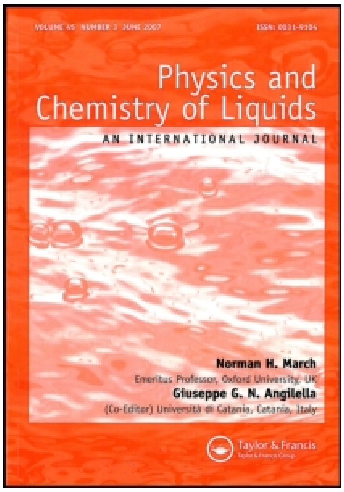

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Supercooled molecular liquids and the glassy phases of chemically bonded N, P, As, Si and Ge

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Glassy phases which have insulating character exist for a variety of monatomic species. By contrast, until recently, it has been possible to make bulk metallic glasses (BMG) by vitrification only for multicomponent systems. After a relatively brief summary on supercooling of a few molecular liquids, we review some of the recently reported results on molecular assemblies of the series N, P, As and amorphous Si and Ge. Based on these results, we suggest that the transition metals with their directional bonding might be suitable candidates for the production of BMG by vitrification.

Keywords: glassy phases; molecular liquids; supercooling

1. Background and outline

While the physical properties of liquids in their equilibrium state are fairly well understood [1], it is true to say that in the supercooled state there is still a lack of such deep understanding. A supercooled liquid is assumed to be a glass if its viscosity is greater than 10^{12} Pa s. The glass transition, characterised by the glass transition temperatures, T_g, is a second-order phase transition. There have been many studies, both experimental and computational, investigating the structure of supercooled liquids. These investigations have shown that supercooling liquids can result in metallic or insulating glasses, polymeric solids or amorphous phases. The factors influencing the type of structures include the detailed nature of the interatomic interactions as well as the liquid density and cooling rates. Two examples demonstrating these are given below.

Recently, Baran *et al.* [2] carried out infrared spectroscopy and differential scanning calorimetry measurements to obtain further information concerning the structural organisations in supercooled liquid 2-biphenylmethanol (2BPM). They found that near the liquid–glass transition, T_g, structural organisation was present in both the glass phase and the liquid phase. They also observed large-scale density fluctuations near T_g as well as

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the phase separation of a one-component liquid to a two-component phase. One conclusion of their work was that these experimental findings are consistent with the predictions of the model of Tanaka [3]. This model is based on the concept that there always exists two competing orderings in the liquid: namely density ordering and bond ordering. Short-range bond ordering can be expected to lead to the formation of stable, locally favoured structures, whose symmetry is often not consistent with crystallographic requirements. In contrast, density ordering leads to crystallisation.

In a similar vein, Ma and Lai (ML) [4] conducted molecular dynamics (MD) simulation studies on the supercooled molecular liquid of diatomic nitrogen. In their MD simulations, ML considered 500 N_2 molecules in a cubic cell. The interaction potential between pairs of atoms on different molecules were taken to have a Lennard-Jones (LJ) form, while each N_2 molecule was modelled as a rigid dumbbell. From their simulations, ML presented specific results for the pair correlation function $g_m(r)$ for the molecular centres. The LJ potential with $e/k_B = 37.2\,\mathrm{K}$ was taken as the reduced unit of temperature T below. Then, for the pair function $g_m(r)$, ML observed a two-stage change at the first maximum position $r_{\max}$ of $g_m(r)$. In the temperature range $1.8 > T > 0.8$, these workers emphasised that $g_m(r)$ gradually increased in height, signalling a slow-down in the translational motion of the molecules, and for $T < 0.8$, $g_m(r)$ remains almost unchanged, except that the left-hand side of $g_m(r)$ develops a well-defined shoulder. To summarise the findings of ML, their detailed structural studies of the supercooled liquid modelling of molecular nitrogen led them to stress the role of molecular rotations for $T < 0.8$ and to note the physical implication that the orientational degree of freedom has dominated the entropy contributions in the distribution of molecules. This has the effect of playing a role in arresting structural transformations.

With this brief background on supercooled molecular liquids, the outline of this article is as follows. Section 2 compares and contrasts the behaviour of insulating and metallic glasses. In particular, it is emphasised that while some eight or more monatomic insulating glasses exist, there is (until recently) no known counterpart for bulk metallic glasses (BMG), all cases being of multicomponent form. Section 3 then sets out some of the results of investigations carried out on the amorphous phases of the nitrogen group of molecules, followed, in less detail, with that carried out on S and Se. In Section 4, we turn our attention to Si and Ge, which have been the subject of much investigation, with Ge possibly providing the first example of monatomic metallic glass. Finally, in Section 5, we summarise the results and indicate some directions for future studies which should prove fruitful.

2. Contrasts between insulating and metallic glasses

In this section we highlight the question which motivated this study: namely as to why, while known (until recently) metallic glasses are multicomponent in character [5], some eight or so insulating monatomic glasses are already well known.

Bulk metallic glasses (BMG) formed from liquid tend to be alloys with three to five metallic components and are dense with small free volumes and viscosities [6]. Close to the crystalline state, the high packing density leads to a propensity to form short-range ordered phases, which together with slow crystallisation kinetics increase the probability of forming glasses. The C-shape in the phase diagram given in Figure 1 demonstrates the competition between the driving force for crystallisation and the slowing of the kinetics of the atoms.

BMG require multicomponents to avoid crystallisation during normal cooling. This can be understood by noting that glasses are formed when crystal nucleation rates are slow or by slowing the diffusivity of atoms. The presence of multicomponents helps to achieve this.

In contrast to multicomponent glasses, the observation that monatomic glasses tend to be insulators suggests that for monatomic liquids, annealing would result in the element undergoing a metal–insulator transition (MIT).

3. Amorphous phases of the nitrogen and sulphur group of materials, including pressure-dependent properties

3.1. *The nitrogen group*

3.1.1. *Phase diagram for N_2*

We begin by summarising some recent first principles MD simulations on compressed nitrogen. Mukherjee and Boehler [7] observed a sharp drop in the slope of the melting curve (dT/dP) above 50 GPa and attributed it to a first-order liquid–liquid polymer transition. They concluded that pressure transforms molecular N_2 to a chain-like polymeric form. More recently, Boates and Bonev [8] summarised the results of their first principles MD simulation of nitrogen in a proposed phase diagram, which is redrawn in Figure 2. It shows a first-order phase transition from molecular to polymeric liquid nitrogen which occurs at about 88 GPa. Also shown are the high-pressure polymeric solid phases, labelled 'amorphous N'. It is important to note that without the pressure investigation, one would have concluded that an assembly of N_2 molecules at atmospheric pressure would preclude the existence of an amorphous phase at high pressure.

3.1.2. *Polymeric phosphorous*

Turning next to the P_2 materials, it is of some relevance to note, first of all, that elemental phosphorous does not exist in nature. It is prepared commercially by heating phosphate ores with sand (SiO_2) and coke in an electric furnace. Elemental P exists in white, red and

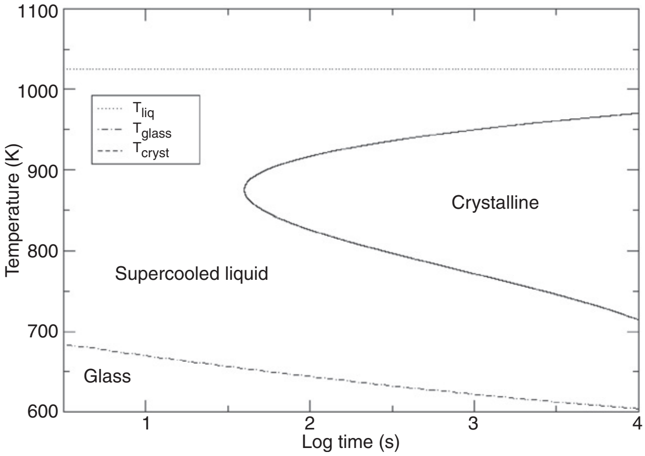

Figure 1. A schematic phase diagram of supercooled liquids. Redrawn from [6].

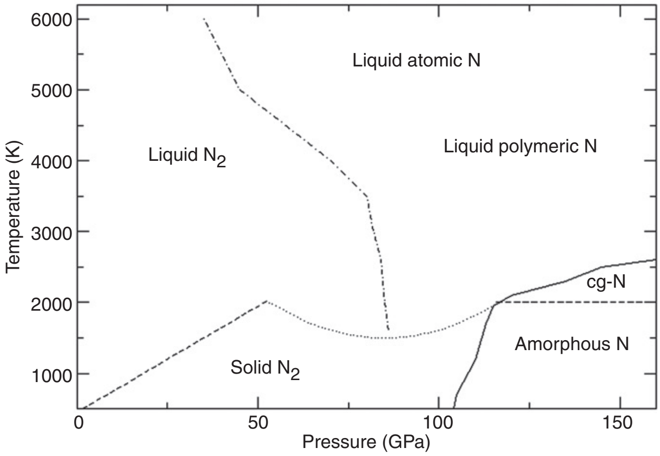

Figure 2. Phase diagram for N_2 assemblies. Redrawn from [8].

black allotropic forms. Black P is similar in structure to graphite and is the most stable of these forms. Pure white phosphorous can be prepared in a cubic crystal structure, with a unit cell containing 56 P_4 tetrameric molecules. We believe it is relevant to this consideration of amorphous elemental P (red phosphorous) to note the fairly recent work of Katayama *et al.* ([9], with earlier references given there) on a first-order liquid–liquid phase transition in phosphorous (see also the review by Angilella *et al.* [10]). In [9], an X-ray diffraction observation of a liquid–liquid transition in phosphorous, involving an abrupt, pressure-induced structural modification between two distinct liquid forms is reported. In addition to a known form of liquid P, which is a molecular liquid built from tetrahedral P_4 molecular (see also [11] for dynamical properties), Katayama *et al.* [9] found a polymeric form at pressures above 1 GPa (see also the theoretical study by Hohl and Jones [12]). They were able to provide the experimental evidence that the liquid–liquid phase transition is first order.

Zaug *et al.* [13] characterised the nature of the medium range order in red phosphorous compressed up to 6.3 GPa by X-ray diffraction. They found that the pressure dependence of the ordering could be qualitatively described by a void distribution function. Senda *et al.* [11] carried out *ab initio* MD simulations aimed at understanding the dynamical properties of P and confirmed the transition from molecular P_4 molecular liquid to the polymeric liquid phase.

3.1.3. *As rings and polymers*

By appealing to quantum chemical calculations, Rodionov *et al.* [14] were able to associate the formation of amorphous As with a random network structure with the formation of As_8 dimers, which in turn gave rise to the polymeric liquid form.

3.2. *Some comments on S and Se*

There has been little recent work done on the group-VI materials. Stolz *et al.* [15] carried out diffraction experiments on sulphur and gave a conclusive demonstration that an

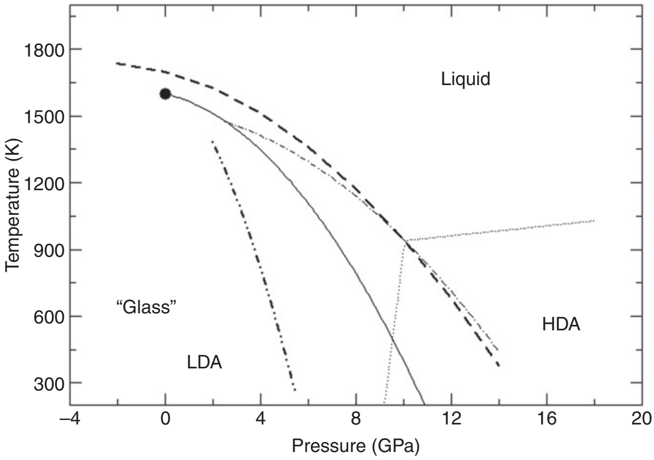

Figure 3. Phase diagram for Si. Redrawn from [20].

amorphous phase of S existed, having the form of a translucent glass. They also suggested that the liquid polymeric phase of S shows a higher local coordination than that in the molecular ring liquid phase. Similar findings were also observed for Se by Popov [16].

4. Metallic liquids Si and Ge: amorphous forms prepared via silane and germane

The amorphous phases of silicon (a-Si) and germanium (a-Ge) might be thought, at least in principle, to be accessible via supercooling liquid metal Si and liquid metal Ge, respectively, these liquids having four conduction electrons per atom, as known from Hall measurements. However, Street [17] observed 'amorphous Si cannot be prepared by quenching from the melt, and is usually made by vacuum evaporation or by the slow discharge of silane'. We expect that the difficulty is, at least partially, connected with the fact that as stressed above, liquid Si is a metal (though with remnants of chemical bonding remaining) with 4 conduction electrons per atom, and thus one must pass through a MIT in order to reach the amorphous counterpart.

In sharp contrast, Greaves *et al.* [18], in their review on amorphous As (in the N, P, etc. group considered earlier), set out in their Table 3 six different ways of producing this structurally disordered solid. We emphasise, however, that for the monatomic glasses cited in this article strong chemical bonding occurs, and it is this element that is quite crucial in the formation of such glasses. Even with directional *d*-bonding in a transition metal like Ni, it has not, to date, proved possible to make a monatomic metallic glass. Returning briefly to Si and Ge, we have already stressed that: (a) in these liquids, both materials are quadrivalent metals; (b) in the amorphous phase they are well described structurally by a continuous random network model [19]; and (c) until very recently, the glassy phases were obtained from silane and germane. Point (c) has been developed in recent studies by Deb *et al.* [20] and by Hedler *et al.* [21]. In particular, in Figure 3 we have redrawn results from [20] showing a calculated temperature–pressure diagram of Si in the stable and metastable crystalline and amorphous states.

We record the facts established by Deb *et al.* [20], using compression measurements on films of porous Si, which contains nanometre-sized domains of diamond structured material. For pressures exceeding 10 GPa, they observed pressure-induced amorphisation. Furthermore, by means of Raman spectroscopy measurements, they demonstrated that the high-density amorphous (HDA) state obtained by this process transforms to a low-density form of amorphous (LDA) Si on decompression. From Figure 3 we note that the glassy state LDA exists 700° or 800° below the melting curve. Such an immense degree of undercooling of liquid Si indicates why earlier workers [17] claimed that one could not produce amorphous Si by quenching from the melt.

Returning briefly to the melting curve under pressure, the slope of this curve is given by:

$$\frac{\partial p}{\partial T} = \frac{\Delta S}{\Delta V} = \frac{S_L - S_S}{V_L - V_S},$$

where L and S subscripts denote liquid and solid, respectively. In the dense liquid metallic Si, $V_L < V_S$, where $S_L > S_S$, and hence from the above equation, the slope of the melting curve is clearly negative, in accordance with Figure 3. We expect entirely similar considerations to hold for the metallic curve of the diamond phase of Ge.

That amorphous Si exhibits a glass transition is verified by the subsequent work of Hedler *et al.* [21]. They report the glass transition temperature for a timescale of 10 ps to be around 1000 K, some 700 K below the melting temperature of diamond-like Si at atmospheric pressure. Hedler *et al.* [21] report that their results support the view that liquid polymorphism is a general phenomenon in tetrahedral networks.

By appealing to the insights gained by ND simulations, Bhat *et al.* [22] were able to create the conditions for the vitrification of metallic liquid germanium. This is the first known instance of a BMG.

5. Summary and future directions

Though the available work on supercooled molecular liquids is presently quite limited, two relevant contributions, one experimental on 2BPM and other on a computational study on liquid nitrogen have been summarised. The model of Tanaka [3] seems particularly useful for interpreting the data on 2BPM. More experimental work on the simpler insulating supercooled liquids (e.g. Se and/or S) should prove instructive in the future.

Turning to the glassy state, we have seen that the degree of supercooling possible on liquid metallic Si and Ge is a huge fraction of the melting temperatures of the diamond phases of these two materials. We have expressed the viewpoint that the MIT required to pass from the metallic liquids to the amorphous solids may provide a reason for the difficulty in trying to produce glassy phases of both Si and Ge from the melt. The additional richness of the phase diagram of molecular assemblies in the N, P, etc. group comes from the use of pressure as an additional variable.

Finally, no monatomic metallic glasses have presently been produced: the many existing disordered solids without long-range order being multicomponent assemblies. It is true that, in general, the viscosity of pure liquid metals is substantially lower than that of monatomic liquid insulators and hence the approach to the glassy state is less accessible. But for a monatomic metallic glass, one presumably will need directional bonding. Thus, we propose the transition metals to be likely candidates for BMG as well as (but now experimentally less accessible) the heavy alkalis, Rb and Cs, which lower their coordination numbers to about two, as one goes along the liquid–vapour coexistence curve towards the critical point.

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