

## Phase transitions in liquids

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Pure substances, other than the 'quantum' systems, exist in some crystalline form or the other at low temperatures at ambient pressure. Different crystalline forms, of monocomponent systems, are referred to as 'polymorphs'. For example, carbon exists in three forms, namely, graphite, diamond and the recently discovered fullerene. The polymorphs possess different crystalline orders (that is, different local structures) with different thermodynamic states. Polymorphs can undergo 'phase transitions' from one polymorphic state to another as a function of one or more thermodynamic variables like pressure or temperature.

In more complex systems like molecular solids, transitions may occur from one 'phase' to another when crystalline periodicity may be preserved but there could be variations in the local structures of 'molecular' constituents. For example, in  $\text{NH}_4$ -halides exhibiting ordered structures with identical orientations of  $\text{NH}_4^+$  at low temperatures, disordering of  $\text{NH}_4^+$  'molecular' ions can take place, as a function of temperature, finally ending up with freely rotating  $\text{NH}_4^+$  'molecular' ions. In liquid crystals, a large variety of phases and transitions among them occur, some of them accompanied by tilting of the molecules as a function of temperature, in addition to positional disorder.

Monocomponent or multicomponent liquids are characterized by fluidity as a result of the domination of dynamical motions of the constituents. There is a constant rearrangement of atomic or molecular configurations as a result of thermal motion. Can one envisage different 'phases' in a liquid with different thermodynamic states and different local structures? For example, are there different allotropes of liquid carbon?

Theoretical studies have shown<sup>1</sup> that thermodynamically different phases can be associated with a pure liquid. One distinguishes between a 'two-state' model and a 'two-phase' model in liquids. In the 'two-state' model, low and high density states coexist within a liquid and the high density state grows relative to the low density state as a function of pressure. The two-state behaviour can go

over into the two-phase behaviour below a certain temperature, the two-phases being characterized by different thermodynamic properties like energy or entropy. Just as there is a liquid-gas critical point in the pressure-temperature phase space, a second liquid-liquid critical point is hypothesized to exist below this critical temperature at some lower temperature. Below such a critical temperature, a first order liquid-liquid phase transition can occur as a function of pressure. Sudden jumps in properties like electrical conductivity can occur within the two-state domain within a single liquid phase or it could happen in two-phase regime of a liquid when liquid-liquid phase transition occurs. An unequivocal proof of occurrence of a liquid-liquid phase transition has to come from other techniques. The diffraction technique can provide such an evidence. However, phase transitions across the liquid-liquid coexistence boundary may not be easily observable in experiments. The observations may be hampered by a transition to a glassy state or even to a crystalline state, as the liquid polymorphs could be metastable. Instability from the metastable state to a relatively stable state is a short step. For quite sometime, any evidence for a liquid-liquid phase transition has been elusive in any one-component system.

Several candidate liquids are expected to exhibit liquid-liquid phase transitions<sup>2</sup>. These include liquids having open molecular coordination at low pressure; liquids having locally tetrahedral molecular structures for example, Si, Ge, C,  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{H}_2\text{O}$  are some of them. For Si, observation of a first order glass to liquid phase transition consistent with an underlying liquid-liquid phase transition has been reported based on flash heating experiments<sup>3</sup> and computer simulation experiments<sup>4</sup>. For  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{H}_2\text{O}$ , liquid polymorphism is suggested from corresponding glass studies at different temperatures. The basis for this is that<sup>2</sup> 'although a glass is not an equilibrium thermodynamic state, if its behaviour parallels that of the corresponding supercooled liquid, then the observation

of a 'polyamorphic transition' (note the word 'polyamorphic'; the transition refers to abrupt changes in density and structure with pressure in an amorphous system) in the glass indicates existence of distinct liquid states'. Evidence for liquid-liquid phase transition in  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  with differing Y/Al ratios while quenching the melts into glassy state and in the organic liquid triphenyl phosphate are also reported (see ref. 2). Indirect evidence for liquid-liquid phase transitions in molecular liquids Se and S have also been suggested by abrupt changes in conductivity as a function of pressure.

Extensive computer simulation experiments have provided 'evidence' for liquid-liquid phase transitions. Stephen Hanington *et al.*<sup>5</sup> reported results of molecular dynamics simulation of a one-component model system, namely, that of ST2 model of water. By evaluating the pressure-density isotherms above and below a critical temperature, they found presence of two coexisting phases differing by 15% in density. By studying the static structure factor  $S(Q)$ , at small wavevectors  $Q$ , they identified the two phases characterized by different local structures and dynamics.

Recently, Japan Atomic Energy Research Institute (JAERI) made an announcement in its webpage<sup>6</sup> titled 'world's first *in situ* observation of sudden change in the atomic structures of a pure liquid - observing a pressure-induced first-order phase transition in liquid phosphorus'. The announcement dealt with an important experimental result achieved in an X-ray diffraction experiment at the Japanese SPring8 synchrotron, using a high temperature-high pressure device, a cubic multianvil press. This announcement of 26 January 2000 had been preceded by a publication of Katayama *et al.*<sup>7</sup> in *Nature* on 13 January 2000.

Phosphorus was chosen for the Japanese studies as it has several allotropes in the solid state, namely, white (MP  $\sim 45^\circ\text{C}$ ), black (MP  $\sim 600^\circ\text{C}$ ) and red (amorphous with MP of  $\sim 600^\circ\text{C}$ ) phosphorus varieties. Molten white, red and black phosphorus are associated with  $\text{P}_4$  molecules. An *ab-initio* molecular dynamics study of liquid phosphorus had

predicted a polymorphic form at high temperatures<sup>8</sup>. The melting curve of black phosphorus has a maximum around 1000°C and 1 GPa. (One gigapascal = 1,000 megapascals = 9,870 atmospheres = 10,000 bar.)

Starting with black or red phosphorus, structures of the molten liquid contained in a BN capsule were studied as a function of temperature and pressure, around 1100°C and 1 GPa respectively, by means of Energy Dispersive X-ray Diffraction Experiments (EDXRD; see Box 1) at the SPring8 synchrotron facility. Figure 1 shows the structure factor  $S(Q)$  of molten phosphorus, as a function of wave-vector transfer  $Q$ , obtained from the X-ray diffraction data. It may be noted that the  $S(Q)$  pattern below 1 GPa is quite different from that above 1 GPa, indicating existence of two different liquid forms below and above 1 GPa. Figure 2 shows the nature of change of the  $S(Q)$  patterns by changing pressure in the forward and reverse cycles. Note that the structure factors are stable and reversible.

From analysis of radial distribution function obtained from experimental results, the authors showed that the liquid exhibits different structures (atomic arrangements) depending on whether the pressure is below or above 1 GPa. Two types of structures were found: (a) a random arrangement of tetrahedral molecules with four phosphorus atoms at low pressure, and (b) an extended network structure with strongly coordinated phosphorus atoms in which no molecular unit is defined under high pressure. It was also observed that a change in pressure results in an abrupt transformation from one type to another. The authors concluded that most

probably, the low pressure 'molecular' form transforms to a 'polymeric' form at high pressure. The phase transformation is reversible and occurring 'within a few minutes over a pressure range of less than 0.02 GPa'. It was also noted that 'the two phases coexist during this transformation'.

These *direct* experimental observations are novel, important and interesting. Paul McMillan<sup>9</sup> commenting on the work of Katayama *et al.*<sup>7</sup> says 'multiple liquid-liquid phase transitions may occur for a given substance as the pressure is varied. At the lowest density the liquid-gas transition is then the 'final' member of a suite of such transitions. . . . An even more intriguing possibility is that first

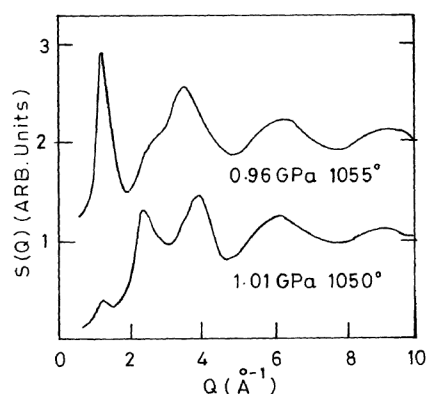
order transitions may occur between gases (gaseous phases)'.

As and when further studies confirm the liquid-liquid phase transition in other materials it 'may lead to synthesis of new, technologically useful families of liquids and glasses, chemically identical to known substances but with quite different thermodynamic, rheological and other properties'.

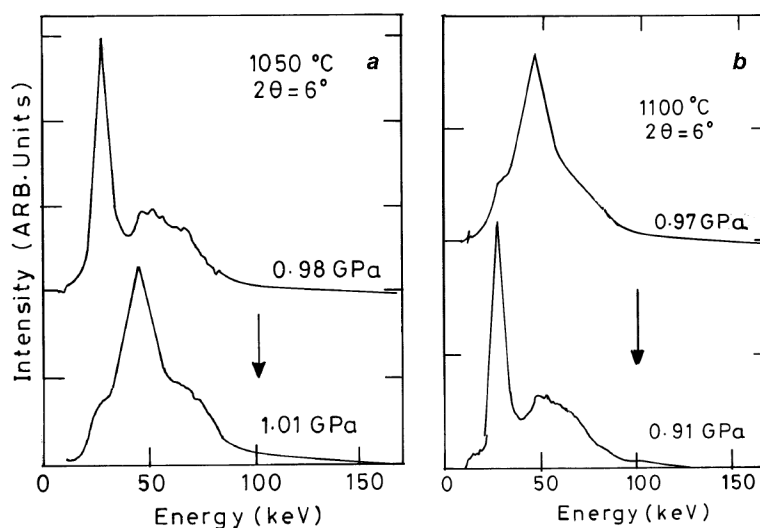
We shall now refer to some theoretical approaches, made recently following the observations narrated in this article, to liquid-liquid phase transitions. Tanaka<sup>10</sup> has, 'to understand these counterintuitive mysterious phenomena' in liquids, proposed in addition to density as an order parameter, another parameter called

### Box 1. Energy Dispersive X-ray Diffraction Experiments (EDXRD)

Crystalline materials produce characteristic diffraction effects when X-rays are incident on them. These diffraction patterns may be measured either by angular dispersion (AD), when monochromatic (or characteristic X-ray) photon scattering is measured as a function of angle or by energy dispersion (ED), when the scattering of photons from the polychromatic source beam itself, is measured at a fixed angle. The latter technique is referred to as 'energy dispersive X-ray diffraction (EDXRD)' technique. The energy distribution of the incident photons is modified by the diffraction effects characteristic of the scatterer and results in a unique pattern dependent upon the crystal structure and atomic constituents of the scattering medium. EDXRD exploits this phenomenon where a measurement is made of the energy distribution of photons scattered at a well-defined angle (typically  $< 10^\circ$ ). The data produced by both these methods (ADXRD or EDXRD), whilst varying with angle and energy, are invariant in momentum transfer and therefore directly comparable.



**Figure 1.** Structure factor of liquid phosphorus as a function of wave vector transfer at 0.96 GPa and 1.01 GPa (adapted from ref. 7).



**Figure 2.** Structure factor of liquid phosphorus obtained by EDXRD as a function of X-ray energy, as pressure (a) increasing (b) decreasing (adapted from ref. 6).

'cooperative medium range bond ordering parameter'. According to this model 'liquid is not homogeneous and in any liquid there exist locally favoured structures which are frustrated with normal structure'. This concept has led to a new possibility that 'even in an ordinary molecular liquid there could be a hidden liquid-liquid phase transition'. Tanaka<sup>10</sup> goes on to state that 'we can straightforwardly generalize our model to a case of  $m$  order parameters. . . . A system of  $m$  order parameters can, in principle, have  $m$  critical points corresponding to the ordering associated with each parameter'.

In yet another study<sup>11</sup>, a 'generic mechanism' has been investigated based on an isotropic pair interaction potential with two characteristic lengths. In addition to an attractive part, the potential has a hard-core as well as a soft core repul-

sive part. Hypernetted chain approximation is made and the resulting integral equation is solved numerically. Although the chosen interaction potential is normally preferred for systems that exhibit a density anomaly, the results show that a low density liquid phase and a high density liquid phase can occur in systems with no density anomaly.

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