2], the known thermodynamic anomalies of water (such as the non-monotonic dependence on T of density and compressibility along isobars) [3] can be explained by the presence of this novel critical point.

For water, the possibility of a liquid–liquid critical point is intimately connected with the possibility of establishing an open local structure with tetrahedral orientation order. One may thus wonder whether this phenomenon could be observed also in other systems, and in particular in other tetrahedral network forming liquids, for example silica, silicon, liquid carbon, germania and beryllium fluoride. Numerical investigations of these systems provide evidence supporting the presence of an additional transition associated with the establishment of the tetrahedral network.

Unfortunately, according to all numerical investigations, the liquid–liquid transition is located in the region of the phase diagram where the crystal phase is thermodynamically stable. For this reason experimental studies—that unlike simulations are hampered by sample crystallization—have not been able to provide direct evidence of a liquid–liquid critical point in a one-component system. In the case of water, the most convincing experimental evidence in favour of multiple liquid states is provided by studies of the different glassy forms of water, by their interconversion and by ingenious estimates of crystal free energy differences [4].

A different example of a liquid–liquid transition is that of phosphorus, where a molecular fluid of tetrahedral clusters appears to convert into a network discontinuously [5]. Unlike in the network liquid models discussed previously, the transition appears to be associated with

changes in the electronic properties, suggesting a possible role of the state point dependence of the effective interatom potential.

An interesting open question, which is addressed in the letter by Rei Kurita and Hajime Tanaka [6] recently published in *J. Phys.: Condens. Matter* is that of the abundance and general nature of the liquid–liquid phase transition in one-component systems. The authors provide experimental evidence in favour of a phase-transformation process, taking place at low T in two samples investigated— n -butanol and triphenyl phosphite—which are clearly different from network forming liquids as well as from each other. If these data are confirmed (and if for these samples the novel critical point can be approached from the equilibrium side) we will need to acknowledge that in molecular systems, significant anisotropies in the intermolecule potential can provide a mechanism able to stabilize competing ordered low energy local structures and disordered but energetically disfavoured arrangements. Although the kinds of locally favoured structures will depend on the details of the molecular structures, the physical scenario of the cooperative emergence of distinct liquid phases may be universal and may come to provide a method for generating glasses with the same composition but significantly different physical properties.

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