

INTERRELATIONSHIP OF POLYAMORPHISM AND THE FRAGILE-TO-STRONG TRANSITION IN LIQUID SILICA

IVAN SAIKA-VOIVOD*, PETER H. POOLE* AND FRANCESCO SCIORTINO†

**Department of Applied Mathematics, University of Western Ontario, London, Ontario N6A 5B7, Canada*

†Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Universita' di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185, Roma, Italy

Abstract.

We study the static and dynamic properties of liquid silica over a wide range of temperature T and density ρ using computer simulations. We find a change in the potential energy landscape as T decreases that underlies a continuous transition from a fragile liquid at high T to a strong liquid at low T . We also show that a specific heat anomaly is associated with this fragile-to-strong transition, and discuss the relationship of this anomaly to the polyamorphic behavior of amorphous solid silica.

1. Introduction

Liquid silica is the canonical “strong liquid”. Almost all liquids display a faster-than-Arrhenius increase of viscosity η as the temperature T decreases toward the glass transition temperature T_g . In Angell’s classification of glass-forming liquids, the greater the deviation from Arrhenius behavior, the greater is the “fragility” of the liquid [1]. Liquids that exhibit behavior that is close to Arrhenius are termed “strong”. Liquid silica is one of only a very few liquids having an essentially perfect Arrhenius behavior as $T \rightarrow T_g$, making it the extreme case of a strong liquid [2].

The strong behavior of liquid silica underlies the central role of silica-based compounds in glass science. η for a strong liquid varies over a smaller range within a given T interval above T_g than does a fragile liquid. This makes it easier to hold the melt just above T_g in a workable, high-viscosity liquid state (suitable e.g. for glass-blowing) without precise temperature

control. The more fragile the system, the narrower is the working range of T within which the liquid must be held, and consequently, the more difficult the material is to manipulate. It is therefore important to understand, at a fundamental level, how it is that silica is such a strong liquid.

Some analyses of experimental data for silica suggest that, rather than being strong at all T , the liquid may be fragile at very high T [3, 4], and converts to a strong liquid only as the liquid is cooled. Recent simulations support this view [5–7]. Simulations [6] of the BKS [8] model of silica between $T = 2750$ and 6000 K show that BKS silica is a fragile liquid at high T , yet starts to transform continuously to a strong liquid near $T = 3300$ K.

Amorphous solid silica, the material formed by cooling the liquid well below T_g , also displays polyamorphism: distinct amorphous solid states, differing in density and structure [9, 10]. The signature of polyamorphism in silica is a relatively abrupt increase in density when the amorphous solid formed at ambient pressure is subjected to high pressures [11]. Polyamorphism is observed even more prominently in amorphous solid water [12], a structural analogue of silica in that both systems exhibit tetrahedral molecular coordination at ambient pressure. In water, it has been proposed that polyamorphism is a sub- T_g manifestation of a liquid-liquid phase transition [13, 14]; this same possibility has recently been shown to be consistent with the thermodynamic behavior of liquid BKS silica [15]. The idea of a “fragile-to-strong” transition was first proposed for the case of deeply supercooled water by Angell [16], who conceptually connected the thermodynamic transition associated with polyamorphism to the dynamical one that occurs as the liquid passes from fragile to strong.

The precise relationship between a polyamorphic thermodynamic transition and a dynamic fragile-to-strong transition can be quantified using the concept of the potential energy hypersurface (PES), or “energy landscape” [17, 18]. Recent studies of the PES of liquids have demonstrated the controlling influence of the PES on transport properties as $T \rightarrow T_g$ [19–23]. However, these studies have only addressed liquids that are fragile at all $T > T_g$, and so the relationship of the PES to a “fragile-to-strong” transition could not be studied.

Here, we present results obtained from extensive simulations of BKS silica over a wide range of T and ρ [24]. These results permit us to (i) examine the fragile-to-strong transition, (ii) identify the energy landscape behavior that underlies it, and (iii) seek the connection between the landscape features found, to polyamorphic thermodynamic anomalies. The results clarify our understanding not only of the origins of silica’s status as a strong liquid, but also of the dynamical behavior of a wider class of liquids that are to some degree silica-like, most notably water and silicon [25], but also other systems such as BeF_2 [26].

2. Dynamics and the Potential Energy Landscape

The results presented here are obtained from molecular dynamics computer simulations, in which the diffusion coefficient D can be evaluated from $\langle r^2 \rangle$, the mean squared particle displacements, using the Einstein relation, $D = \lim_{t \rightarrow \infty} \langle r^2 \rangle / 6t$. Like η , D is a characteristic transport property whose deviations from the Arrhenius law serve to classify a liquid as strong or fragile.

The theory of Adam and Gibbs (AG) [27] states that D is related to the configurational entropy, S_c via,

$$D = D_0 \exp(-A/TS_c), \quad (1)$$

where the parameters D_0 and A are commonly assumed to be T -independent. S_c quantifies the number of distinct configurational states explored by the liquid in equilibrium. These states have been proposed to correspond to the “basins” of the PES sampled by the liquid [17, 18]. A basin is the set of points in phase space representing configurations having the same local minimum. The local minimum configuration is termed an inherent structure (IS), and is identified in simulation by a steepest descent minimization of the potential energy.

Following the IS thermodynamic formalism of Stillinger and Weber [17], the internal energy of the liquid can be expressed as $E = e_{IS} + E_{harm} + E_{anh}$, where e_{IS} is the average IS energy and the last two terms are the average contributions to E due to thermal excitations about the IS. E_{harm} is the average harmonic contribution determined from a quadratic approximation to E around each IS minimum, while E_{anh} is the remaining, necessarily anharmonic contribution. The harmonic and anharmonic potentials characterize the shape of the basin.

If the shape of a basin does not depend on the basin’s IS energy (a condition satisfied here; see below), then S_c can be calculated along an isochore by integrating the T dependence of e_{IS} at constant volume V [20]:

$$S_c = S_c^0 + \int_{T_0}^T \frac{1}{T'} \left(\frac{\partial e_{IS}}{\partial T'} \right)_V dT', \quad (2)$$

where S_c^0 is the value of S_c at a reference $T = T_0$. Eq. 2 highlights that the T dependence of S_c arises solely from changes in e_{IS} [17, 20]. Evaluation of S_c when the basin shape depends on e_{IS} is also feasible [22, 28, 29].

For a strong liquid that satisfies Eq. 1, the T dependence of S_c must approach a constant to recover Arrhenius behavior. From Eq. 2, if S_c is constant, then so must be the variation of e_{IS} with T . This behavior would be qualitatively different from that found in simulations of fragile liquids. For example, recent studies [21, 22] of a binary Lennard-Jones liquid have

shown that $e_{IS} \propto -1/T$, a dependence that is not consistent with the approach to a constant at low T .

3. Methods

Our results are based on molecular dynamics simulations of BKS silica. All data are obtained from systems of $N = 1332$ atoms (888 O and 444 Si atoms), except for the $\rho = 2.36$ g/cm³ isochore, where we employ 999 atoms to facilitate equilibration at low T . At $\rho = 2.36$ g/cm³ 8 independent runs for each state point are performed. All data reported here are for liquid states in equilibrium. Equilibration is confirmed by ensuring that runs are longer than the slowest relaxation time in the system as evaluated from the collective (coherent) density-density correlation function. The lowest T runs exceed 80 ns. Simulations are carried out in the constant- (N, V, E) ensemble, and long-range electrostatic interactions are accounted for by Ewald summation. We evaluate e_{IS} by conducting conjugate gradient minimizations of up to 1000 equilibrium liquid configurations and averaging the results.

We calculate the configurational entropy as the difference between the total entropy and the vibrational entropy: $S_c = S - S_{vib}$. Details of our calculations of S and S_{vib} may be found in Ref. [24]. The assumption that underlies the validity of Eq. 2, that the shape of the basins is independent of e_{IS} along an isochore, is based on two observations: (i) We find that the vibrational density of states is independent of e_{IS} along an isochore. (ii) The anharmonic energy of IS configurations heated from $T = 0$ to a chosen T follows the $E_{anh} = E - E_{harm} - e_{IS}$ curve calculated from equilibrium simulations. This is only possible if the anharmonic character of the basins is also independent of e_{IS} .

4. Results

The fragile-to-strong transition of BKS silica is demonstrated in Fig. 1. The curvature of the data for $\log D$ vs $1/T$ at high T , both along an isochore and an isobar, fades as T decreases, approaching a linear behavior at low T .

Fig. 2 shows the T dependence of e_{IS} along two isochores. The shape of the higher ρ isochore is similar to that found for fragile liquids. However, at the lower ρ —which is close to the experimental ρ at ambient pressure— e_{IS} exhibits an inflection, passing from concave downward at high T to concave upward at low T . Fig. 2 also shows the potential energy E_0 at $T = 0$ of the corresponding equilibrium crystalline system for the same ρ . Since the energy of the lowest IS cannot be less than E_0 , E_0 sets a lower bound on

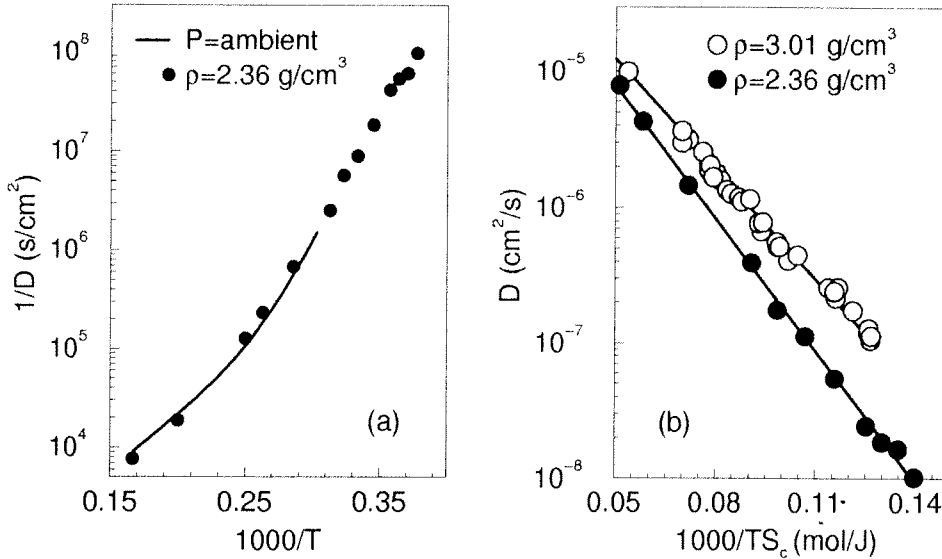


Figure 1. (a) Arrhenius plot of $1/D$ along the ambient pressure isobar, found by interpolating our isochoric data; and along the $\rho = 2.36 \text{ g/cm}^3$ isochore. Note the non-Arrhenius to Arrhenius crossover observed both at constant ρ and at constant P . All D values reported here are for Si atoms. (b) Plot of D versus $1/TS_c$ along two isochores.

e_{IS} . The value of E_0 relative to the measured e_{IS} curves confirms that an inflection occurs.

Like e_{IS} , S_c also exhibits an inflection along our lower ρ isochore (Fig. 2). In the same range of T , we find (Fig. 1) that along each isochore D satisfies the AG relation within numerical error. That is, despite the change in the nature of the T dependence of S_c , the transport properties of the liquid adjust (from non-Arrhenius to Arrhenius) so as to maintain the AG relation, a finding that demonstrates of the robustness of Eq. 1 [22, 30, 31]. The low ρ data thus reveal the signature in the energy landscape of a fragile-to-strong transition. The rapid variation of landscape properties at high T corresponds to a fragile regime. As T decreases, the inflections of e_{IS} and S_c mark the onset of a regime in which the rate of change of these quantities decreases, consistent with the system's approach to the strong liquid limit.

The influence of the energy landscape is sufficiently prominent to appear in the total thermodynamic properties [32]. The isochoric specific heat C_V can be written as $C_V = C_V^{IS} + 3R + C_V^{anh}$, where each term is the derivative with respect to T of the corresponding contribution to E , and R is the gas constant. The inflection in the T dependence of e_{IS} corresponds to a maximum in C_V^{IS} (Fig. 3) that is the origin of a C_V anomaly, in the form of a peak, in the interval of T corresponding to the fragile-to-strong transition.

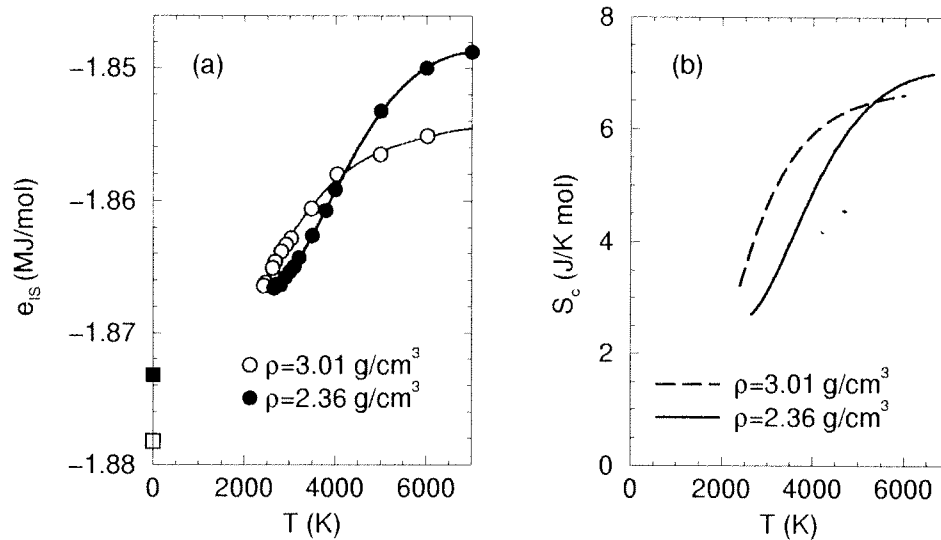


Figure 2. (a) e_{IS} as a function of T along two isochores. At $T = 0$ we show the energy E_0 of the crystalline system at $\rho = 2.36 \text{ g/cm}^3$ (filled square) and $\rho = 3.01 \text{ g/cm}^3$ (open square). E_0 is found by calculating the V dependence of the potential energy at $T = 0$ of three crystal polymorphs of silica (stishovite, coesite and quartz), and then using the common tangent construction to determine the potential energy of the heterophase of coexisting crystals that would be the ground state at the required bulk value of ρ . (b) S_c as a function of T along two isochores.

An analogous C_V anomaly has recently been predicted to occur in the silica-like liquid BeF_2 [26], and in theoretical models designed to reproduce a fragile-to-strong transition [33]. High T experiments that test for this anomaly, though challenging, can thus directly seek the thermodynamic signature of the fragile-to-strong transition in these systems.

5. Discussion

As shown in Fig. 4, the peak we find in C_V occurs at T near the temperature of maximum density of BKS silica, and in the vicinity of a maximum of the isothermal compressibility K_T predicted for this model [15]. Thermodynamic anomalies, such as peaks in C_V and K_T , are associated with the physics of liquid-liquid transitions and with polyamorphism in glasses. The C_V maximum we observe in connection with the fragile-to-strong transition is located in the appropriate region of the phase diagram to be the thermal anomaly associated with polyamorphism. Along different isochores we find that the T at which the C_V maximum occurs decreases with increasing ρ , as would be expected for an anomaly related to polyamorphism in silica.

In sum, these results indicate that the fragile-to-strong transition of

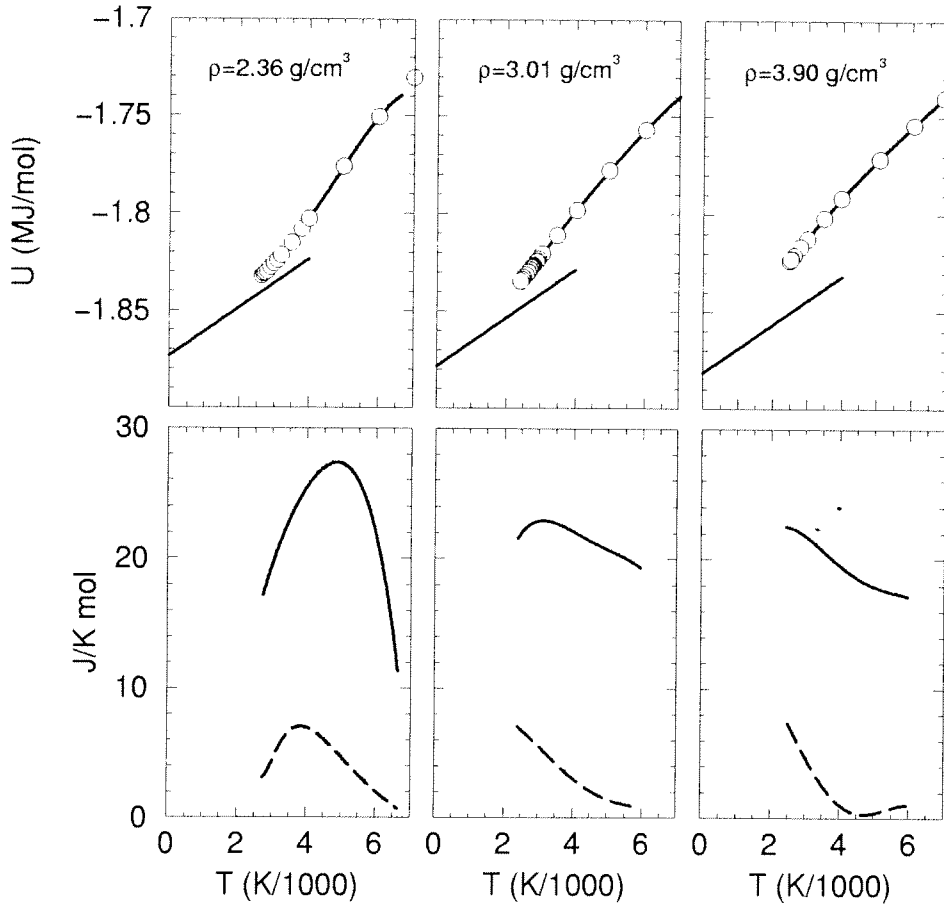


Figure 3. Upper panels: Isochores of the liquid potential energy U . Lower panels: $C_V - (3/2)R$ (solid lines) and C_V^{LS} (dashed lines) as a function of T . In the upper panels are shown lines of slope $\frac{3}{2}R$ whose values at $T = 0$ are the potential energies of the corresponding crystalline systems, calculated as described in Fig. 2; these lines are lower bounds for U of the liquid.

BKS silica is the dynamical transition corresponding to the thermodynamic crossover in the liquid that presages polyamorphism [33]. The phase behavior proposed in Fig. 4 for BKS silica accounts for the continuous nature of the fragile-to-strong transition that we observe, despite the fact that a discontinuous, first-order liquid-liquid phase transition may occur in BKS silica: the fragile-to-strong transition seen in Fig. 1 occurs along paths that do not intersect the line of first order transitions. This line of first order transitions is predicted to occur in a region where it is extremely difficult (at present) to conduct equilibrium simulations from which D would be calculated. However, when such simulations are feasible, we expect that

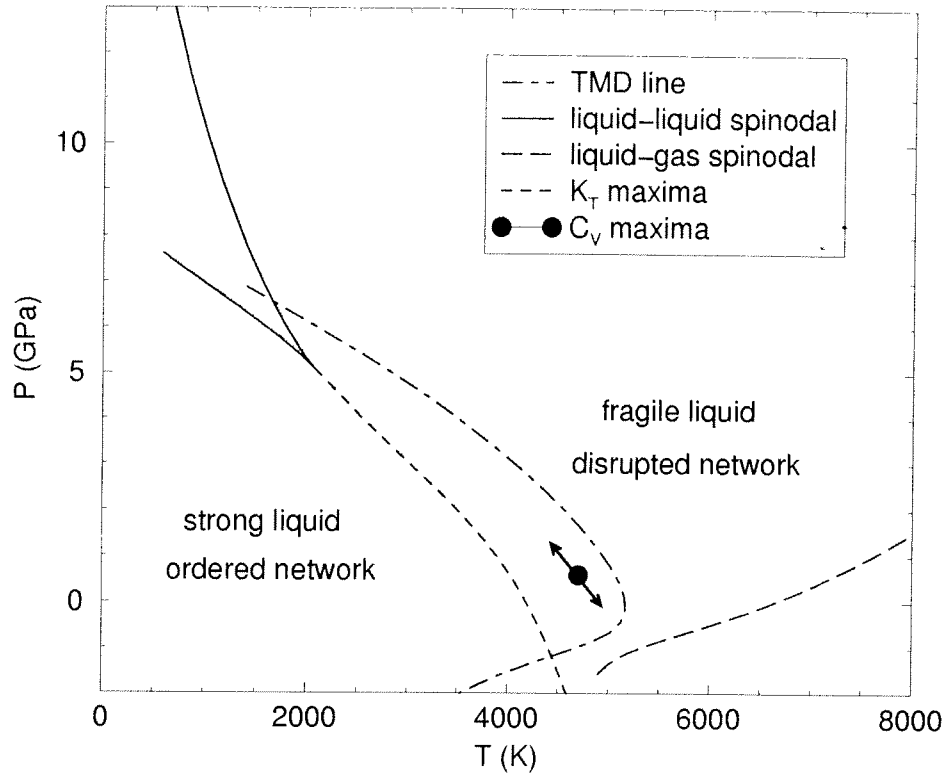


Figure 4. Phase behavior of liquid BKS silica. Lines are estimates for liquid state features calculated in Ref. [15]: spinodal lines (stability limits) for both the liquid-liquid and liquid-gas phase transitions; the line of K_T maxima; and the temperature of maximum density (TMD) line. The filled circle locates the maximum of C_V identified at $\rho = 2.36 \text{ g/cm}^3$. The arrows indicate the estimated slope of the line of C_V maxima at this point. The anomalies of density, K_T and C_V demarcate the boundary between the region of strong liquid behavior at low T and P , and that of fragile liquid behavior at higher T and P .

the fragile-to-strong transition so observed would itself be discontinuous, and similar to that found in simulations of liquid silicon [25].

Taken together, the above results provide a basis for conjecturing that all strong liquids are candidates for polyamorphism: a strong liquid arises via a fragile-to-strong transition, associated with which may be thermodynamic anomalies that are the liquid-state precursors to polyamorphism.

It is also interesting to note, at low ρ , how close U for the liquid approaches that for the crystal ground state (Fig. 3, upper left panel). The rate of decrease of U with T up to the inflection point is sufficiently great that, if not for the inflection, the liquid U would easily cross below that of the crystal at finite T . In this sense, the inflection in the T -dependence of

U has the effect of avoiding an “energy crisis,” in analogy to the “entropy crisis” of the so-called “Kauzmann paradox” [34]. Although such an “energy crisis” would not be a violation of any thermodynamic law, it would lead to the surprising case where the liquid (or, more precisely, its ideal glass) would be the ground state of the system at $T = 0$.

In the present case, the energy crisis is avoided via a thermodynamic anomaly, which is in turn associated with a fragile-to-strong crossover in the dynamics mediated by the shape of the energy landscape. Hence, for BKS silica, fundamental phenomena associated with (i) the Kauzmann Paradox, (ii) polyamorphism, and (iii) a fragile-to-strong transition, are all inextricably interconnected.

6. Acknowledgments

We thank C.A. Angell, W. Kob, S. Sastry and R. Speedy for useful discussions. ISV and PHP acknowledge NSERC (Canada) for financial support, and SHARCNET for computing resources. FS acknowledges support from the INFM “Iniziativa Calcolo Parallelo,” PRE-HOP and from MURST PRIN 2000.

References

1. C.A. Angell, *J. Non-Cryst. Solids* **131-133**, 13 (1991).
2. P. Richet, *Geochimica et Cosmochimica Acta* **48**, 471 (1984).
3. E. Rossler, K.-U. Hess and V.N. Novikov, *J. Non-Cryst. Solids* **223**, 207 (1998).
4. K.-U. Hess, D.B. Dingwell and E. Rossler, *Chemical Geology* **128**, 155 (1996).
5. J.-L. Barrat, J. Badro and P. Gillet, *Molecular Simulation* **20**, 17 (1997).
6. J. Horbach and W. Kob, *Phys. Rev. B* **60**, 3169 (1999).
7. P. Jund and R. Jullien, *Phys. Rev. Lett.* **83**, 2210 (1999).
8. B.W.H. Van Beest, G.J. Kramer and R.A. van Santen, *Phys. Rev. Lett.* **64**, 1955 (1990).
9. G.H. Wolf, S. Wang, C.A. Herbst, D.J. Durben, W.J. Oliver, Z.C. Kang, and C. Halvorsen, in *High-Pressure Research: Application to Earth and Planetary Sciences*, edited by Y.S. Manghnani and M.H. Manghnani (American Geophysical Union, Washington, 1992) p. 503.
10. P.H. Poole, T. Grande, C.A. Angell and P.F. McMillan, *Science* **275**, 322 (1997).
11. H. Sugiura, K.-I. Kondo and A. Sawaoka in *High-Pressure Research in Geophysics* (eds S. Akimoto and M.H. Manghnani) 551 (Reidel, Dordrecht, 1982).
12. O. Mishima, L.D. Calvert and E. Whalley, *Nature* **314**, 76 (1985).
13. P.H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, *Nature* **360**, 324 (1992).
14. O. Mishima and H.E. Stanley, *Nature* **396**, 329 (1998).
15. I. Saika-Voivod, F. Sciortino and P.H. Poole, *Phys. Rev. E* **63**, 011202 (2001).
16. C.A. Angell, *J. Phys. Chem.* **97**, 6339 (1993).
17. F.H. Stillinger and T.A. Weber, *Science* **225**, 983 (1984).
18. F.H. Stillinger, *Science* **267**, 1935 (1995).
19. S. Sastry, P.G. Debenedetti and F.H. Stillinger, *Nature* **393**, 554 (1998).
20. F. Sciortino, W. Kob and P. Tartaglia, *Phys. Rev. Lett.* **83**, 3214 (1999).
21. S. Buechner and A. Heuer, *Phys. Rev. E* **60**, 6507 (1999).
22. S. Sastry, *Nature* **409**, 164 (2001).

23. L.-M. Martinez and C.A. Angell, *Nature* **410**, 663 (2001).
24. I. Saika-Voivod, P.H. Poole and F. Sciortino, cond-mat 0105084 (2001).
25. S. Sastry, private communication.
26. M. Hemmati, C.T. Moynihan and C.A. Angell, *J. Chem. Phys.*, in press (2001).
27. G. Adam and J.H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
28. F. Sciortino and P. Tartaglia, *Phys. Rev. Lett.* **86**, 107 (2001).
29. F.W. Starr, S. Sastry, E. La Nave, A. Scala, H.E. Stanley and F. Sciortino, *Phys. Rev. E* **63**, 041201 (2001).
30. R.J. Speedy, *Mol. Phys.* **95**, 169 (1998).
31. A. Scala, F.W. Starr, E. La Nave, F. Sciortino and H.E. Stanley, *Nature* **406**, 166 (2000).
32. F. H. Stillinger, P. G. Debenedetti and S. Sastry, *J. Chem. Phys.* **109**, 3983, (1998).
33. E. A. Jagla, cond-mat/0008218 (2000).
34. P.G. Debenedetti and F.H. Stillinger, *Nature* **410** 259 (2001).