

Simulated silica

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We review how molecular dynamics computer simulations are providing a comprehensive picture of the behaviour of silica, as modelled by the van Beest–Kramer–van Santen (BKS) potential. We have recently evaluated a number of key properties of this model system: the phase diagram, including melting lines of three crystal phases; the equation of state and free energy of the liquid phase; the dynamical equation of state; the average energy of inherent structures, and configurational entropy, associated with the potential energy landscape of the liquid; and a characterization of the local coordination environments in the supercooled liquid. The results reveal the interplay among a number of phenomena, in particular, the relationship between the energy landscape and the fragile-to-strong crossover of the liquid dynamics; and the relation of both of these to the possibility of a liquid–liquid phase transition in the supercooled liquid.

Keywords: silica; computer simulations; energy landscape; liquid–liquid transitions

1. Introduction

Materials with a tetrahedral molecular structure at ambient pressure P play important roles in many areas of science and technology. Water, silicon, carbon and silica are all examples of this class of material. Silica in particular has received much attention because it is commonly encountered in an amorphous solid state, or glass, consisting of a random tetrahedral network (RTN), as opposed to the ordered tetrahedral network found in crystalline phases such as quartz. The RTN of silica glass has its origins in the RTN-like structure of the liquid phase above the glass transition temperature, T_g . The robustness of the RTN structure in the liquid underlies the fact that silica, according to Angell’s strong–fragile classification of glass-forming liquids (Angell 1991), is among the strongest of all liquids known (Richet 1984). That is, the

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temperature dependence of the transport properties of the liquid are nearly perfectly Arrhenius on approach to T_g , in contrast to almost all other liquids.

In computer simulations of fragile liquids (i.e. those with non-Arrhenius behaviour approaching T_g) the potential energy landscape, or potential energy surface (PES), has proved to be a useful conceptual tool for elucidating the connection between dynamics and thermodynamics (Goldstein 1969; Stillinger & Weber 1984; Stillinger 1995; Sastry *et al.* 1998; Sciortino *et al.* 1999; Sastry 2001; Debenedetti & Stillinger 2001). In this context, the PES refers to the potential energy hypersurface of the system, expressed as a function of the $3N$ coordinates that specify the positions of the N atoms of the system.

However, understanding the interrelationship of the PES, the dynamics and thermodynamics of strong RTN-based liquids presents new challenges and opportunities. Liquids such as silica, silicon and water exhibit a range of exotic behaviour, notably density maxima, and the possibility of liquid–liquid phase transitions (Poole *et al.* 1997). As we will describe below, recent computer simulation studies have allowed us to show that the origins of silica’s strong behaviour can be found in the behaviour of its PES (Saika-Voivod *et al.* 2001b). Yet, at the same time, we also find that these observations are intimately related to the thermodynamic anomalies of the system. Hence, from a coordinated simulation study of structure, dynamics and thermodynamics (including phase behaviour), we illustrate the pervasive role played by the RTN in determining the properties of liquid silica: how its formation on cooling relates to strong liquid behaviour and how its breakdown with pressure relates to the density maximum and the possibility of a liquid–liquid transition.

2. Simulation methods

All of the results described here are obtained via molecular dynamics simulations employing the van Beest–Kramer–van Santen (BKS) potential (van Beest *et al.* 1990), a widely used model of atomic interactions in silica. Detailed descriptions of the simulation protocols and techniques are given by Saika-Voivod *et al.* (2004a, b). As described in these works, we evaluate the properties of the liquid over a wide range of temperatures T and volumes V , yielding structural, thermodynamic and dynamical information on the liquid phase over greatly varying conditions. Employing a conjugate gradient quenching technique, we also evaluate the inherent structures of the liquid over this wide range of states, and evaluate the average inherent structure energy, e_{IS} . As outlined below, the dependence of e_{IS} on T is then used to estimate the T dependence of S_c , the configurational entropy of the liquid. In this context, S_c quantifies the number of basins of the PES explored by the liquid at a given state.

We also carry out free-energy calculations for the liquid phase, and for three crystal phases: β -quartz, coesite and stishovite. This information allows us to construct the phase diagram of BKS silica (Saika-Voivod *et al.* 2004b). As we will show below, this phase diagram provides a key perspective on the behaviour of this model material, allowing us to self-consistently relate the behaviour of the liquid to the location of its phase boundaries, as is common practice in experiments.

3. Fragile-to-strong dynamical crossover

While silica is a strong liquid in experiments conducted near and below the melting T , the simulation study of Horbach & Kob (1999) showed that BKS silica behaves as

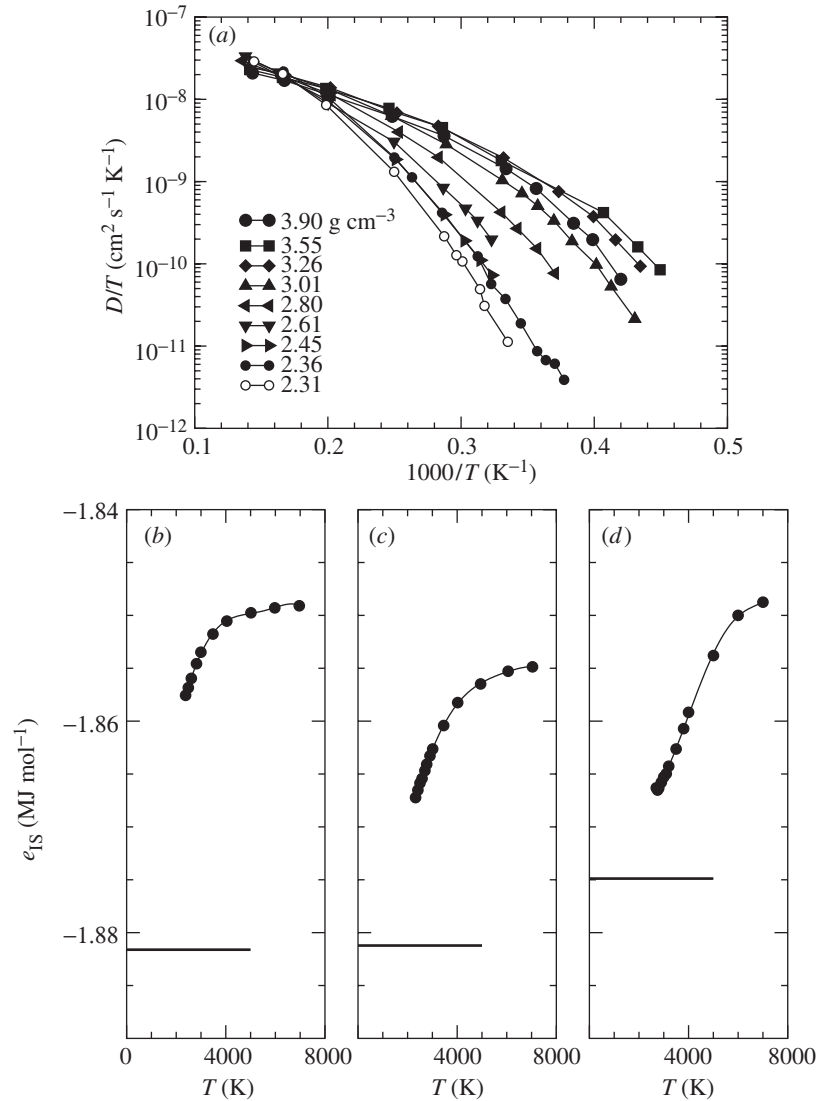


Figure 1. (a) Isochores of D/T . For the low density isochores, the curvature is greater at high T than at low T , indicating that the liquid is crossing over from fragile to strong behaviour as T decreases. (b)–(d) Isochores of e_{IS} for three densities spanning the range of our calculations: (b) 3.90 g cm^{-3} ; (c) 3.01 g cm^{-3} ; (d) 2.36 g cm^{-3} . The thick horizontal lines show the value of the $T = 0$ ground state crystal energies for each density.

a fragile liquid at the very highest T . However, in the vicinity of 4000 K, the dynamics crosses over to that of a strong liquid, establishing an Arrhenius dependence of relaxation on T consistent with experimental results obtained at lower T (figure 1). This ‘fragile-to-strong’ crossover (FSC) represents a valuable opportunity to test the robustness of the Adam–Gibbs (AG) relation (Adam & Gibbs 1965), which predicts a relationship between the characteristic relaxation time of the system and the configurational entropy, S_c . Using the diffusion coefficient D , we substitute D/T for the

relaxation time, and write the AG relation as

$$\frac{D}{T} = \mu_0 \exp\left(-\frac{A}{TS_c}\right), \quad (3.1)$$

where μ_0 and A are presumed to be constant with respect to T . BKS silica provides a context in which we can test if equation (3.1) is obeyed throughout the region in which an FSC occurs. If so, we can then use the AG relation to connect transport properties, such as D , to properties of the PES, such as S_c and e_{IS} .

As explained in detail by Saika-Voivod *et al.* (2004a), for BKS silica the T dependence of S_c along an isochore can be evaluated from that of e_{IS} using

$$S_c(T) = S_c(T_0) + \int_{T_0}^T \frac{1}{T'} \left(\frac{\partial e_{\text{IS}}}{\partial T'} \right)_V dT', \quad (3.2)$$

where $S_c(T_0)$ is the configurational entropy at a reference $T = T_0$. Assuming that the AG relation holds, one scenario consistent with the occurrence of an FSC is for S_c to decrease with T at high T (yielding non-Arrhenius, fragile behaviour), but then saturate to a constant value at low T (giving Arrhenius, strong behaviour). Based on equation (3.2), this implies that e_{IS} also decreases with T at high T , and then approaches a constant at low T . Hence the signature of the FSC can be sought in the properties of the PES by evaluating the T dependence of e_{IS} .

Figure 1 shows the T dependence of e_{IS} for liquid BKS silica along three isochores (Saika-Voivod *et al.* 2001b, 2004a). The lowest density corresponds to that at which the clearest indications of an FSC exist. In line with the scenario proposed above, e_{IS} does indeed vary rapidly at high T , but then exhibits an inflection at the lowest T that we can reach on our computational time-scale. This inflection is consistent with the early stages of e_{IS} approaching a constant. Also shown in figure 1 are the energies of crystalline ground states of the BKS system at each density. We find that the inflection of the e_{IS} curve at the lowest density is consistent with the expectation that the inherent structure energy of the liquid should not become less than that of the crystalline state at the same density.

Hence, the behaviour of the PES shows us that the FSC in liquid BKS silica is, in some sense, inevitable on purely energetic grounds. The formation of an RTN in the liquid carries the configurational energy to values close to that of crystalline phases. Compared with higher T , relatively little configurational improvement is possible in the liquid as T decreases, and so the dynamics begins to take on an Arrhenius form.

4. Phase diagram

As shown in Saika-Voivod *et al.* (2004a, fig. 17), the PES signature of the FSC in liquid BKS silica is also reflected in the total thermodynamic properties, in the form of a maximum of the isochoric specific heat C_V . Since this feature and the density maximum of liquid silica are both related to the formation of an RTN in the liquid, it is useful to compare their locations to each other and to the phase boundaries of the model system.

Figure 2 shows our evaluation of the phase diagram of BKS silica. As described in Saika-Voivod *et al.* (2004b), we locate all possible coexistence conditions, both stable and metastable, occurring among the liquid phase (L) and the crystalline

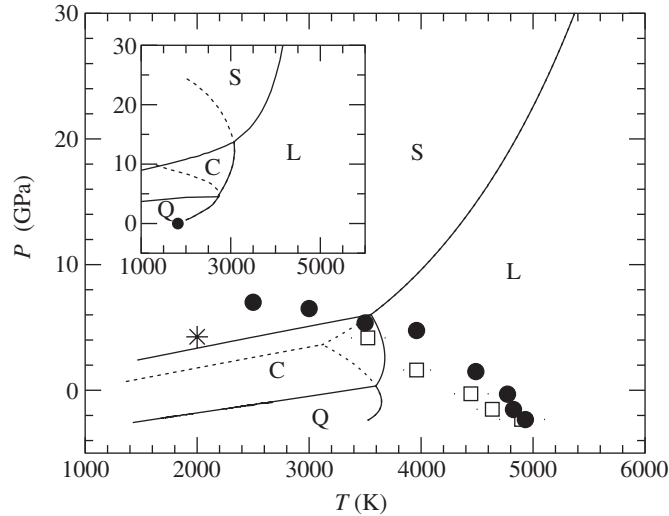


Figure 2. Phase diagram of BKS silica in the P - T plane. The solid lines locate the phase boundaries for the liquid (L), stishovite (S), coesite (C) and β -quartz (Q). Metastable coexistence lines (dashed) are also shown that meet at the metastable S-L-Q triple point. The locations of the TMD line (filled circles) and C_V maxima (open squares) are indicated. The star locates a state point of the supercooled liquid at which simulation evidence for liquid-liquid phase separation was reported in Saika-Voivod *et al.* (2001a). The inset shows the experimentally determined coexistence lines, and their metastable extensions, for the same phases as in the main figure. The location of the observed TMD of the real liquid is shown as a filled circle.

phases β -quartz (Q), coesite (C) and stishovite (S). We compare the model phase diagram to that determined experimentally in figure 2. The quantitative comparison is poor, especially the pressures at which corresponding features occur. For example, the S-L-C triple point occurs at 13.4 GPa in real silica, but at only 5.8 GPa in the model. Overall the P range of the crystal stability fields is substantially lower in the model. The correspondence in the thermal properties is better, but not impressive. The T of the S-L-C and C-L-Q triple points are respectively 15% and 32% higher than their experimental values. At the same time, it is noteworthy that the topology of the real silica phase diagram is preserved in the model. Characteristic features, such as the melting line maxima in both the Q-L and C-L coexistence lines are also reproduced. Thus, despite its quantitative deficiencies, the model is appropriate for studying the qualitative behaviour of a substance with a silica-like phase diagram.

As shown in figure 2, the location of the lines of maxima of C_V and of density approximately coincide, consistent with the connection of both to the RTN formation in the liquid. At the same time, one perplexing feature of the BKS liquid stands out when placed in the context of the phase boundaries: the location of the density maximum. The occurrence of a temperature of maximum density (TMD) in liquid silica is a feature that is characteristic of tetrahedral liquids (Angell & Kanno 1976), the TMD in liquid water at 277 K being the best known example. The experimentally observed TMD in silica occurs at $T = 1823$ K at ambient P , in the supercooled liquid. Yet in BKS silica it occurs well above melting at T as high as 4950 K, an increase on the experimental value of 170%. This is much larger than the increase in T of other characteristic features, such as the triple points, which are not more than 32%

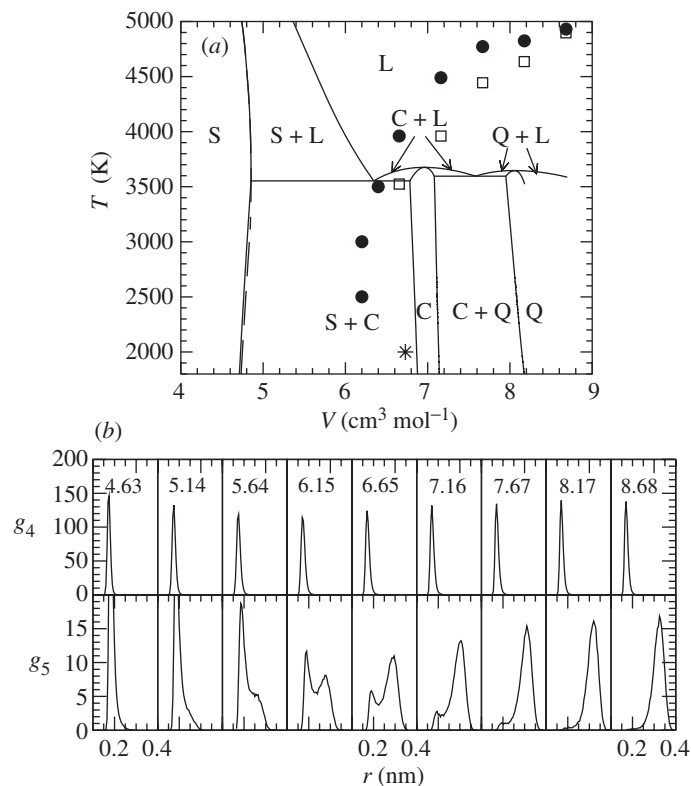


Figure 3. (a) Phase diagram of BKS silica in the V - T plane. The notation and symbols used have the same meaning as in figure 2. Note that in this projection, both one-phase stability fields and two-phase coexistence regions are located. (b) Structural change in the equilibrium liquid at $T = 3000$ K as a function of V . The top row presents $g_4(r)$, with V (in $\text{cm}^3 \text{mol}^{-1}$) indicated in each panel. The bottom row shows the corresponding plots of $g_5(r)$.

higher in the model. Although this discrepancy may simply indicate a particularly acute limitation of the BKS model, the physical implications for the behaviour of high- T liquid silica merit further investigation.

5. Liquid-liquid phase transition

Finally, we relate the behaviour described above to the possibility of a low- T liquid-liquid phase transition (LLPT) in the BKS model, for which evidence was presented by Saika-Voivod *et al.* (2001a). For an LLPT in a multi-component system, the chemical composition x is an appropriate order parameter, and phase diagrams for such systems are often plotted in the x - T plane. For the type of LLPT proposed for tetrahedral liquids, density is predicted to be an order parameter. Hence, a phase diagram analogous to the x - T plot of a multi-component system is a V - T plot, shown for the BKS model in figure 3. This type of plot is rarely constructed for materials at fixed composition, due to the challenge of determining the densities of coexisting phases, especially at high pressure. However, it is readily constructed from simulation data.

We see in figure 3 that the line of C_V maxima and the TMD line envelop the low- T , high- V region of the V - T plane in which the one-phase stability fields of coesite and β -quartz occur. Both of these crystals are based on four-coordinate Si atoms and, as will be shown below, this is also the region in which four-coordinate Si atoms dominate the liquid structure. Notable in figure 3 is the large two-phase coexistence region between the one-phase stability fields of coesite and stishovite, across which the density changes by *ca.* 30%. The point studied for signs of an LLPT occurs near the high- V side of this region, and at V just above that of the TMD. In multi-component systems, there are numerous cases where liquid-liquid demixing occurs in a supercooled melt at compositions within that of a broad crystal-crystal coexistence region. The simulations on which our phase boundary evaluations are based do not penetrate to low enough T to reveal an explicit LLPT in the supercooled liquid phase, if indeed one occurs at all. At the same time, the thermodynamic and structural properties of the supercooled liquid in the vicinity of the stishovite-coesite coexistence region exhibit striking mixture-like behaviour.

To characterize the local structure, we consider $g(r)$, the Si-O radial distribution function (RDF); $4\pi r^2 g(r) dr$ is the probability that an oxygen atom will be found at a distance between r and $r + dr$ from a reference Si atom. We decompose $g(r)$ according to the contributions made by successive nearest-neighbour (NN) O atoms of a given Si atom, labelled in ascending order of distance from an Si atom. That is, we define sub-RDFs $g_i(r)$ according to

$$g(r) = \sum_{i=1}^{\infty} g_i(r),$$

where $4\pi r^2 g_i(r) dr$ is the probability that the i th NN O atom of a given Si atom will be found at a distance between r and $r + dr$. In figure 3*b* we show $g_4(r)$ and $g_5(r)$, the contributions to the conventional Si-O radial distribution function made by those O atoms that are, respectively, a fourth and fifth NN of an Si atom.

We use $g_4(r)$ and $g_5(r)$ to monitor the structural evolution of the supercooled liquid as the density changes across the phase diagram in figure 3. The change in $g_4(r)$ with V is unremarkable. The progression simply shows that there are always at least four NN O atoms in the first coordination shell of Si atoms. We use the position of the peak in $g_4(r)$ as a reference, approximately locating the first coordination shell.

The change in $g_5(r)$ with V is much more interesting. Over a range of V , from 5.5 to 7.5 cm³ mol⁻¹, the $g_5(r)$ distribution is bimodal, with one of the peaks occurring at a distance consistent with the first coordination shell, and the second outside it. This indicates that two distinct populations of Si atoms occur under these conditions: those having four O atoms in the first coordination shell, and those having five. That is, the liquid in this regime is behaving as a mixture of two ‘species’ of Si atom, distinguished by their coordination environments.

The thermodynamic behaviour of the supercooled liquid also suggests mixture-like properties. Notably, the V where the numbers of these species are equal coincides with the V at which isotherms of S versus V exhibit a maximum, shown in figure 4. (Note that this maximum formally corresponds to the TMD line of the liquid, plotted in figure 3.) Analogous behaviour is observed in multi-component systems, where the entropy maximum arises due to the entropy of mixing of the chemical species. The Helmholtz free energy A and potential energy E are also shown in figure 4. As in

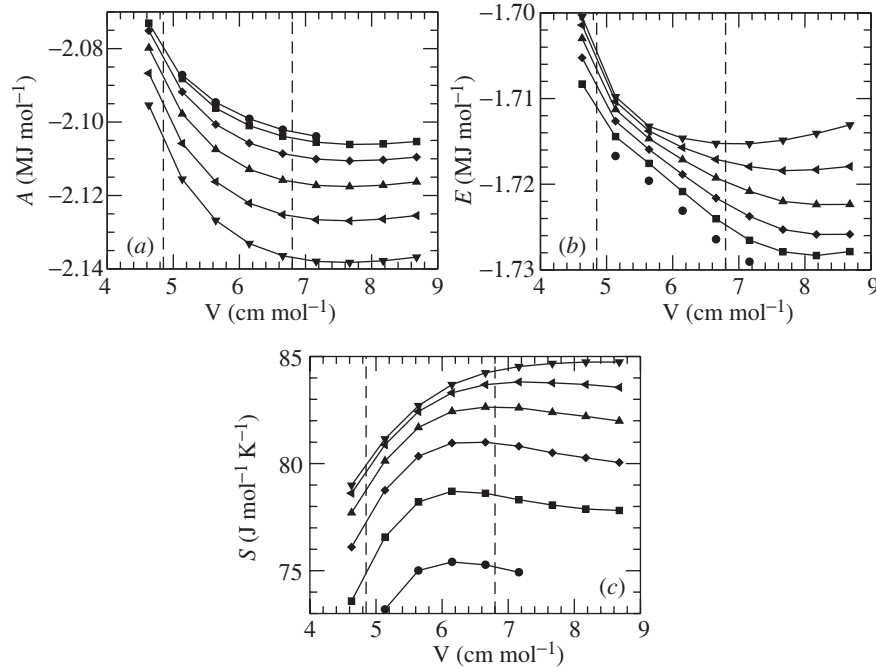


Figure 4. Isotherms of (a) A , (b) E and (c) S as a function of V . Note that all curves have been shifted by arbitrary amounts for clarity. As a reference, the vertical dashed lines indicate the volumes of stishovite and coesite at the S–L–C triple point. The temperatures shown are 2500 K (circles), 3000 K (squares), 3500 K (diamonds), 4000 K (triangles), 4500 K (left triangles) and 5000 K (down triangles).

the case of S , these quantities display a pattern of behaviour (as a function of V) analogous to that of the Gibbs free energy and enthalpy in a two-component system (as a function of x). At high T , the contributions from the curvature of both $S(V)$ and $E(V)$ to the thermodynamic stability of the homogeneous liquid phase are positive. At low T in the vicinity of the S maximum, the contribution of $E(V)$ decreases to nearly zero, and so the homogeneous liquid is ‘entropy stabilized’ in this range of V . If the trend in the curvature of $E(V)$ continues to lower T , an LLPT may occur. At higher V , the trends are reversed. $E(V)$ contributes more strongly to stability, while $S(V)$ contributes negatively: the liquid is ‘energy stabilized’. At intermediate V lies a locus of states along which $(\partial^2 S / \partial V^2)_T = 0$. In this region, $(\partial^2 E / \partial V^2)_T$ seems also to be decreasing toward zero, making this the most likely V at which the LLPT can be observed at the highest T . This interplay of behaviour almost certainly underlies why evidence was found for an LLPT near this particular V by Saika-Voivod *et al.* (2001a).

In summary, our phase diagram, thermodynamic and structural results on BKS silica all suggest a picture in which, as T decreases, the liquid phase self-organizes into a mixture of two distinct coordination species. An LLPT need not necessarily occur in such a ‘self-organized mixture’, for the same reasons that an LLPT does not necessarily occur in all chemical mixtures. However, our results make clear that the explicit mixture-like behaviour of BKS silica (and potentially, of the large class of related tetrahedral materials, both real and simulated) needs to be considered to fully

understand their behaviour. ‘Mixture’ or ‘two-state’ models of chemically pure liquids have a long history in theoretical treatments of the liquid state (see, for example, Rapoport 1968), but most studies in recent decades have opted to consider liquids in terms of an undifferentiated continuum of local configurations. The present results indicate that a reconsideration of the mixture model approach, for some materials, is justified at low T .

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Discussion

C. R. A. CATLOW (*Department of Chemistry, University College London, UK*). Have you considered using more sophisticated potentials for SiO₂, such as those which include the effects of covalence and polarizability?

P. H. POOLE. It will certainly be important to confirm the qualitative aspects of the results with better potentials. Ours is an initial survey, requiring of the order of 100 state points to be equilibrated, many at the lowest temperatures accessible to current computing power. This approach leads us to use an approximate, but computationally efficient potential.

P. G. WOLYNES (*Department of Chemistry and Biochemistry, Department of Physics and Center for Theoretical Biological Physics, University of California, San Diego, La Jolla, CA, USA*). According to the random first-order transition approach to glass formation there is a crossover temperature for activated behaviour. Can you tell us where this occurs for BKS silica? Is it distinguishable from the fragile-strong crossover?

P. H. POOLE. Horbach & Kob (1999) estimated that the critical temperature of mode coupling theory (MCT) occurs in BKS silica at 3330 K. A crossover to activated behaviour is suggested by the temperature range in which the liquid dynamics deviates significantly from the prediction of MCT; this occurs in the vicinity of 3600 K. This temperature range is in approximate correspondence with the crossover in the landscape properties that we find underlies the fragile-to-strong crossover: the inflection in the inherent structure energy occurs at *ca.* 3900 K. This is the temperature at which deviations from high-temperature fragile behaviour can be expected to begin, with a fully developed activated behaviour emerging as the temperature decreases below this value. We have not examined the microscopic dynamics in detail to assess the degree to which purely activated behaviour has set in at the lowest temperatures studied, but it would be enlightening to do so for the reasons you suggest.

J. L. FINNEY (*Department of Physics and Astronomy, University College London, UK*). The theoretical work of George Stell and others convinces me that, in principle, a liquid–liquid transition can exist in a system whose structure is determined by a potential function with particular—one might say pathological—properties. In looking at candidate systems for the possible existence of a liquid–liquid transition phase boundary, rather than trying to decide if such a transition exists by calculating or simulating the system’s behaviour, would it be more effective to focus on sorting out the details of the appropriate potential function to see if it has the properties appropriate to the existence of two liquid phases? Or are the necessary potential function characteristics not that well defined?

P. H. POOLE. I agree that this should be the long-term goal: to identify the possibility of a liquid–liquid phase transition from the properties of the intermolecular potential. As you point out, Stell and others have identified potential properties sufficient to induce the occurrence of a liquid–liquid phase transition in certain classes of system, particularly spherically symmetric atomic potentials. The properties that

a multi-site molecular potential should have to yield a liquid–liquid transition are much less well understood. Computational work can serve to identify candidate systems and suggest trends, as we have tried to do here. The pursuit of a general analytical theory connecting potential properties to the thermodynamics of a liquid–liquid phase instability is a daunting theoretical task, yet a successful attempt would generate some much needed insight. It deserves more attention.