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Locally preferred structure and frustration in glass-forming liquids: a clue to polyamorphism?

G Tarjus¹, C Alba-Simionesco², M Grousson^{1,3}, P Viot¹ and D Kivelson³

¹ Laboratoire de Physique Theorique des Liquides, Université Pierre et Marie Curie,
4 Place Jussieu, Paris 75005, France

² Laboratoire de Chimie Physique, Bâtiment 349, Université Paris Sud, Orsay 91405, France

³ Department of Chemistry and Biochemistry, University of California, Los Angeles,
CA 90095, USA

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Abstract

We propose that the concept of liquids characterized by a given locally preferred structure (LPS) could help in understanding the observed phenomenon of polyamorphism. ‘True polyamorphism’ would involve the competition between two (or more) distinct LPSs, one favoured at low pressure because of its low energy and one favoured at high pressure because of its small specific volume, as in tetrahedrally coordinated systems. ‘Apparent polyamorphism’ could be associated with the existence of a poorly crystallized defect-ordered phase with a large unit cell and small crystallites, which may be illustrated by the metastable glacial phase of the fragile glass-former triphenylphosphite; the apparent polyamorphism might result from structural frustration, i.e., a competition between the tendency to extend the LPS and a global constraint that prevents tiling of the whole space by the LPS.

1. Locally preferred structures in liquids

Polyamorphism is the coexistence of condensed phases of identical chemical composition that appear amorphous, i.e., with no obvious long-range order. This is to be distinguished from those situations such as concentration-driven transitions in multi-component liquids or from gas–liquid coexistence. This puzzling phenomenon, not to be confused with the long-recognized polymorphism between phases of different symmetries (be they crystals, liquid crystals, plastic crystals, etc), has recently attracted much attention [1–9]. It has been observed in liquids at low temperature, usually in the vicinity of the glass transition. In this paper, we suggest that the concept of *locally preferred structure* (LPS) in liquids is central to understanding polyamorphism. A LPS can be loosely defined as an arrangement of molecules which, in a given region of the pressure–temperature phase diagram, minimizes some local free energy.

Most recorded examples of polyamorphism are tetrahedrally coordinated systems, such as H₂O, SiO₂, or GeO₂ [1, 2, 4, 5, 8, 9], in which low-temperature coexistence of amorphous

phases is observed under sufficiently high pressure. This phenomenon can be rationalized in terms of a *competition between different LPSs*. This is best illustrated by the case of water, a system that has been thoroughly studied by Stanley and his co-workers [5, 10, 11].

Following the picture put forward by Stanley and co-workers [5, 11], liquid water has been characterized schematically by two kinds of LPSs that are favoured in different regions of the pressure–temperature phase diagram. This can be seen by considering the arrangements of five-molecule clusters, also known as Walrafen pentamers. In one LPS, two neighbouring pentamers are oriented relative to each other so as to form two linking hydrogen bonds; this is a low-energy, but open (large-specific-volume) structure, and due to the directional nature of the H bonding, it has a low entropy. In the other arrangement, the two pentamers come closer to each other, but are no longer bonded: the structure is then better packed (small specific volume) and has a higher entropy, but at the expense of a higher energy. The former structure is locally favoured at low pressure whereas the latter is locally preferred at high pressure. As has been shown via a description of the intermolecular interactions in terms of an effective, spherically symmetric pair potential [12], the competition between two such LPSs may lead to a *bona fide* phase transition between a low-density liquid and a high-density liquid in the pressure–temperature diagram. Similar reasoning could apply to glass-forming liquids such as SiO₂ and GeO₂ whose LPS is a four-coordinated cation at low pressure and a six-coordinated one at high pressure [4]. Another extreme example is also provided by the polyamorphism of liquid phosphorus, one liquid phase being characterized by a local organization formed by P₄ molecules and the other one being a polymeric-like phase of phosphorus atoms [7].

We suggest here that in some systems, in addition to the alternative LPSs, there can also be a competition associated with the inability of a given LPS to tile space, i.e., with *structural frustration*. In this case the polyamorphism may incorporate a very poorly developed mesoscopic order and so might be described as ‘apparent polyamorphism’. Such ‘apparent polyamorphism’ appears to be illustrated by triphenylphosphite (TPP).

2. Apparent polyamorphism in TPP

TPP is one of the most fragile glass-formers, i.e., one for which the increase of viscosity and relaxation time with decreasing temperature is most dramatic. A new metastable phase, denoted as the ‘glacial phase’, has recently been observed at atmospheric pressure [3]. This phase transforms to and from the supercooled liquid and is metastable with respect to the normal crystal [3, 13–15].

Since its discovery, the glacial phase of TPP has been studied by many groups and by means of a variety of experimental techniques [3, 14–21]. A number of conjectures have been proposed concerning the structure of the glacial phase, and most of them describe the phase as amorphous. The reason for this is that in normal x-ray or neutron scattering, the structure of the glacial phase does not show well defined Bragg peaks as observed in crystalline materials. This is illustrated in figure 1, where we display the result of a series of neutron scattering experiments carried out both on the D7 spectrometer of the ILL in Grenoble (in the range of wavevector Q from 0.1 to 2.5 Å⁻¹) and on the small-angle spectrometer PAXE at the LLB in Saclay (in the Q -range between 0.01 and 0.12 Å⁻¹) [19]. The static structure factor $S(Q)$ of the glacial phase is distinct from that of the liquid, the glass, and the crystal, and, although the peaks are somewhat sharper than those of the liquid and the glass, they are much broader than those of the crystal. However, what clearly distinguishes the structure factor of the glacial phase is an unusual feature at small Q s, a feature that is visible in the experiment on D7 but shows up more clearly in the small-angle scattering data: in sharp contrast with the $S(Q)$ s of the other phases, the $S(Q)$ of the glacial phase has a pronounced shoulder for $Q < 0.2$ Å⁻¹,

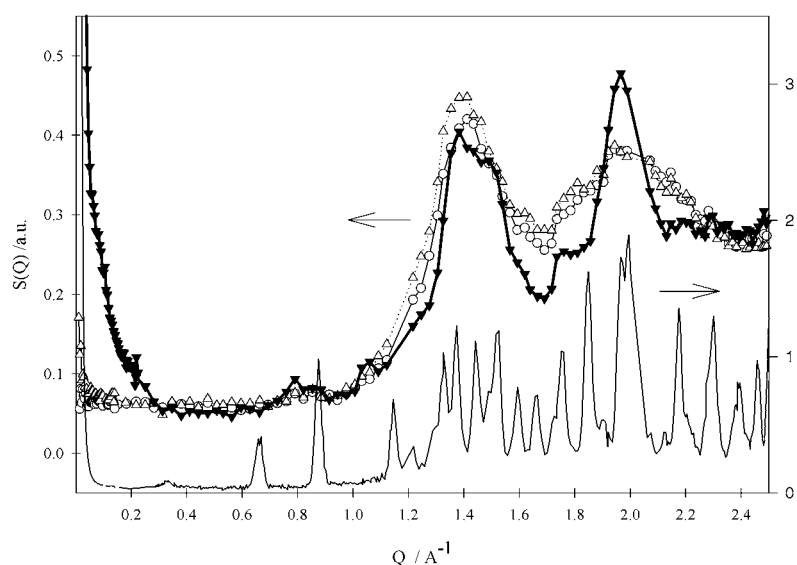


Figure 1. Combined low- and wide-angle neutron scattering data (in arbitrary units) for the static structure factor $S(Q)$ of TPP in its different phases: supercooled liquid (open triangles, $T = 218$ K), glass (open circles, $T = 183$ – 184 K), crystal (thin continuous curve, $T = 270$ and 183 K at low Q), and glacial phase (filled triangles, $T = 225$ K) phases. For clarity the $S(Q)$ of the crystal is shifted downwards, and the associated scale is on the right. The melting temperature is 295 K, the glass transition temperature of the supercooled liquid is around 195 K, and the liquid–glacial transition temperature is around 240 K.

and, in addition, the scattered intensity keeps rising very steeply at the lowest Q s in a manner that is compatible with the Porod Q^{-4} -law observed for powders of crystalline materials: see figure 2.

By analysing the low- Q scattering data described above (and shown in figure 2) as the superposition of a Porod tail and a broad peak centred at $Q_p \simeq 0.07 \text{ \AA}^{-1}$, standard arguments used in studying polycrystals indicate that the ‘apparently amorphous’ glacial phase could be a powder of an unusual crystalline material characterized by a large unit cell of typical size $2\pi/Q_p = 80 \text{ \AA}$, with small polydisperse crystallites of about 100 – 250 \AA [19]: this is sketched in figure 3. The premelting phenomenon reported in [15] is also consistent with this picture of a crystalline structure with small crystallites. In such a ‘poorly crystallized’ material, the small number of unit cells contained in the crystallites, the polydispersity of the crystallites, the rotational disorder, and strain effects could all combine to explain the absence of well defined Bragg peaks, thus resulting in a structure that at first glance looks amorphous.

What then is the physical origin of this ‘apparent’ polyamorphism at atmospheric pressure?

3. Structural frustration

If one accepts the premise that there exists a LPS in a liquid (say, at atmospheric pressure so that competition between two different LPSs is unlikely), one must worry about a competition between a tendency to extend the LPS and a global constraint. It has been suggested that *structural frustration*, i.e., the impossibility of tiling the whole space by periodically replicating the LPS, might be ubiquitous in glass-forming liquids [22–25]. One manifestation of frustration can be perceived in the fact that liquids restructure and undergo a strong first-order transition

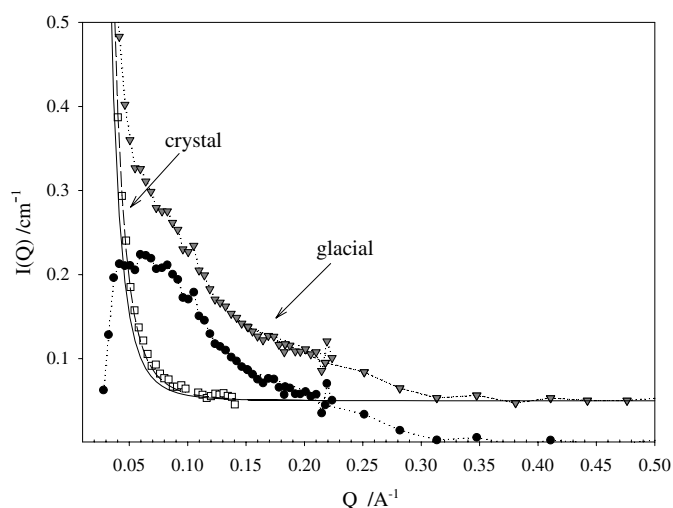


Figure 2. The low- Q region for the crystal (open squares) and the glacial phase (filled triangles): it shows the Porod Q^{-4} -regime (plus a constant background) for the crystal (full curve) and the glacial phase (dashed curve), as well as the distinct shoulder in the glacial phase data; this latter can be interpreted as the superposition of a Porod contribution and a broad peak (filled circles) that is indicative of structural organization on a mesoscopic scale (see also [19]).

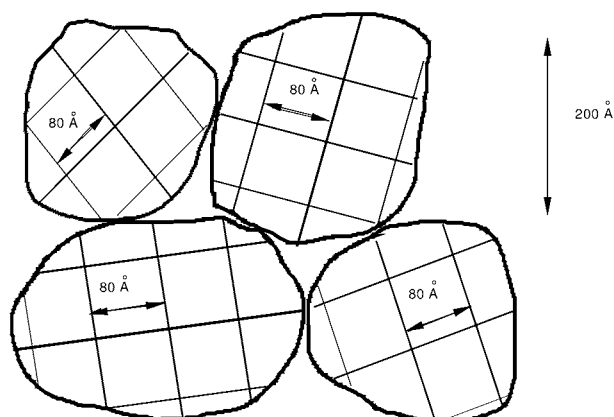


Figure 3. A speculative picture of the structure of the glacial phase of TPP: a poorly crystallized material with a large unit cell (80 Å), small polydisperse crystallites (typically, 200 Å), and interstitial liquid.

to a crystal whose local structure is different from the LPS; this transition occurs in order to avert the increasing strain that develops as the temperature decreases and the LPS grows. The frustration may also play a dominant role in glass formation.

The canonical example of structural frustration is provided by single-component systems of spherical particles interacting via simple pair potentials, and the phenomenon is best illustrated by comparing the situations encountered in two and three dimensions. In two dimensions, the arrangement of discs that is locally preferred is a hexagon of six discs around a central one, and this hexagonal structure can be extended to the whole space to form a triangular lattice. In three dimensions, as was shown long ago by Frank [26], the LPS of spheres is an

icosahedron, but the fivefold rotational symmetry of the icosahedron is incompatible with translational periodicity, and formation of an icosahedral crystal is precluded. Frustration is thus absent in two dimensions, but present in three dimensions. As a result, crystallization is essentially continuous in the former case, and neither supercooling of the liquid nor glass formation are possible. On the other hand, crystallization of spheres in three dimensions is a strongly first-order transition that involves a restructuring of the local order to form the face-centred-cubic (or the hexagonal-close-packed) order that can tile space periodically. Studies of structural frustration for spheres in three dimensions have been further developed to describe metallic glasses [22, 24, 27].

Two points are worth stressing. First, frustration can be relieved by ‘curving’ the regular three-dimensional Euclidean space, so that an ideal world without frustration is generated where periodic tiling by the LPS (e.g., icosahedral order) is possible. Forcing the ideal order into the real world leads to the formation of defects (disclination lines in the example of spherical particles in three dimensions) and to the growth of a strain free energy that opposes the extension of the LPS. Secondly, back in the Euclidean space, ordered phases can still be formed which are different from the usual and more stable crystal in that their structure is partly based on the LPS. The system can indeed get around frustration and form ‘defect-ordered phases’ in which the defects themselves form periodic structures with long-range order, as in the Frank–Kasper phases [22, 24]. In real metallic systems such phases are only observed in alloys made of two or more components, but a recent simulation study has shown that a one-component atomic liquid whose particles interact with a spherically symmetric potential that favours local icosahedral order can form a metastable ‘defect-ordered phase’ [28]; this latter is a dodecagonal quasi-crystal that is essentially a layered phase with translational periodicity in one direction but quasi-periodic, icosahedral-like order in the transverse directions.

The example of spheres and their local icosahedral packing symmetry has been introduced only for illustration. More generally, one can envisage competition between the tendency to extend the LPS and the global constraint embodied in the structural frustration as an intrinsic feature of all liquids. A coarse-grained description should thus be sufficient, and it has been argued that a minimal model could be built, based on competing effective interactions acting on very different length scales [23, 25]: a short-ranged ordering interaction, that describes the tendency to extend the LPS and leads to a continuous transition to an ideal crystal in the absence of frustration, and a weak but long-ranged ($1/r$) frustrating interaction that generates a super-extensive strain free energy opposing the growth of the ideal structure. It has been recently shown by means of model calculations that such ingredients do indeed lead to a strong slowing down of the relaxations as the temperature is lowered, and that the characteristics of this slowing down (super-Arrhenius activated temperature dependence of the primary relaxation time and non-exponential decay of the relaxation function) are similar to those observed for fragile glass-forming liquids [29]. As in liquids, glassiness is self-generated and does not result from the introduction of quenched spin-glass-like randomness or of dynamical constraints. An important property of these models is that by varying the frustration strength, i.e., the relative amplitude of the long-ranged frustrating interaction, one can span the whole range of glass-forming behaviour, from strong (Arrhenius T -dependence) to very fragile (marked super-Arrhenius T -dependence); the less frustrated a system, the more fragile it is.

4. Frustration and defect-ordered phases

It has been shown that, generically, frustration does indeed lead to formation of low- T defect-ordered phases [30]. The situation is schematically illustrated in figure 4(a) for the Coulomb frustrated Ising ferromagnet [30]. In the frustration–temperature diagram, there is a line of

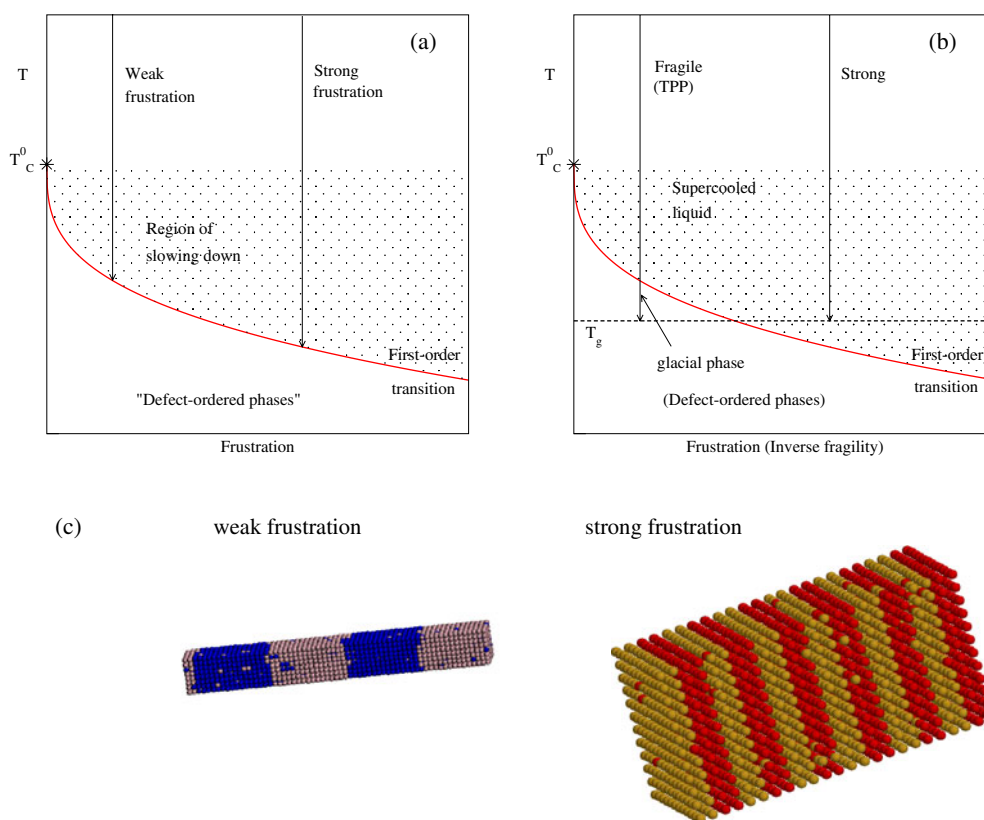


Figure 4. (a) A schematic temperature–frustration phase diagram of frustrated models with a long-range frustrating interaction. The defect-ordered phases are illustrated in (c). (b) Transposition of the temperature–frustration phase diagram to a temperature–fragility diagram for glass-forming liquids. A liquid is characterized by a given frustration and a given fragility; the smaller the former, the larger the latter. The dotted line represent the hypothetical position of the experimental glass transition temperature that may come above or below the line of transition to the defect-ordered phases. (c) Low-temperature configurations of the Coulomb frustrated Ising model obtained by Monte Carlo simulation for weak and strong frustration [29].

(This figure is in colour only in the electronic version)

first-order phase transition from the high- T disordered phase to the low- T defect-ordered phases. (Recall that the usual crystal, which is more stable than the liquid and the defect-ordered phases below the melting point, is not included in this picture.) The region of strong slowing down is above the transition line. For the Ising model considered here for illustration, the defect-ordered phases at low frustration are lamellar phases whose period increases as frustration decreases: see figure 4(c). Stated differently, the size of the unit cell (here, as in the dodecagonal quasi-crystal, there is a one-dimensional periodic pattern and ideal order in the transverse directions) increases as frustration decreases, and thus, as discussed above, as fragility increases. The details, e.g., the microscopic characterization of the ideal order, may be model dependent, but the overall trends are robust.

Transposing the above results to glass-forming liquids, a liquid being characterized by a given value of the frustration strength, one may speculate that fragile glass-formers would tend to form low- T defect-ordered phases with large unit cells: see figure 4(b). It is possible

that due to their large unit cells and the fact that they appear in the viscous liquid regime, these phases would be poorly crystallized, i.e., appear as powders with small polydisperse crystallites when formed upon decreasing the temperature. This leads us to suggest that the ‘apparently amorphous’ glacial phase of fragile TPP is a frustration-induced defect-ordered phase with a large unit cell. Note that the possibility of observing such phases depends on a non-universal property, the relative position of the transition temperature T_{DO} with respect to the glass transition temperature T_g . Only if T_g is less than T_{DO} can a defect-ordered phase be experimentally obtained, and this may be a rare situation.

5. Conclusions

We have proposed that characterizing liquids by their LPS could help in understanding the observed phenomenon of polyamorphism. ‘True polyamorphism’ would involve the competition between two (or more) distinct LPSs, one favoured at low pressure because of its low energy and one favoured at high pressure because of its small specific volume, as in tetrahedrally coordinated systems. ‘Apparent polyamorphism’ that we associate with the existence of a poorly crystallized defect-ordered phase with a large unit cell and small crystallites could result from structural frustration, i.e., a competition between the tendency to extend the short-ranged LPS and a long-ranged global constraint that prevents tiling of the whole space by the LPS. The fragile glass-former triphenylphosphite, in which a first-order transition is observed between the supercooled liquid and the mesoscopically structured glacial phase, may be one example of such ‘apparent polyamorphism’. Although some of these ideas have been previously considered, this is the first time that they have been incorporated within a consistent picture.

Finally, it is tempting to speculate that the low-density ‘amorphous’ phase of water, a phase that shows none of the canonical low- T features of truly amorphous glasses (excess in the density of states at low frequency over the value expected from harmonic vibrations, and violation of the Debye T^3 -law due to the presence of low-energy two-level systems) [31], could also be only apparently amorphous, thereby adding more to the ‘puzzling behaviour of water at very low temperature’ [11].

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