On liquid polymorphism and liquid–liquid phase transitions

VIEWPOINT

On liquid polymorphism and liquid–liquid phase transitions

Leif Gerward

Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

E-mail: gerward@fysik.dtu.dk

Abstract
Liquids are not just amorphous phases as commonly believed. It is pointed out that recent pioneering work on liquid phase transitions has shed new light on the phase behaviour of matter in the non-crystalline state.

Interatomic forces and the prevailing physical conditions dictate the atomic arrangements in matter [1]. Ice, for example, melts if its temperature rises above 0 °C. The reason for this melting is that the effect of the interatomic forces is overcome by thermal agitation. Most solids are crystalline solids where the constituent atoms, ions or molecules are situated in an orderly array. Liquids, on the other hand, are amorphous substances. Although the molecules in a liquid are in contact with their neighbours, they have enough energy to push through to a new neighbourhood, and the entire substance is a fluid. A crystal is like an audience seated in a theatre for an opera performance, while a liquid at rest is like the crowd of people milling about during the break (a flowing liquid would be like the crowd of people leaving the opera house).

Gases, at least in the ideal approximation, are characterized by complete randomness on the molecular scale. The ideal crystal, on the other hand, is one of Nature's most orderly arrangements. The physical properties of gases and crystals are well understood, because the extremes of perfect randomness and perfect order are relatively simple to treat mathematically. The theory of liquids and glasses, representing a peculiar compromise between order and disorder, is at a much less advanced stage.

The subtlety of the melting transition lies in the fact that both crystals and liquids constitute condensed matter, the volume occupied by these phases usually differing by no more than a few per cent. In this transition, the molecules are not able to escape from the influences of each other, yet something does happen to break down the orderly array of the crystal. John Bernal, in 1962, simulated a liquid by packing steel spheres into an irregularly shaped container. Although the spheres are still in contact, they have, on average, fewer neighbour contacts than they would have in regular packing. The model has a flaw, however: it is static, whereas the molecules in a

liquid are in rather vigorous motion. More recently, the structure of liquids has been described in terms of small regions of free volume, which open up instantaneously at random locations, enabling nearby molecules to jump into them.

Polymorphic transformations are usually defined as changes in a pure metal from one form to another. A well-known example is provided by iron, for which the stable crystal structure below 910 °C is of the body-centred cubic type, while above this temperature the most stable form is face-centred cubic. Polymorphism, however, is abundant in many other types of material. For example, ionic compounds with the NaCl-type structure often have a high-pressure form of the CsCl-type structure. The general rule for these pressure-induced solid–solid transformations is that the coordination number, i.e. the number of atoms surrounding a particular central atom, increases with increasing pressure. Common belief has it that in a liquid there is some short-range order but no long-range order. The possibility of liquid–liquid phase transitions has therefore, with few exceptions, not been considered seriously in the past, although some interest has been afforded to the glass–liquid transition.

Sciortino, in a recent Viewpoint article [2], has discussed the interesting possibility that liquid and gas are not just two disordered phases emerging below the critical temperature. The liquid may undergo a further separation into two different forms of liquids. Molecular dynamics simulations by Poole *et al* [3] have provided the first evidence for this possibility in a study of the phase behaviour of water. The result was later confirmed in several studies. In a recent theoretical work, Tanaka [4] has pointed out that a liquid also may have some medium-range order arising from many-body interactions. He concludes that a liquid–liquid transition in principle can exist in any liquid. Very recently, Cotterill and Madsen [5] have explored the topology of the energy landscape for the glassy state. A central result of their study is the existence of pockets of preferred occupation of the system, many of these pockets being linked by constant potential energy tubes.

Experimentally, Kurita and Tanaka [6] have verified the existence of liquid–liquid transitions in molecular liquids, such as triphenyl phosphite and *n*-butanol. It has also been shown that liquids may contain reminiscences of the solid-state structure. Thus, Urakawa *et al* [7] have demonstrated that liquid NaCl under pressure has a rocksalt-like structure with large vacancies. Substances exhibiting polymorphism in the solid state should therefore be good candidates for showing liquid polymorphism.

In a recent pioneering work, Katayama *et al* [8, 9] have demonstrated the existence of a first-order liquid–liquid phase transition in phosphorus. The two phases are identified as a molecular low-pressure form, consisting of tetrahedral P_4 molecules, and a polymerized high-pressure form. The transition is found to take place above the melting temperature of phosphorus at about 1000 °C at pressures of about 1 GPa. The local atomic arrangement has been derived from measurements of the structure factor, $S(Q)$, and the radial distribution function, RDF, using synchrotron radiation and *in situ* x-ray diffraction. The density of the two phases has been studied by a radiographic technique. Monaco *et al* [10] have confirmed the first-order transition between a high-density molecular fluid and a low-density polymeric liquid. They have also shown that the transition can be temperature driven as well as pressure driven.

In the present issue of *Journal of Physics: Condensed Matter*, there is a highly interesting paper '*In situ* XAFS and XRD studies of pressure-induced local structural change in liquid AgI' by Arima, Ohtaka, Hattori, Katayama, Utsumi and Yoshiasa of Osaka University, SPring-8 and Kumamoto University, Japan [11]. The authors have extended the study of liquid polymorphism to silver iodide (AgI) at pressures up to 6 GPa and temperatures up to 1500 °C. Using synchrotron x-rays with their inherent narrow collimation and high intensity, and advanced experimental techniques using high-resolution x-ray diffraction (XRD) and x-ray

absorption fine structure (XAFS), Arima *et al* [11] have derived the local atomic structures in the liquid phase.

AgI is a promising candidate for exhibiting pressure-induced liquid polymorphism. Because of its mixed ionic and covalent bonding, it has a variety of allotropes in the solid state: fourfold-coordinated structures of wurtzite and zincblende type, and a sixfold-coordinated structure of rocksalt (NaCl) type. It is to be expected that liquid AgI should undergo a pressure-induced structural change corresponding to the solid–solid transformation from fourfold to sixfold coordination. Arima *et al* [11] have been able to demonstrate that liquid AgI has two distinct local structures within the observed pressure range.

Generally, the interatomic bond length decreases with increasing pressure. However, Arima *et al* [11] demonstrate that the I–Ag bond length first increases with pressure up to 2 GPa, and then decreases at larger pressures. They also show that, at ambient pressure, liquid AgI has a zincblende-like structure characterized by fourfold coordination of iodine, and they explain the increasing bond length on the basis of the introduction of components with higher coordination number. The structural change is completed below 2 GPa, and then a high-pressure polymorph is stabilized. The high-pressure form of liquid AgI is shown to have a rocksalt-like structure with large vacancies, similar to the structure suggested for liquid NaCl by Urakawa *et al* [7]. The average coordination number of iodine in the high-pressure phase of liquid AgI is therefore larger than four but smaller than six, i.e. five.

In conclusion, liquids are not just amorphous phases as commonly believed. At closer inspection, they exhibit interesting local structures resembling those of the solid state. The pioneering work by Arima *et al* [11] and their predecessors has convincingly demonstrated that studies of liquid polymorphism and liquid–liquid phase transitions represent important research fields, where many interesting phenomena are awaiting exploration. Further studies along these lines will certainly shed light on the phase behaviour of matter in the non-crystalline state.

References

[1] Cotterill R 1985 *The Cambridge Guide to the Material World* (Cambridge: Cambridge University Press) pp 37–52
[2] Sciortino F 2005 *J. Phys.: Condens. Matter* **17** V7
[3] Poole P H, Sciortino F, Essmann U and Stanley H E 1992 *Nature* **360** 324
[4] Tanaka H 2000 *Phys. Rev.* E **62** 6968
[5] Cotterill R M J and Madsen J U 2006 *J. Phys.: Condens. Matter* **18** 6507
[6] Kurita R and Tanaka H 2005 *J. Phys.: Condens. Matter* **17** L293
[7] Urakawa S, Igawa N, Shimomura O and Ohno H 1999 *Am. Mineral* **88** 341
[8] Katayama Y, Mizutani T, Utsumi W, Shimomura O, Yamakata M and Funakoshi K-I 2000 *Nature* **403** 170
[9] Katayama Y, Inamura Y, Mizutani T, Yamakata M, Utsumi W and Shimomura O 2004 *Science* **306** 848
[10] Monaco G, Falconi S, Crichton W A and Mezouar M 2003 *Phys. Rev. Lett.* **90** 255701
[11] Arima H, Ohtaka O, Hattori T, Katayama Y, Utsumi W and Yoshiasa A 2007 *J. Phys.: Condens. Matter* **19** 076104