ELSEVIER

Computational Materials Science 4 (1995) 373–382

COMPUTATIONAL MATERIALS SCIENCE

Amorphous polymorphism [1]

Peter H. Poole [a,b,*], Tor Grande [a,c], F. Sciortino [d], H.E. Stanley [e], C. Austen Angell [a]

[a] Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA

[b] Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

[c] Department of Inorganic Chemistry, Norwegian Institute of Technology, N-7034 Trondheim, Norway

[d] Dipartimento di Fisica, Universita' "La Sapienza", Piazzale Aldo Moro, 00185 Roma, Italy

[e] Center for Polymer Studies and Physics Department, Boston University, Boston, MA 02215, USA

Received 3 July 1995

Abstract

Recent studies of amorphous solid materials have revealed the possibility that more than one distinct amorphous phase may be formed from the same substance. In analogy with the phenomenon of crystalline polymorphism, this behavior has been termed "amorphous polymorphism". We review the experimental manifestation of amorphous polymorphism, especially in tetrahedrally coordinated materials such as H_2O and SiO_2. Guided by computer simulation results on these substances we show how a thermodynamic explanation of these phenomena is possible, specifically that amorphous polymorphism occurs in substances where the thermodynamic behavior of the liquid state exhibits liquid–liquid phase separation, or a tendency toward it. We identify a number of systems which may also display amorphous polymorphism, and emphasize the central role to be played by computer simulation in the elucidation of this phenomenon.

1. Introduction

Many pure substances are known which exist in more than one crystal structure, or crystal polymorph [1]. The diamond and graphite polymorphs of carbon are a classic example. Each crystal polymorph has a well-defined region of thermodynamic stability in the phase diagram of the substance, and first-order phase transitions from one polymorph to another are observed through changes in temperature T or pressure P. In such phase transitions, the density ρ (or equivalently the specific volume V) is usually a reliable order parameter since the different atomic structures of each polymorph usually result in distinct values of ρ.

In this paper we will address the possibility that an analogous phenomenon occurs in amorphous solid materials, or glasses. The reasons to consider such a possibility are two-fold.

(i) Experimentally, it is known that certain substances in their amorphous solid form can occur in more than one distinct state [2,3]. The state observed depends on the particular thermodynamic conditions and preparation route employed, and the resulting "amorphous polymorphs" [4] exhibit markedly different bulk properties and atomic structure. In materi-

* Corresponding author. Present address: Department of Applied Mathematics, The University of Western Ontario, London, Ontario N6A 5B7, Canada.

[1] Contribution to proceedings from a workshop on Glasses and the Glass Transition: Challenges in Materials Theory and Simulation, organized by the Center for Theoretical and Computational Materials Science at the National Institute of Standards and Technology. The workshop was held in Kent Island, Maryland, 16–18 February, 1995.

0927-0256/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0927-0256(95)00044-5

als where tetrahedral coordination dominates the local atomic structure (as in H_2O, SiO_2 and Si), abrupt transformations from one polymorph to another as a function of P or T have been reported [3,5–7]

(ii) Conceptually, amorphous polymorphism follows naturally from the possibility that first-order phase transitions occur in the *liquid* state of certain substances. By this we do not refer to *compositional* phase separation in multicomponent melts. Liquid–liquid phase transitions, in which *density* and not composition is the order parameter, have been reported experimentally in a number of substances [2], and predicted by a variety of theoretical treatments [8–15]. In the following we refer to this phenomenon as "liquid polymorphism" [16]. Glasses are often formed by quenching an equilibrium or supercooled liquid to a temperature below the glass transition temperature T_g [17]. Hence, in a case where two thermodynamically distinct phases of the liquid exist above T_g, two distinct amorphous solid states of the same substance can be prepared by separately quenching each liquid phase.

Despite the above considerations, there are numerous open questions and unresolved difficulties surrounding the phenomenon of amorphous polymorphism – including most notably the appropriateness of associating the experimental observations with a true thermodynamically-based polymorphism. Yet the observed mechanical and thermal properties of amorphous polymorphs suggest that a thermodynamic description of this phenomenon is possible. In the present paper, we first discuss some recent experimental observations of amorphous polymorphism. These results, combined with unique insights presently available only from computer simulations, demonstrate that amorphous polymorphism may arise in some systems because of an actual phase transition (or a tendency toward a phase transition) occurring in the equilibrium or supercooled liquid from which the glass forms. We find that such a description permits prediction of a range of systems in which amorphous polymorphism may be found, and we suggest how experiments and computer simulations can together be used to confirm such predictions.

2. Experimental observations of amorphous polymorphism

2.1. Al_2O_3–Y_2O_3

One of the most recently discovered examples of amorphous polymorphism is perhaps the most spectacular: Aasland and McMillan [2] have reported that after quenching the technologically important oxide system Al_2O_3–Y_2O_3, the amorphous solid product contained two distinct amorphous phases. Compositional phase separation is a well-known phenomenon in multi-component melts. However, in this particular experiment it was shown that the two phases arrested during quenching were *identical* in chemical composition, and were distinguished instead by different densities and atomic structures. This system apparently undergoes a liquid–liquid phase transition during quenching, after which each phase separately passes through its respective glass transition. The result was a sample in which spherical inclusions of one phase embedded in the other were clearly visible. (See Fig. 1 of Ref. [2].) Although the origin of this phenomenon in terms of the microscopic interatomic interactions is not understood, there clearly exists a thermodynamic driving force for a phase transition in which density (and not chemical composition) is the order parameter.

The behavior in the Al_2O_3–Y_2O_3 system is a revealing case. Two distinct glassy phases were prepared apparently through the vitrification of two distinct liquid phases. In this case, labeling the two glassy phases as amorphous polymorphs seems justified, since the supercooled liquids from which they apparently formed were themselves thermodynamically distinct liquid polymorphs. A schematic diagram showing how the coexistence curve of a liquid–liquid transition in a generic substance might relate to other thermodynamic features, and also to the glass transition, is shown in Fig. 1.

2.2. H_2O

Perhaps the best characterized case of amorphous polymorphism is found in H_2O. The first report of an amorphous solid form of H_2O appeared in 1935 [18]. After much experimental effort, it has become clear that several preparation routes (e.g., vapor deposi-

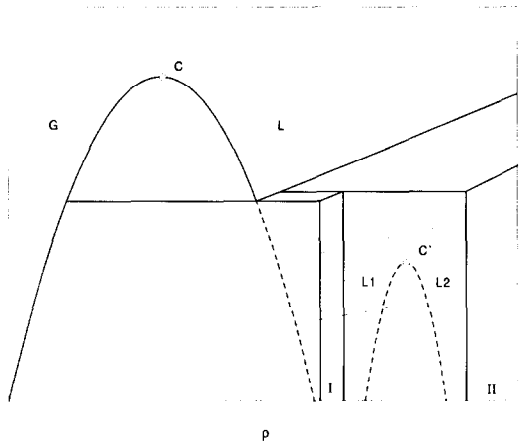

Fig. 1. Schematic T versus ρ coexistence curves of a hypothetical substance exhibiting liquid polymorphism. Labeled are the stability fields of the pure phases of the gas (G), the liquid (L) and two crystal polymorphs (I and II). The critical point C terminates the liquid–gas coexistence curve. The dotted lines represent metastable coexistence curves. C′ terminates a metastable coexistence curve separating two distinct phases of the supercooled liquid, L1 and L2. The two dot-dashed lines represent possible locations for the line of glass transitions in the supercooled liquid. If the lower T_g line occurs, liquid polymorphism will be directly observed in the supercooled liquid. If the higher T_g line occurs, explicit liquid polymorphism will not be seen, though amorphous polymorphism may still occur.

tion [18] and hyperquenching [19–21]) produce a well-defined amorphous solid material at ambient P, called "low-density amorphous" (LDA) ice. Furthermore, Mishima and co-workers [3] have shown that LDA ice undergoes a sudden transformation to a higher-density form when compressed at 77 K. This "high-density amorphous" (HDA) ice was found to be recoverable at ambient pressure, and distinct from the original (LDA) ice, both in its structure and density.

The first report of the densification of LDA ice into HDA ice upon compression was found to be sufficiently abrupt to motivate the authors to refer to this transformation as an "apparently first-order phase transition" [3]. Experimental P–V data [22] for this transformation are shown in Fig. 2a. The LDA–HDA ice transition is clearly visible in this data in the form of a rapid change in V over a small P range, resulting in a characteristic S-shaped curve.

The similarity of this transformation to some kind of thermodynamic phase transition was further supported by the behavior of HDA ice when heated at

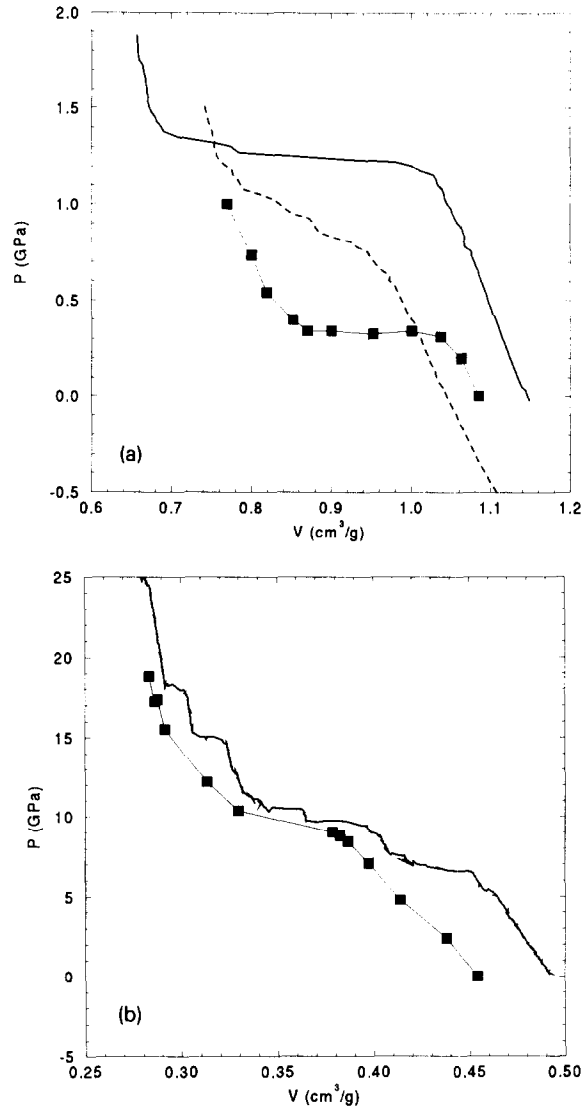

Fig. 2. (a) P versus V plots for compression of H_2O amorphous solid as observed in experiment at 135 K (■; data taken from Ref. [22]) and MD simulations at 80 K (ST2, solid line; TIP4P, dotted line). (b) P versus V plots for compression of SiO_2 amorphous solid as observed in shock compression experiments on fused silica (■; data taken from Ref. [36]) and MD simulations at 100 K (solid line).

ambient P. The HDA ice was observed to convert to LDA ice, establishing that the transformation from one amorphous ice to the other could be induced thermally, as well as through compression. Although significant hysteresis effects common in non-ergodic systems were observed, these observations are reminiscent of the path independence and reversibility that

occurs in equilibrium thermodynamic transitions. Extensive work [23,22] has established several other behaviors in this system consistent with the description of the transformations between the LDA and HDA ice in terms of a phase transition.

Yet clearly there are difficulties in understanding the observed behavior of the amorphous ices in the same way as the behavior of the Al_2O_3–Y_2O_3 system. First, there is the obvious problem that the liquid polymorphism observed in the case of Al_2O_3–Y_2O_3 does not occur in the behavior of equilibrium liquid H_2O for T greater than the melting point. Second, the experimental results on H_2O focus not only on the distinctness of the amorphous polymorphs, as in Al_2O_3–Y_2O_3, but also on the direct transformation of one amorphous polymorph to the other when $T < T_g$, a process not yet studied in Al_2O_3–Y_2O_3. The identification of the transformation of one amorphous ice directly to another as a "phase transition" suggests that concepts of equilibrium thermodynamics can be used. However, the language of equilibrium thermodynamics cannot be applied easily to amorphous solids, or to the changes observed in them as T and P change [17,24]. Amorphous solids are characteristically non-ergodic systems [25]. They are out of equilibrium with respect to the supercooled liquid from which they are quenched. They are also metastable with respect to the true equilibrium state, the crystal. Hence, an equilibrium concept like a phase transition technically has no meaning in the context of an amorphous solid. This is a severe complication, which casts doubt on the appropriateness of characterizing this phenomenon as any kind of thermodynamic phase transition.

Computer simulation investigations of amorphous solid H_2O have typically focussed on clarifying the microscopic origin of amorphous polymorphism in this material, and have elucidated the atomic displacements and local structural instabilities responsible for the abrupt changes observed between amorphous polymorphs [26,27]. However, as described in the next section, computer simulations have also directly addressed the thermodynamic difficulties described above.

3. Computer simulations of amorphous polymorphism

3.1. H_2O

The behavior in liquid Al_2O_3–Y_2O_3 raises the possibility that amorphous polymorphism is observed in the amorphous solid when the liquid state that exists at $T > T_g$ exhibits liquid polymorphism. If true, the equilibrium thermodynamic behavior observed above T_g in H_2O should show either this phase transition, or at least the characteristic supercritical behavior expected close to the onset of the phase transition. As stated above, the equilibrium thermodynamic behavior of liquid H_2O, though anomalous, does not unambiguously indicate any liquid polymorphism. However, the thermodynamic properties of supercooled H_2O are much less well known [28]. Experimentally, the study of supercooled H_2O is problematic because crystallization becomes difficult to prevent below −30°C at ambient P.

In this context, computer simulations have been found to be useful, in that system sizes and observation times can be studied for which crystallization will not interfere [29]. As a result, a wide range of thermodynamic states, spanning the behavior of both the supercooled liquid and amorphous solid, can be evaluated with relative ease and within the same methodological scheme. To this end, we also show in Fig. 2a the results of molecular dynamics (MD) computer simulations of two models of H_2O [30], respectively designated ST2 [31] and TIP4P [32]. The simulation protocol employed is described in detail in Refs. [30,33]. The experimental behavior of the amorphous ices is well reproduced in the computer simulation, as evidenced by the abrupt decrease in V observed upon compression.

In Fig. 3a the MD simulation results for the same H_2O model (ST2) are shown, but now describing the $P(V,T)$ equation of state (EOS) of the ergodic supercooled liquid [34,33]. The high T isotherms of P against V qualitatively reproduce the experimentally observed behavior of the equilibrium liquid. However, deep in the supercooled region the shape of the isotherms has changed, and qualitatively has the same S-shape found in the amorphous solid behavior.

Notably, such S-shaped isotherms also have the shape expected if the T considered is above, but in

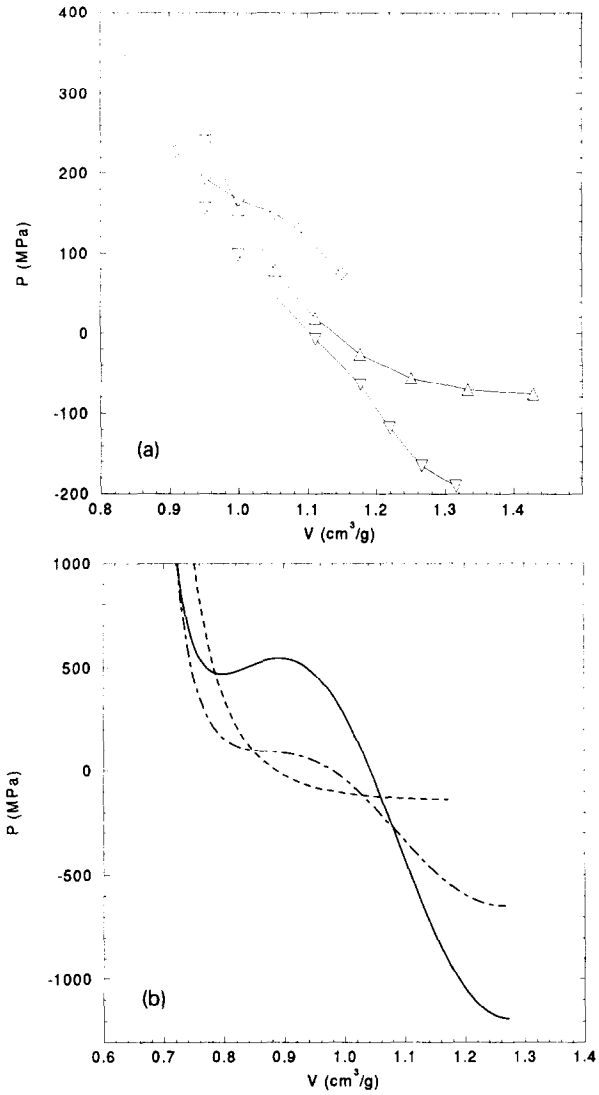

Fig. 3. (a) P versus V plots for simulated liquid H_2O (ST2 model), at T = 390 (△), T = 290 (▽) and T = 250 (◇). (b) Schematic P–V isotherms of a liquid displaying liquid polymorphism. The dashed line gives the behavior well above $T_{C'}$, the dot-dashed line is just above but near to $T_{C'}$, while the solid line exhibits the "van der Waals" loop expected below $T_{C'}$.

the vicinity of, a second-order phase transition. As in the case of a liquid–gas transition (as modeled by, e.g., the van der Waals equation), P–V isotherms take on the characteristic S-shape seen in Fig. 3 as a region of phase separation is approached from high T. The scenario suggested by the trend in the data of Fig. 3a is shown schematically in Fig. 3b. The phase transition itself occurs when the slope of the isotherm becomes zero for the first time, followed at lower T by a "van der Waals loop" as a coexistence gap appears between the densities of the now distinct phases. In simulations of the ST2 model, there is evidence that such a liquid–liquid phase transition is observed directly [34,35]. In the TIP4P model the trend in the P–V isotherms is the same, but a first-order phase transition is not observed due to prohibitively long relaxation times in the relevant range of T [33,35].

In any case, it is apparent that simulations can (i) reproduce the signature densification of the amorphous solid indicating amorphous polymorphism, and (ii) reveal behavior in the liquid state indicating, if not liquid polymorphism, then at least a trend in that direction. The liquid state behavior in Fig. 3 has not been confirmed experimentally because the appropriate EOS measurements have not yet been made under the degree of supercooling required. However, it is important to note that the prediction of Fig. 3 has been shown to be consistent with the properties of H_2O at higher T [34].

3.2. Other tetrahedral liquids and amorphous solids

The geologically important material SiO_2 is also dominated by tetrahedral coordination (at ambient P) and has also been studied in the amorphous solid form. Its experimental behavior under compression at well below T_g is shown in Fig. 2b [36]. The mechanical response of this amorphous solid has a form similar to that observed for amorphous ice, suggesting that this geological material is also a candidate for displaying amorphous polymorphism. MD simulations of SiO_2, both in the non-ergodic (Fig. 2b) and ergodic (Fig. 4a) regimes, support this view: the behavior is very similar to that found in the H_2O simulations [37,38]. (The simulation protocol for the SiO_2 data shown in the figures is given in Refs. [38,39].) Behavior strongly indicating amorphous polymorphism has further been observed in simulations of BeF_2 [40], in which the local atomic structure is also roughly tetrahedral at low P, but converts to a higher coordination under compression. Notably, this transformation was observed to be quasi-reversible under decompression.

While the nature of the interatomic bonds in SiO_2 and BeF_2 is different from the hydrogen bonds found

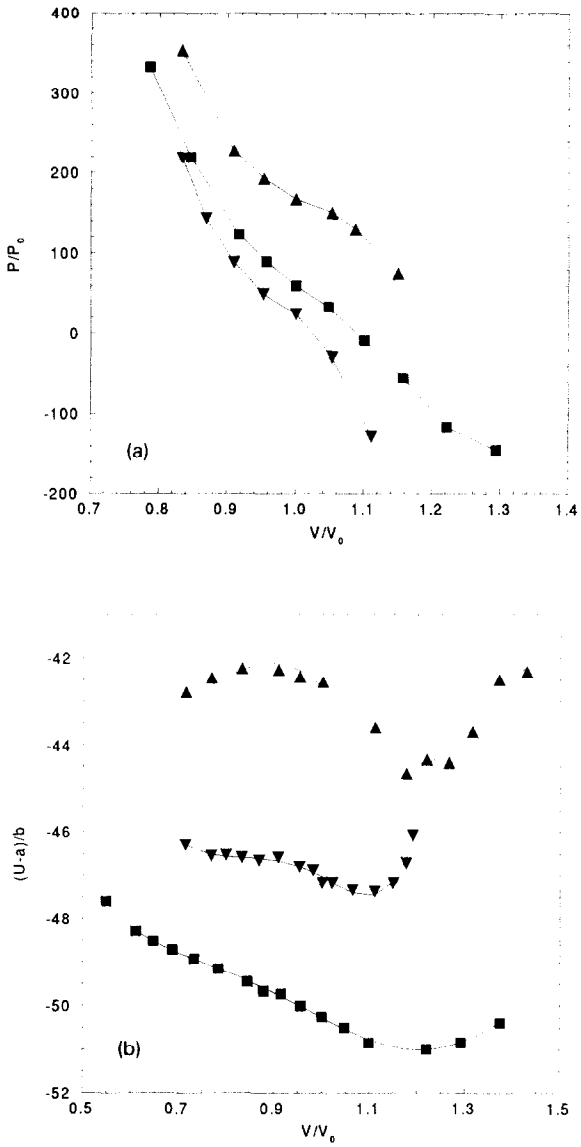

Fig. 4. (a) Comparison of low T isotherms of P versus V for two H_2O models, ST2 (▲; T = 250 K, V_0 = 1.0 cm^3/g, P_0 = 1.0 MPa), TIP4P (▼; T = 200 K, V_0 = 1.0 cm^3/g, P_0 = 0.5 MPa), and for SiO_2 as modeled by a rigid-ion potential (■; T = 7000 K, V_0 = 0.455 cm^3/g, P_0 = 20 MPa). (b) U versus V plots for the liquid state of two H_2O models, ST2 (▲; T = 290 K, V_0 = 1.0 cm^3/g, a = 0, b = 1.0 kJ/mol), TIP4P (▼; T = 225 K, V_0 = 1.0 cm^3/g, a = 0, b = 1.0 kJ/mol), and for SiO_2 as modeled by a rigid-ion potential (■; T = 7000 K, V_0 = 0.455 cm^3/g, a = 10.467 MJ/mol, b = 0.0333 MJ/mol). Note that the a and b parameters occur only to allow all the data to appear on the same scale. The line through each data set is a fit to a fifth-order polynomial.

in H_2O, the local geometry of bonding in all these systems has the same tetrahedral character throughout the crystal, amorphous solid and liquid regimes at ambient P. Hence, the possibility exists that amorphous polymorphism is a phenomenon observed to some degree in all tetrahedrally coordinated materials.

3.3. The internal energy

Further insight is provided by additional information easily obtained from computer simulations, but difficult to obtain experimentally. Specifically, we examine the behavior of the configurational internal energy, U, as a function of V at constant T, as measured in the H_2O and SiO_2 simulations [33,38]. The isotherms of U have positive curvature at high T in the regime of the equilibrium liquid. However, as shown in Fig 4b, at lower T the isotherms display segments with both positive and negative curvature.

These curvature changes are significant because of their influence on the thermodynamic stability of the system. Recall that the Helmholtz free energy A is given by

$$A = U - TS, \tag{1}$$

where S is the entropy. For a single phase of the system to be thermodynamically stable the curvature of A as a function of V, $(\partial^2 A/\partial V^2)_T$, must be positive. From Eq. (1), the curvature of A can be written as

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T = \left(\frac{\partial^2 U}{\partial V^2}\right)_T - T\left(\frac{\partial^2 S}{\partial V^2}\right)_T. \tag{2}$$

The sign of $(\partial^2 A/\partial V^2)_T$, and hence the stability, is therefore determined by the relative signs and magnitudes of $(\partial^2 U/\partial V^2)_T$, $(\partial^2 S/\partial V^2)_T$ and T.

For a simple liquid, one could argue that typically the sign of $(\partial^2 U/\partial V^2)_T$ will be the same as the sign of the average value of $(\partial^2 \phi/\partial r^2)$, where $\phi(r)$ is the function giving the energy of interaction of a pair of molecules separated by a distance r. In the liquid state of a system modeled by, say, the Lennard–Jones potential, the total interaction energy will be dominated by relatively close pairs. The interaction energy of these pairs will be found in the region of the minimum of $\phi(r)$, where the curvature (and hence the second derivative) is positive. One would therefore typically expect that $(\partial^2 U/\partial V^2)_T > 0$ in the liquid state, and

this is indeed seen in the simulations of H_2O and SiO_2 at high T [33,38].

Fig. 4b shows that this simple picture becomes more subtle in certain liquids as T decreases toward the supercooled region. In the interval of V where $(\partial^2 U/\partial V^2)_T < 0$ we see that U no longer contributes to the thermodynamic stability of the liquid phase; instead it makes a destabilizing contribution which increases in magnitude as T decreases. Under these conditions it is the behavior of S which maintains the stability of the liquid as a single phase. Furthermore, the contribution of S to the thermodynamic stability is subject to a prefactor of T, as seen in Eq. (2). This prefactor suppresses the contribution of S to the stability of the single phase liquid as T decreases.

Another (though cruder) way to express the above observations is to simply note that (i) the shape of U as a function of V is qualitatively the shape that A would take in a phase-separated system, and that (ii) in the limit $T \to 0$, $A \to U$.

The observation of Fig. 4b is then that U has a functional form appropriate for the appearance of liquid polymorphism at lower T. These observations do not demonstrate that liquid–liquid phase separation *must* occur – the functional behavior of S can always vary sufficiently strongly so that stability is maintained to arbitrarily low T. Yet they demonstrate that thermodynamic precursors to a first-order liquid–liquid phase transition exist in the properties of simulated H_2O and SiO_2 [41]. Notably, the experimental data on liquid H_2O also confirm this picture: $(\partial^2 U/\partial V^2)_T$ changes sign from positive to negative as T decreases toward the melting temperature [35].

3.4. Pseudo-thermodynamic behavior of non-ergodic systems

The computer simulation results described above show how a tendency toward liquid polymorphism can be observed in the low T behavior of the liquid state. Yet it remains true that the same system below T_g is no longer an equilibrium liquid state, but rather a non-ergodic glass. In spite of what the behavior "might have been" in the ergodic state, there is no compelling reason for such a glass to respond to changes in T or P according to the extrapolated equilibrium liquid behavior.

Yet the experimental and simulation data both show that even though the amorphous solid is manifestly an out-of-equilibrium state, it still responds to changes in T and P so as to follow, at least weakly, the behavior that might be expected in an ergodic state. Hence, despite the obvious difficulty in using thermodynamic language to describe a non-thermodynamic state, we are able to observe a measurable correspondence with the equilibrium behavior.

A more precise understanding of this correspondence is clearly required. For example, one possibility is that the non-ergodic amorphous solid behaves at $T < T_g$ so as to follow the thermodynamic behavior that would exist in equilibrium at the same T. Another possibility is that the amorphous solid behavior follows the higher T behavior that is "frozen in" as the system passed through T_g.

Also, the relationship between T_g and the onset temperature for liquid–liquid phase separation $T_{C'}$ (if it exists) is clearly important. Fig. 1 illustrates two possible positions of the glass transition line with respect to a liquid–liquid coexistence curve. The Al_2O_3–Y_2O_3 system seems to be a system where $T_{C'} > T_g$. The case of H_2O and SiO_2 is less clear. If $T_{C'}$ exists in these liquids, it may very well be near or below T_g, which would presumably reduce the relative sharpness of the amorphous solid transitions. The case where supercritical precursors to liquid polymorphism exist, but where actual liquid polymorphism is not realized at any T, is also potentially important: it may be sufficient to "freeze in" only the *precursor* behavior to liquid polymorphism in order to observe quite sharp expressions of amorphous polymorphism.

Whatever the origin, the pseudo-thermodynamic behavior of these amorphous solids does suggest that the equilibrium EOS behavior of the liquid state for $T > T_g$ can be used to anticipate the properties of the material at $T < T_g$, and vice versa.

4. The search for other amorphous polymorphic materials

In order to confirm or refute the scenario described here accounting for the occurrence of amorphous polymorphism, there needs to be a systematic experimental observation of the behavior found in the computer simulation data of Figs. 2 and 3: that is, the same sub-

stance must be be shown to exhibit (i) the characteristic sudden densification during compression of the amorphous solid state, and (ii) either fully-developed liquid polymorphism in the ergodic liquid for $T > T_g$, or at least a tendency in that direction as revealed by S-shaped liquid-state P–V isotherms. Despite the indirect evidence that such results can be realized, they do not yet exist for a single substance. Hence this is a vital first step to establish or refute the existence and phenomenology of amorphous polymorphism as described above.

The tetrahedrally coordinated materials seem to offer the richest opportunity to achieve this goal. Historically, the extensive work of Ponyatovsky, Barkalov and co-workers [10,11] on liquid semiconductors such as molten Ge and Si seems to represent the first attempt to systematically link liquid and amorphous polymorphism in tetrahedrally coordinated materials. Their thermodynamic models of these substances predict liquid polymorphism in the supercooled melt. They also predict a line of first-order liquid–liquid phase transitions ending in a critical point. Their work therefore anticipates the behavior found in the H_2O simulations [34]. Also, theoretical treatments of the thermodynamic behavior of carbon explicitly predict a liquid–liquid phase transition between diamond-like and graphite-like liquid phases [42,43]. Most recently, a number of detailed theoretical studies of models of H_2O (both microscopic and thermodynamic) have elucidated the rich phase behaviors possible in this system [11–15]. Hence new experimental results are clearly needed to confirm or refute the many theoretical scenarios now coming to light.

Experimentally, the prediction of liquid polymorphism in the behavior of Si seems to have been confirmed [6,7], in that it has been observed that the semiconducting amorphous solid form apparently undergoes a reversible first-order phase transition directly to a supercooled metallic liquid. However, the experimental protocols from which this conclusion was drawn were complex. It would be informative if this result could be reproduced under conditions where EOS information could simultaneously be extracted.

Despite extensive work on liquid and amorphous solid H_2O, crystal nucleation in the supercooled regime has so far prevented an experimental determination of the EOS of the supercooled liquid which would test the prediction of Fig. 3. An appropriate measurement would be to determine the isothermal compressibility $K_T = -(1/V)(\partial V/\partial P)_T$ of the liquid as a function of P at constant T, as deeply as possible into the supercooled region. The S-shaped P–V behavior of Fig. 3 would appear in such a plot as a maximum in K_T at that P at which the slope of the P–V isotherm is a minimum. Crystal nucleation becomes relatively less of a difficulty in supercooled H_2O as P increases, so such an experiment should be easier than one at ambient P.

The possibility of liquid polymorphism in supercooled H_2O has also been used to develop a novel interpretation of the dynamic behavior of H_2O as a function of T [44]. The viscosity of liquid H_2O as it is cooled below the melting point shows non-Arrhenius behavior, making it a "fragile" liquid. Yet an analysis of the liquid behavior observed just above the glass transition suggests that it is a strong liquid. Such a fragile-to-strong transition in dynamic properties can be explained by an accompanying thermodynamic phase transition. Experimental confirmation of this analysis through a direct measurement of the relaxation time as a function of T just above T_g would be revealing. Note that it has also been argued that the transition in the Al_2O_3–Y_2O_3 system involves a similar fragile-to-strong transition [24].

The experimental situation is similar to that of H_2O in the case of SiO_2 [5,36,45,46] and also for GeO_2 [47], in that the behavior of the amorphous solid is much better known than the thermodynamic properties of the supercooled liquid. Here too measurements of the EOS (through measurements of K_T as a function of P at constant T) of SiO_2 or GeO_2 melts could confirm or refute the prediction of Fig. 4a. Such measurements may be much easier than for H_2O, since these melts are well-known for their ability to avoid crystallization. It is the high T and P required which makes these experiments difficult, but it is our impression that the measurements are achievable with existing technology, especially in GeO_2.

Yet it is clear from the dramatic observations of amorphous polymorphism in the Al_2O_3–Y_2O_3 system that amorphous polymorphism is not a phenomenon restricted only to tetrahedrally coordinated materials. In the Al_2O_3–Y_2O_3 system the behavior of the low density glass under compression should be measured, to determine if abrupt densification occurs. Fortunately, both the low and high density glasses of this

melt can be obtained at ambient P by choosing the appropriate quenching conditions [2].

A number of other systems would appear to be candidates for amorphous polymorphism. For example, the thermodynamic models of Rapoport [8,9], developed to explain melting point maxima in the phase diagrams of Te and Cs, also predict the occurrence of a first-order phase transition in the liquid. Also, certain molecular liquids (e.g., Se [48], S [49] and I_2 [50]) under compression display abrupt changes in conductivity. These semiconductor-to-metal transitions may be associated with liquid–liquid phase transitions, either in the equilibrium or supercooled liquid. Again, EOS data on these liquids combined with an examination of the properties of the glasses formed on quenching, would test the possibility that these materials display amorphous polymorphism.

5. Conclusions

In summary, the combined results of experiments and computer simulations show that amorphous polymorphism found at $T < T_g$ may be related to liquid polymorphism occurring at $T > T_g$. The pseudo-thermodynamic behavior of an amorphous solid, required for this proposal to be true, is perplexing and merits deeper study. A central motivating factor for such work is the evidence that this phenomenon occurs in some of the most common and important substances in nature and technology, including H_2O and SiO_2. An exploration of other candidate systems is needed, to obtain a deeper understanding of the underlying phenomenon, and (perhaps more importantly) to discover previously unknown but technologically useful amorphous polymorphs.

Also worthy of note has been the role played by computer simulations in characterizing the conditions under which amorphous polymorphism is observed. A contributing factor to the uncertainty which still surrounds this idea is that experimental results on a given material typically pertain either to the liquid or glassy states, but very rarely to both. Hence the possibility of a correlation between the ergodic liquid behavior and the amorphous solid behavior has been slow to emerge. On the other hand, computer simulations can very easily evaluate the properties of a single system across the ergodic and non-ergodic regimes. As a direct result, it is from computer simulations that we have perhaps first glimpsed the origin and significance of amorphous polymorphism. Although experimental confirmation of this picture is vital, this progression of understanding represents a good example of how computer simulations can, under the right conditions, play a *leading* role in the exploration of a new phenomenon.

Acknowledgements

We would like to thank S. Aasland, P.G. Debenedetti, P.F. McMillan, S. Sastry, J. Shao and G.H. Wolf for enlightening discussions, and S.C. Glotzer for suggestions on the manuscript. Financial support was provided by NSF. PHP acknowledges the support of NSERC (Canada) and the Killam Trust.

References

[1] A.F. Wells, Structural Inorganic Chemistry (Clarendon Press, Oxford, 1984).
[2] S. Aasland and P.F. McMillan, Nature 369 (1994) 633.
[3] O. Mishima, L.D. Calvert and E. Whalley, Nature 314 (1985) 76.
[4] G.H. Wolf (private communication) has suggested that the more compact, and etymologically appropriate, name "polyamorphism" should be used in place of "amorphous polymorphism". While agreeing with this proposal, we use the latter term in this work to retain a parallelism with the term "crystal polymorph".
[5] M. Grimsditch, Phys. Rev. Lett. 52 (1984) 2379.
[6] M.O. Thompson, G.J. Galvin, J.W. Mayer, P.S. Peercy, J.M. Poate, D.C. Jacobson, A.G. Cullis and N.G. Chew, Phys. Rev. Lett. 52 (1984) 2360.
[7] E.P. Donovan, F. Saepen, D. Turnbull, J.M. Poate and D.C. Jacobson, J. Appl. Phys. 57 (1985) 1795.
[8] E. Rapoport, J. Chem. Phys. 46 (1967) 2891.
[9] E. Rapoport, J. Chem. Phys. 48 (1968) 1433.
[10] E.G. Ponyatovsky and O.I. Barkalov, Mater. Sci. Rep. 8 (1992) 147.
[11] E.G. Ponyatovsky, V.V. Sinard and T.A. Pozdnyakova, JETP Lett. 60 (1994) 360.
[12] S. Sastry, F. Sciortino and H.E. Stanley, J. Chem. Phys. 98 (1993) 9863.
[13] S.S. Borick and P.G. Debenedetti, J. Phys. Chem. 97 (1993) 6292.
[14] P.H. Poole, F. Sciortino, T. Grande, H.E. Stanley and C.A. Angell, Phys. Rev. Lett. 73 (1994) 1632.
[15] S.S. Borick, P.G. Debenedetti and S. Sastry, J. Phys. Chem. 99 (1995) 3781.

[16] In the same spirit, note that the well-known phenomenon of liquid–gas phase separation could be discussed in terms of "fluid polymorphism".
[17] W. Kauzmann, Chem. Rev. 43 (1948) 219.
[18] E.F Burton and W.F. Oliver, Nature 135 (1935) 505; Proc. R. Soc. London A 153 (1935) 166.
[19] P. Brügeller and E. Mayer, Nature 288 (1980) 569.
[20] J. Dubochet and A.W. McDowall, J. Microsc. 124 (1981) RP3.
[21] E. Mayer and P. Brüggeller, Nature 298 (1982) 715.
[22] O. Mishima, J. Chem. Phys. 100 (1994) 5910.
[23] O. Mishima, K. Takemura and K. Aoki, Science 254 (1991) 406.
[24] C.A. Angell, Science 267 (1995) 1924.
[25] F. Stillinger, Science 267 (1995) 1935.
[26] J.S. Tse and M.L. Klein, Phys. Rev. Lett. 58 (1987) 1672.
[27] J.S. Tse and M.L. Klein, J. Chem. Phys. 92 (1990) 3992.
[28] C.A. Angell, Annu. Rev. Phys. Chem. 34 (1983) 593.
[29] M.P. Allen and D.J. Tildesley, Computer Simulations of Liquids (Oxford University Press, Oxford, 1987).
[30] P.H. Poole, U. Essmann and H.E. Stanley, Phys. Rev. E 48 (1993) 4605.
[31] F.H. Stillinger and A. Rahman, J. Chem. Phys. 60 (1974) 1545.
[32] W.L. Jorgensen, J. Chandrasekhar, J. Madura, R.W. Impey and M. Klein, J. Chem. Phys. 79 (1983) 926.
[33] P.H. Poole, F. Sciortino, U. Essmann and H.E. Stanley, Phys. Rev. E 48 (1993) 3799.
[34] P.H. Poole, F. Sciortino, U. Essmann and H.E. Stanley, Nature 360 (1992) 324.
[35] F. Sciortino, U. Essmann, P.H. Poole and H.E. Stanley, preprint.
[36] H. Sugiura, K.-I. Kondo and A. Sawaoka, in: High-pressure Research in Geophysics, eds. S. Akimoto and M.H. Manghnani (Reidel, Dordrecht, 1982) p. 551.
[37] M.S. Somayazulu, S.M. Sharma, N. Garg, S.L. Chaplot and S.K. Sikka, J. Phys. Condensed Matter 5 (1993) 6345.
[38] P.H. Poole, M. Hemmati and C.A. Angell, preprint.
[39] H.E. Stanley, C.A. Angell, U. Essmann, M. Hemmati, P.H. Poole and F. Sciortino, Physica A 205 (1994) 122.
[40] B. Boulard, J. Kieffer, C. Phifer and C.A. Angell, J. Non-Cryst. Solids 140 (1992) 350.
[41] The behavior is analogous to the way that phase separation is characterized in multi-component systems: In this case, the behavior of the enthalpy H as a function of composition x is often measured to assess the potential for phase separation at low T. If a plot of H as a function of x has a pronounced negative curvature, then the contribution of H to the stability of the mixture (as determined by the curvature of the Gibbs free energy $G = H - ST$) has the potential to overcome the entropy of mixing as T decreases.
[42] A. Ferraz and N.H. March, Phys. Chem. Liq. 8 (1979) 289.
[43] M. van Thiel and F.H. Ree, Phys. Rev. B 48 (1993) 3591.
[44] C.A. Angell, J. Phys. Chem. 97 (1993) 6339.
[45] J. Wackerle, J. Appl. Phys. 33 (1962) 922.
[46] R.V. Gibbons and T.J. Ahrens, J. Geophys. Res. 76 (1971) 5489.
[47] K.H. Smith, A.V.G. Chizmeshya and G.H. Wolf, EOS 74 (1993) 630; in press, Phys. Rev. B (1995).
[48] H. Endo, K. Tamura and M. Yao, Can. J. Phys. 65 (1987) 266.
[49] V.V. Brazhkin, R.N. Voloshin, S.V. Popova and A.G. Umnov, Phys. Lett. A 154 (1991) 413.
[50] V.V. Brazhkin, S.V. Popova, R.N. Voloshin and A.G. Umnov, High Pressure Res. 6 (1992) 363.