

## Amorphous silica from the Rigid Unit Mode approach

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### ABSTRACT

We apply the Rigid Unit Mode model, which was initially developed for crystalline silicates, to the study of the flexibility of silica glass. Using a density-of-states approach we show that silica glass has the same flexibility against infinitesimal displacements of crystalline phases. Molecular dynamics simulations also show that parts of the silica structure are able to undergo large spontaneous changes through reorientations of the SiO<sub>4</sub> tetrahedra with no energy cost.

**KEYWORDS:** amorphous silica, Rigid Unit Mode theory, silica glass.

### Introduction

IN this paper we begin to tie together two related — but not yet connected — strands of work on the dynamics of silicate materials, specifically those whose atomic structures consist of an infinite network of SiO<sub>4</sub> tetrahedra linked at the corners. Both strands concern the degree of rigidity or floppiness of the structures. The first strand concerns the dynamics of general amorphous networks, for which a general theoretical framework has been developed that links the rigidity of the network to the number of chemical bonds of specific type (Phillips, 1979; Thorpe, 1983; Thorpe *et al.*, 1997). At the heart of this theory is the analysis of the balance between the number of degrees of freedom of the network and the number of constraints that reduce the overall flexibility of the network, a theory that was initially used by Maxwell (1864) to analyse the stability of engineering structures. The second strand concerns the dynamics of crystalline silicates, using our ‘Rigid Unit Mode’ (RUM) model (Giddy *et al.*, 1993; Dove *et al.*, 1993, 1995*b*; Dove, 1997*a*; Hammonds *et al.*, 1996).

This also is based upon the balance between degrees of freedom and constraints, but symmetry now has a role that is not taken into account in the analysis of amorphous networks. In both cases, if the number of degrees of freedom exceeds the number of independent constraints, there will be some patterns of deformation that cost no energy, which could correspond to zero frequency normal modes of vibration. Of course, when the full range of all the real interatomic forces are taken into account the zero frequency will be modified to a non-zero value, but will remain small since the constraints are always those associated with the stiffest bonds.

To point towards the convergence of the two approaches, we work out the application of the Maxwell approach to silica when we consider the basic objects to be rigid SiO<sub>4</sub> tetrahedra (Dove *et al.*, 1993, 1995*b*, 1999; Dove, 1997*a*). Each tetrahedron has six degrees of freedom, three translations and three rotations. For the constraints, there are three constraints per vertex which force the vertex of one tetrahedron to be at exactly the same position as the vertex of the neighbouring linked tetrahedron. Since each set of three constraints is shared equally between the two linked tetrahedra, and there are four vertices in each tetrahedron, there are six constraints for each tetrahedron. Thus, in an infinite system, or

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one with periodic boundary conditions, there is an exact balance between the numbers of degrees of freedom and constraints. The number of zero-frequency modes in this system will be equal to the difference between the number of degrees of freedom and the number of constraints, which in this case is equal to zero. This way of counting is exact, but for crystalline silicates we have shown that symmetry can cause some of the constraints to become degenerate (Giddy *et al.*, 1993; Dove *et al.*, 1995*a,b*; Dove, 1997*a*). This means that there are more degrees of freedom than independent constraints rather than there being an exact balance, so that there will be a finite number of zero-frequency normal modes. Because these will involve the tetrahedra moving as rigid units without internal deformations, we call these modes of motion the rigid unit modes (RUMs). Moreover, we have found in crystalline silicates that it is also important to widen the issue to consider not just the zero-frequency modes, but also the vibrational modes with very low, but non-zero, frequencies (Hammonds *et al.*, 1997*a*).

Our objective in this paper is to try to identify the similarities between the low-frequency RUM motions found in glasses, and the low-frequency dynamics of silica glass, using the methods we have developed for crystalline silicates. Our scientific goals are defined by a number of features of the low-frequency dynamics of glass phases. At very low temperatures there are low-frequency excitations that give rise to a linear variation of the heat capacity with temperature above the normal  $T^3$  Debye dependence (Zeller and Pohl, 1971). Raman and neutron spectroscopy experiments (Levelut *et al.*, 1997) show a broad spectrum of excitations over the frequency range 0–1 THz (0–4 meV) that have a strong temperature dependence. This range is the same as that for RUMs in crystalline silicates, as shown for  $\beta$ -cristobalite (Swainson and Dove, 1993) and cubic-leucite (Boysen, 1990). Finally, Raman and neutron spectroscopy experiments (Levelut *et al.*, 1997) on many glasses show a peak at  $\sim 1$  THz (4–5 meV) that has provoked a lot of discussion in the literature, and it has been suggested that this may have a RUM-type origin (Buchenau *et al.*, 1986, 1988). Our own inelastic neutron scattering data (Dove *et al.*, 1997*a*; Harris *et al.*, 1999, 2000), and those from the work of others (Foret *et al.*, 1996), suggest that this is not the case, and that the Boson peak arises from acoustic-like excitations (Harris *et al.*, 1999, 2000). Initially we had thought that the RUM spectrum of glasses

would not be as significant as it is for crystalline silicates because of the absence of symmetry which, in crystalline silicates, allows the existence of zero-frequency RUMs. However, in this paper we show that silica glass has the same RUM flexibility as the crystalline phases.

The outline of this paper is as follows. We first review the essential details of the RUM model and our methods for calculating the RUMs in a given structure. Following this we consider how the existence of RUMs in crystalline phases is important in allowing the glass structure to ‘borrow’ elements of the crystalline structures. Then we turn to think about the possible existence of RUMs in silica glass. Finally we show how the glass can undergo large changes in the structure which preserve the topology of the structure. The technical details associated with the calculations are given in the Appendix.

### Brief review of the Rigid Unit Mode model

The rigid unit mode model originated as an attempt to determine the ways in which the crystal structure of a framework silicate can distort in order to allow a displacive phase transition to occur (Giddy *et al.*, 1993; Hammonds *et al.*, 1996; Dove, 1997*a,b*). The basic idea is that any low-energy distortion of a silicate structure will have a minimal deformation of the constituent  $\text{SiO}_4$  tetrahedra, since these units are fairly stiff and any significant deformation will carry a high energy penalty. The search for possible distortions in quartz was first carried out by Vallade and co-workers (Berge *et al.*, 1986; Vallade *et al.*, 1992), who enumerated all the normal modes of motion that are allowed to propagate without the tetrahedra having to deform as part of the motion. This work used direct analytical methods, which unfortunately were not easy to apply to more complicated silicates. Our way around this problem was to develop the ‘split-atom method’ (Giddy *et al.*, 1993), in which the  $\text{SiO}_4$  tetrahedra are treated as being completely rigid, and pairs of linked oxygens are replaced by two atoms, notionally located at the same point in space, with a spring force between them which acts to resist any motion that moves them apart. This model is represented in Fig. 1, and in many applications no additional forces are added (we have, however, implemented a modification which contains forces between the nearest-neighbour Si atoms). The model is relatively easy to implement within the formalism of

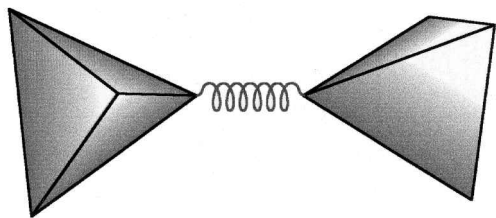


FIG. 1. Representation of the split-atom method. As two tetrahedra move in a way that strains the common vertices, the model represents the required distortions of the two tetrahedra by the stretching of a spring linking the two vertices. Formally, the stiffness of the spring is equivalent to the stiffness of the tetrahedra against deformation.

molecular lattice dynamics, and we have developed the CRUSH code (Giddy *et al.*, 1993; Hammonds *et al.*, 1994) to evaluate all the normal modes of motion for any given wave vector in which the tetrahedra can move as rigid units (i.e. without the tetrahedra needing to distort). These modes of motion are called 'rigid unit modes', and within this approach are strictly the normal modes of motion that are calculated to have zero frequency.

Initially we mostly considered RUMs with wave vectors of special symmetry within the Brillouin zone, and we have compiled tables for a number of important crystal structures which give the numbers of RUMs for special points, lines and planes of wave vectors (Hammonds *et al.*, 1996). Most crystalline silicates we have investigated (e.g. the phases of silica and their aluminosilicate derivatives) have RUMs on planes of wave vectors. Zeolites are exceptions, for a number of zeolite structures have one or more RUMs for each wave vector (Hammonds *et al.*, 1997*a,b*, 1998*a*). Recently we have realized that it is quite common for a crystal structure to also have a significant number of RUMs that lie on exotic curved surfaces in reciprocal space (Dove *et al.*, 1995*b*, 1999; Pryde *et al.*, in prep. A gallery of curved RUM surfaces can be found on the worldwide web at <http://www.esc.cam.ac.uk/rums>).

In our work on crystalline silicates the initial objective of the RUM model was to attempt to explain the origins of displacive phase transitions. Specific RUMs can act as the classical soft modes for these phase transitions, and the task of explaining the origin of a particular displacive phase transition reduces to identifying a RUM of the correct symmetry and wave vector to match

the associated soft mode (Giddy *et al.*, 1993; Hammonds *et al.*, 1996; Dove, 1997*a,b*). Subsequently it was realized that the RUM model also provided an explanation of the thermodynamic behaviour of many displacive phase transitions (Dove *et al.*, 1995*b*; Dove, 1997*a,b*). The RUM model has also been applied to the problems of negative thermal expansion in ceramics (Pryde *et al.*, 1996; Heine *et al.*, 1998; Welche *et al.*, 1998) and the catalytic behaviour of zeolites (Hammonds *et al.*, 1997*a,b*, 1998*a*).

Much of our work to date has focused on the importance of RUMs as zero frequency modes within the simplified model of rigid tetrahedra and no inter-tetrahedral forces (Hammonds *et al.*, 1996). This is appropriate when searching for soft modes for phase transitions, but it is important to appreciate that the number of RUMs as a proportion of the total number of phonon modes in a crystal is tiny. To illustrate this we take the common situation where the RUMs are found with wave vectors lying on particular planes in the Brillouin zone. For a crystal containing  $N$  unit cells there will be  $N$  wave vectors, so that the number of wave vectors lying on a single plane in the Brillouin zone will be of order  $N^{2/3}$ . Therefore the proportion of phonon modes that are RUMs will be of order  $N^{-1/3}$ , and it should be recalled that  $N$  will be of the order  $10^{20}$ – $10^{24}$  for an experimental sample.

When the proportion of modes that are RUMs is so small, to simply count the number of RUMs has limited value. Instead, we have developed a new way of thinking about the flexibility of crystal structures that is based on the calculation of the vibrational density of states,  $g(\omega)$ , using the split-atom model (Giddy *et al.*, 1993), where  $g(\omega)d\omega$  gives the number of modes with angular frequencies between  $\omega$  and  $\omega + d\omega$ . In effect, by focusing on the zero frequency solutions we are basing our evaluation of the RUM flexibility on the enumeration of  $g(0)$ . When taking account of the exotic curved surfaces of RUMs, (Dove *et al.*, 1995*a*, 1999; Pryde *et al.*, in prep.),  $g(0)$  can be difficult to evaluate accurately. Instead, it is more instructive to evaluate the flexibility of a structure by evaluating  $g(\omega)$  in the limit  $\omega \rightarrow 0$  (Hammonds *et al.*, 1998*b*). The single force constant in the split-atom model actually represents the finite stiffness of the tetrahedra against deformations, and allows the phonon frequency to vary continuously with wave vector on moving away from RUM wave vectors (where the RUM

frequency is zero) into the Brillouin zone (where the phonon frequency is determined by the extent to which the vibration distorts the tetrahedra). We find that for a system containing no RUMs, e.g. crystals containing octahedra linked to tetrahedra,  $g(\omega) \propto \omega^2$  as  $\omega \rightarrow 0$  (Hammonds *et al.*, 1998*b*). This result arises in any normal phonon treatment and reflects the case where the only low-frequency vibrations are the long-wavelength acoustic modes. On the other hand, we find for many systems containing RUMs that  $g(\omega) \approx$  constant as  $\omega \rightarrow 0$ , with the size of  $g(\omega)$  reflecting the flexibility. For very flexible systems, such as zeolites,  $g(\omega)$  has a peak at  $\omega \propto 0$ . We use the approach of analysing the low  $\omega$  behaviour of  $g(\omega)$  in our comparison of glass and crystalline phases below.

### Rigid Unit Modes in crystalline silica and the implications for the atomic structure of silica glass

Both  $\beta$ -cristobalite and the hexagonal phases of tridymite have planes of RUMs (Hammonds *et al.*, 1996; Swainson and Dove, 1993; Dove *et al.*, 2000). These impart considerable flexibility to the structure. In these high-temperature phases the average structures have linear Si–O–Si bonds, but there are considerable local distortions that allow the Si–O–Si bonds to relax to lower-energy angles (Swainson and Dove, 1995; Dove *et al.*, 1997*b*; Keen and Dove, 1999, 2000; Gambhir *et al.*, 1997, 1999). Some authors have proposed that for  $\beta$ -cristobalite this arises through the spontaneous formation of small domains of lower symmetry structures (Wright and Leadbetter, 1975; Hatch and Ghose, 1991), but we have shown that, instead, the RUMs provide enough flexibility for the structure to dynamically distort on a local scale as a result of the dynamic superposition of the atomic displacements associated with many RUMs (Swainson and Dove, 1993; Hammonds *et al.*, 1996). This idea is supported by the experimental results shown by Keen and Dove (1999, 2000). This flexibility is highlighted by a series of snapshot images of a ring of six tetrahedra in the high-tridymite structure obtained from a molecular dynamics simulation (Dove *et al.*, 2000), Fig. 2. This series of snapshots forms part of an animation that is part of a collection of animations of the tridymite structures that is available for public viewing on the world-wide web (<http://www.esc.cam.ac.uk/rums>).

Keen and Dove (1999, 2000) have shown that there is a close relationship between the atomic configurations of silica glass and the  $\beta$ -cristobalite and high-tridymite forms of crystalline silica over the length scale 0–10 Å. The possibility for the glass structure to ‘borrow’ elements of the structures of these crystalline phases arises because of the inherent RUM flexibility of these structures. The snapshot images of the rings of tetrahedra in tridymite in Fig. 2 show how distorted these rings can become. Of course, the rings are not isolated but are part of the crystalline matrix, and the distortion of one ring must be correlated with the distortion of a wider part of the crystalline environment. However, there are planes of RUMs in tridymite parallel to (001), and dynamic linear superposition of these RUMs will allow a high degree of localization of ring distortions. The RUMs in cristobalite are of a different form, but molecular dynamics simulations have shown that they can yield similar localized distortions (Gambhir *et al.*, 1999). The same idea has been developed in more detail for the prediction of localized static RUM distortions in zeolites (Hammonds *et al.*, 1997*a,b*, 1998*b*). The fact that the structure of silica glass has similarities to that of the disordered phases of cristobalite and tridymite means that the glass is able to use the same localized RUM flexibility.

### Atomic configurations of silica glass

The issue of constructing an atomic model for silica glass has long been problematic. For our analysis we require a model of linked SiO<sub>4</sub> tetrahedra with periodic boundaries and, initially, with no defects leading to the existence of non-bridging oxygens. To develop such a configuration from molecular dynamics simulations is not easy. Our approach was to start with a number of defect-free models for amorphous-silicon developed using the Wooten-Weaire algorithm (Wooten *et al.*, 1985; Wooten and Weaire, 1987), kindly provided by Prof. M.F. Thorpe, and to adapt these by placing an oxygen atom midway between each pair of bonded silicon atoms. The length scale was chosen to give first-neighbour Si...Si distances in agreement with experiment. This procedure automatically produces linear Si–O–Si linkages with shortened Si–O bonds. The structure was then allowed to relax to have more reasonable Si–O–Si angles by running the configurations through a molecular dynamics simulation with the interatomic poten-

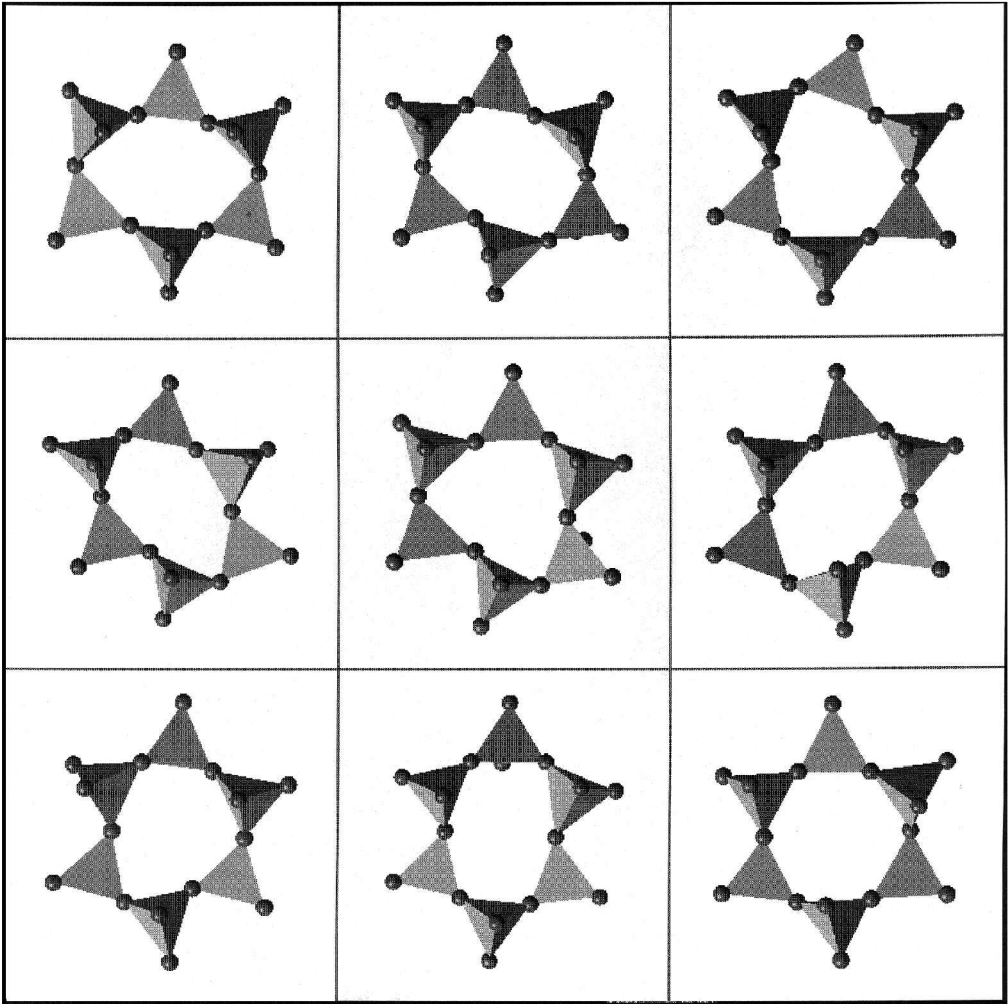


FIG. 2. A series of snapshot images of a ring of six tetrahedra in the high-tridymite structure obtained from a molecular dynamics simulation.

tials of Tsuneyuki *et al.* (1988), initially at a relatively high temperature, and then cooling down to 10 K to allow the system to relax into a local potential energy minimum. From the final configurations we were able to calculate the pair distribution functions  $g(r)$ , and from these we constructed the neutron scattering  $T(r)$  functions

$$T(r) = 4\pi r \sum_{\alpha\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} g_{\alpha\beta}(r)$$

where  $\alpha$  and  $\beta$  are two atomic species (Si or O),  $b_{\alpha}$  and  $c_{\alpha}$  are the neutron scattering length and

atomic concentration of atomic species  $\alpha$  respectively, and  $g_{\alpha\beta}(r)$  is the pair distribution function for atomic species  $\alpha$  and  $\beta$ . The calculated  $T(r)$  is compared with experimental data in Fig. 3. It can be seen that the agreement is reasonable.

#### RUMs in silica glass

Using our silica glass configurations we have calculated the phonon density of states using the split-atom model (Giddy *et al.*, 1993), and our results are compared with those for  $\beta$ -cristobalite in Fig. 4. The similarities of  $g(\omega)$  for the two

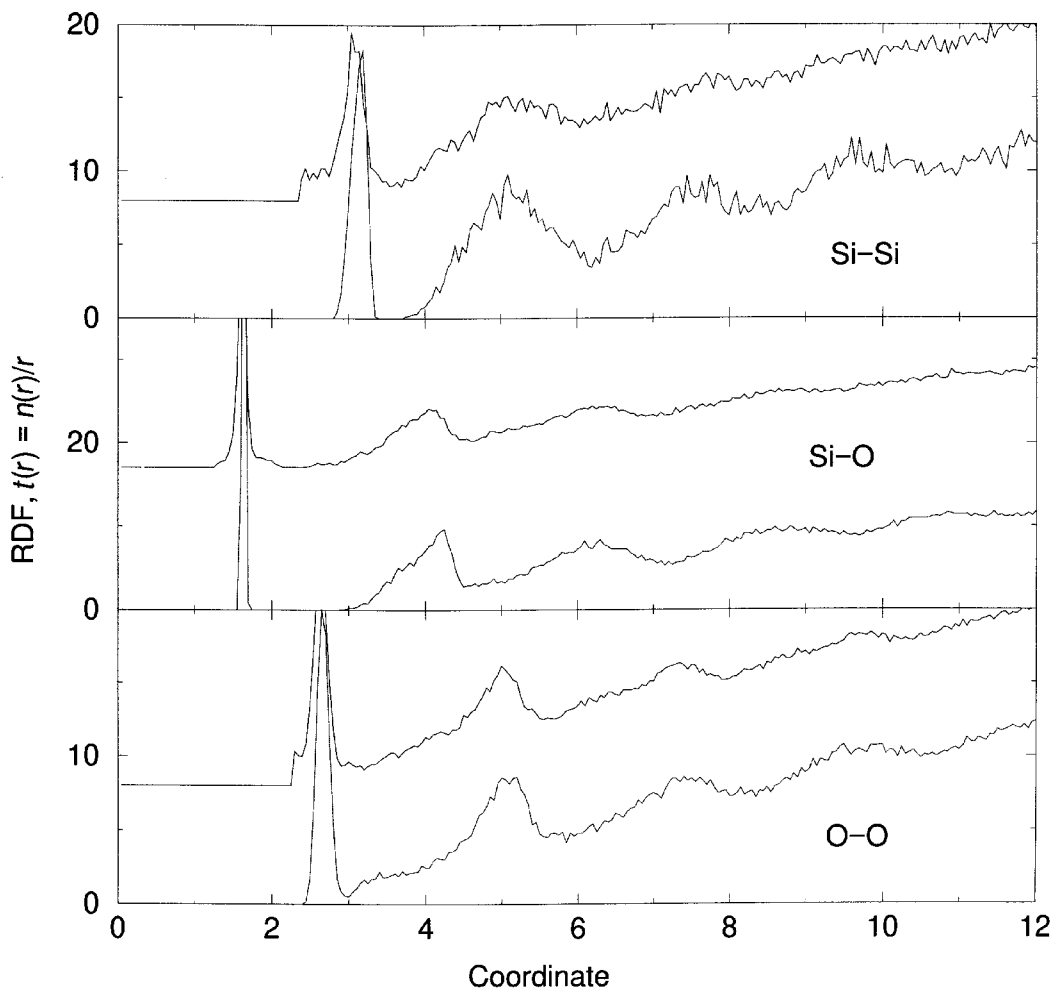


FIG. 3. Comparison of the calculated (lower curves) and experimental  $T(r)$  functions for silica glass.

systems is striking — one can view  $g(\omega)$  of silica glass simply as a lower-resolution version of  $g(\omega)$  of  $\beta$ -cristobalite. This implies that silica glass has the same RUM flexibility as  $\beta$ -cristobalite, contrary to our initial expectations as detailed in the introduction to this paper.

It is common to quantify the localization of the atomic motions associated with vibrations in glasses through the participation ratio  $\mathcal{P}$ . If  $\mathbf{u}_j$  represents the displacement of atom  $j$  in any given vibration, the participation ratio is defined as:

$$\mathcal{P} = \frac{(\sum |\mathbf{u}_j|^2)^2}{N \sum |\mathbf{u}_j|^4}$$

For a vibration in which all atoms participate equally,  $\mathcal{P} \approx 1$ , whereas for a vibration involving only a single atom  $\mathcal{P} \approx 1/N$ . For the  $g(\omega)$  of silica glass shown in Fig. 4,  $\mathcal{P} \approx 0.8$  for all  $\omega$ , including the low- $\omega$  modes. This means that the low- $\omega$  RUM-like vibrations involve all tetrahedra in the glass, and are not localized to particularly flexible segments of the glass structure.

We have investigated the effect of introducing non-bridging Si-O bonds into the glass structure by removing some of the Si centres. An example of the resultant  $g(\omega)$  is shown in Fig. 4. The interesting feature is the formation of a peak in  $g(\omega)$  at  $\omega \approx 0$ . This is not surprising since the Maxwell counting scheme indicates that by

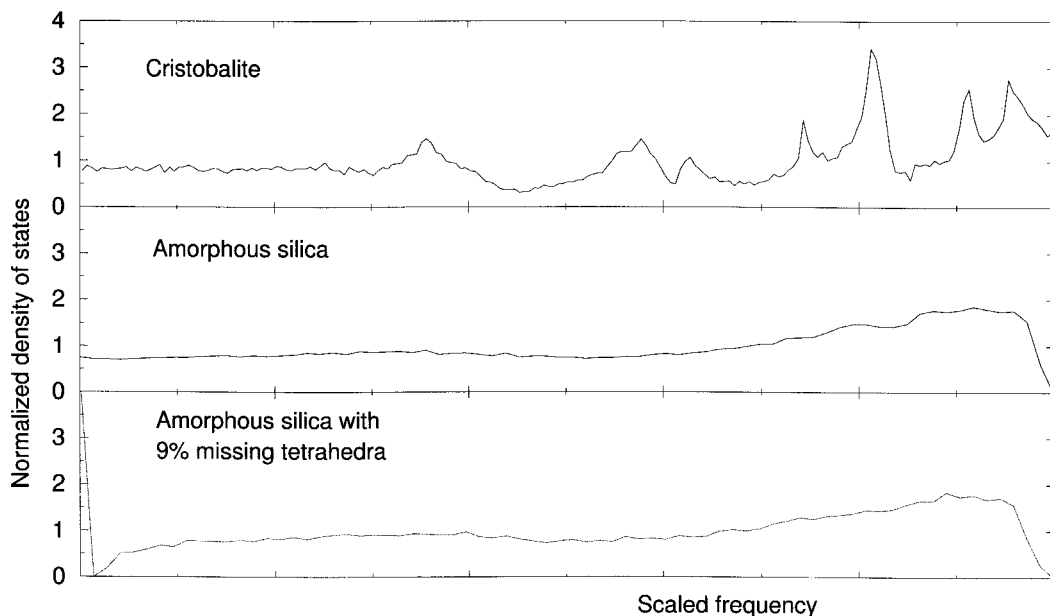


FIG. 4. Calculated phonon density of states,  $g(\omega)$ , for a silica glass configuration,  $\beta$ -cristobalite, and a silica glass configuration containing some Si-vacancies, constructed using the split-atom method.

removing one tetrahedron there is a reduction of 6 in the number of degrees of freedom, but a reduction of 12 in the number of constraints, so there will be  $12 - 6 = 6$  new zero-frequency vibrations. The interesting point from Fig. 4 is that the new zero-frequency modes come from the low-frequency part of the RUM density of states. Moreover, the calculated participation ratios for the new zero-frequency modes vary uniformly from 0–0.8, showing that some are highly localized and others are as delocalized as other vibrations.

#### An interesting aside – the heat capacity of a RUM system

There has been considerable interest in the observation that the heat capacity of amorphous materials tends to vary as  $C \approx T$  at low temperatures, rather than following the usual Debye form  $C \approx T^3$ . If the density of states follows the RUM form shown in Fig. 4, it can be idealized as having a constant value for frequencies below a cut-off frequency  $\omega_R$ , i.e. for one mole of Si atoms  $g(\omega) = 6N_A/\omega_R$ . For this density of states the heat capacity (per mole of Si) at low temperatures has the form

$$C = \frac{2\pi^2 RT}{T_R}$$

where  $k_B T_R = \hbar \omega_R$ . We estimate that a reasonable value of  $T_R$  is 1000 K for silica, taking account of the highest vibrational frequency. Compared with experimental data (Zeller and Pohl, 1971), however, this function gives results that are too high, in the low-temperature limit, by about a factor of 10. This of course is not surprising. The RUM density of states cannot be a true representation of the true density of states since it neglects all inter-tetrahedra interactions. On the other hand, there may be a smaller continuum of vibrations down to zero frequency remaining after the true interatomic potentials are taken into account.

#### Large-amplitude changes in the glass structure

The RUM flexibility of a structure is properly concerned with low-energy infinitesimal distortions of the structure. In practice the RUMs will have relatively large amplitudes, and with a superposition of a large number of RUMs, the actual atomic displacements can be quite large,

but they always refer to continuous distortions about a set of mean positions. On the other hand, it has been proposed that the tetrahedra in silica glass may be able to undergo large reorientations from one potential energy minimum to another. The Maxwell counting scheme for silica glass leads to the same result for crystalline silica phases, namely that there is an exact balance between the numbers of constraints and degrees of freedom, so it is difficult to predict whether or not these types of motion are possible.

We have explored this issue by performing molecular dynamics simulations on our silica glass configurations at temperatures of  $\sim 50$  K. We have identified a number of events whereby small groups of tetrahedra suddenly jump from one orientation to another. An example is shown in Fig. 5, where we superimpose the orientations of a small group of tetrahedra before and after a sudden jump. The jump motion is highlighted in Fig. 6, which shows the time-dependence of the  $x, y, z$  coordinates of one of the oxygen atoms in this group of tetrahedra. In Fig. 6 we also show the time-dependence of the  $x, y, z$  coordinates of an oxygen atom involved in a different event, in which a jump is subsequently reversed a short time later. These jump events can be viewed as animations on the world-wide web (<http://www.esc.cam.ac.uk/rums>).

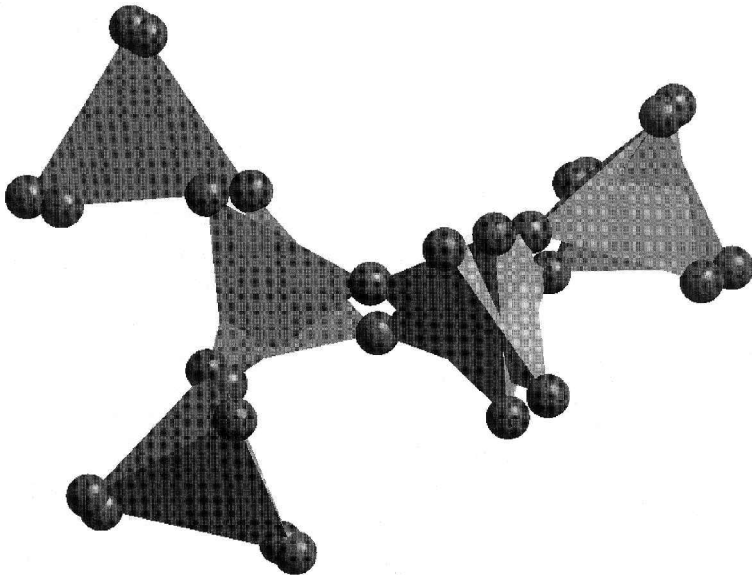


FIG. 5. Superposition of the orientations of a small group of tetrahedra within a larger configuration of silica glass before and after a sudden jump in the orientations of the group of tetrahedra.

In Fig. 7 we show the time-dependence of the potential energy of the system through the jump event shown in Fig. 5. The results in Fig. 7 show that any change in the potential energy through the jump event is substantially lower than the normal fluctuations. On the other hand, it is evident from Fig. 6 that the system can remain in one potential minimum for times corresponding to many periods of oscillation of  $\text{SiO}_4$  tetrahedra before jumping to another state which implies that the energy barrier separating two minima is much larger than the thermal energy fluctuations. We have estimated that the value of the potential energy barrier is  $\sim 0.06$  eV, and the change in energy of the sample on flipping from one state to another is  $< 0.01$  eV. This suggests that the system finds a path in the phase space with the energy barrier small enough to allow it to jump in another potential minimum with little energy cost.

For these and other jump events the analysis of the participation ratio  $\mathcal{P}$  shows that  $\sim 30$  tetrahedra are involved, and for a single configuration, different jump events involve a common set of tetrahedra. We have investigated this aspect further by performing molecular dynamics simulations on a single initial configuration, that is the configuration with linear Si–O–Si bonds, with different initial velocities, and comparing the final relaxed structures. The simulations are not able to change



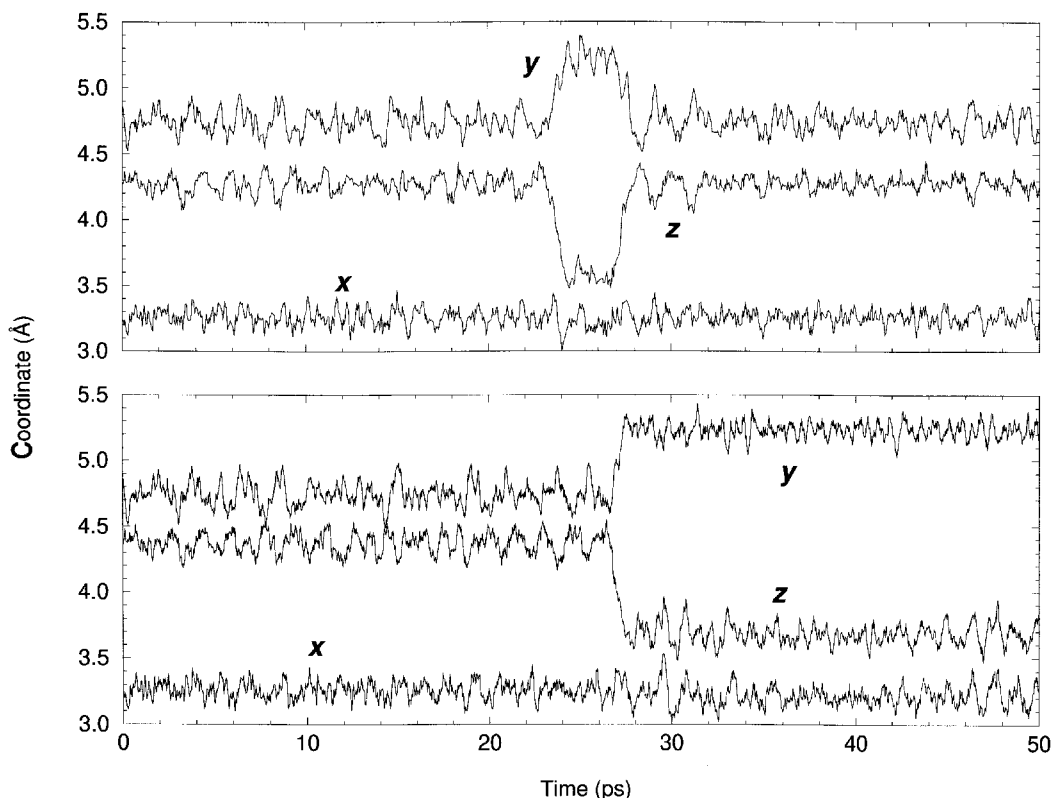


FIG. 6. The atomic coordinates  $x, y, z$  (in Å) of individual oxygen atoms within the part of the silica glass configuration that undergoes sudden tetrahedra reorientational jump events. The upper plot shows the behaviour of one of the oxygen atoms in the group shown in Fig. 5. The lower plot shows the behaviour of one of the oxygen atoms that participates in a separate jump event, in which the jump motion is subsequently reversed.

the basic topology and connectivity, but may allow the configuration to relax with different orientations of the  $\text{SiO}_4$  tetrahedra. The comparisons of the different structures showed that the main differences involve a common group of  $\sim 100$  tetrahedra, which contained the smaller groups involved in the jump motions described above. The main conclusion from this is that the glass network contains floppy regions, floppy in the sense of being able to undergo large amplitude RUM distortions, as islands within a more rigid network.

## Summary

The simulation results presented in this paper have shown the following:

(1) The RUMs in crystalline phases of silica allow sufficient flexibility for the  $\text{SiO}_4$  tetrahedra to rotate in order to avoid forming the linear

$\text{Si-O-Si}$  bonds suggested by the average structure. This flexibility is dynamic and gives the appearance of considerable disorder in the orientations of the tetrahedra and in the distortions of the 6-membered rings of tetrahedra.

(2) The ability of the structures of the high-tridymite and  $\beta$ -cristobalite phases of silica to have quasi-localized RUM distortions gives the structure of silica glass the ability to employ the elements of its crystalline phases.

(3) Silica glass has the same RUM flexibility as  $\beta$ -cristobalite when viewed from the perspective of the phonon density of states. Creation of Si defects gives a large increase in the number of RUMs.

(4) The network structure of silica glass is also able to support large-scale jump reorientations of  $\text{SiO}_4$  tetrahedra, with very little cost in energy and with a dynamic collapse in the energy barriers.

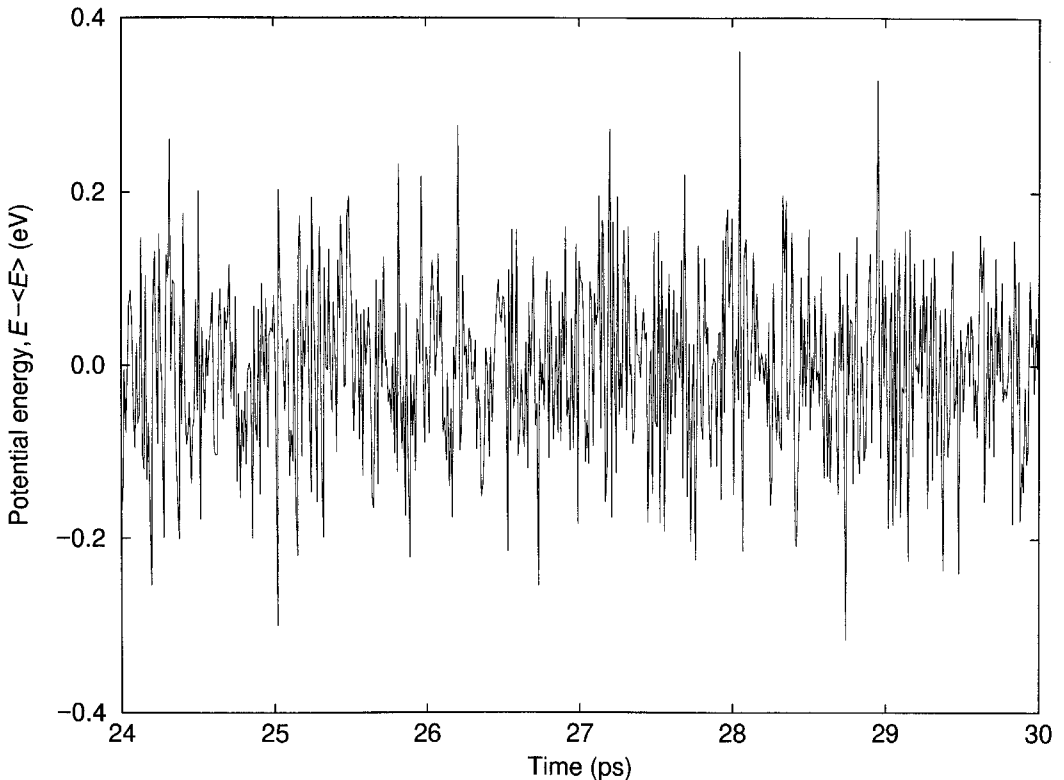


FIG. 7. The time-dependence of the sample potential energy through the jump event shown in Fig. 5.

## Appendix: Technical details

### RUM calculations

A vectorized version of the CRUSH program (Hammonds *et al.*, 1994) for the enumeration of RUMs in the glass phase was run on the Hitachi S3600 vector processor of the High-Performance Computing Facility of the University of Cambridge.

### Molecular Dynamics Simulations

The molecular dynamics simulations were performed using the DLPOLY code (Smith and Forrester, 1996), kindly provided by the Daresbury Laboratory (UK). The simulations were carried out on the Hitachi SR2201 parallel computer of the High-Performance Computing Facility of the University of Cambridge. Constant-energy, constant-volume ensembles were used following an initial equilibration stage.

For simulations of tridymite we used the shell model interatomic potential model of Sanders *et al.* (1984). In fact we investigated a wide range of

model potentials, and found that this model best reproduced the experimental phase transition behaviour, although even this model did not give a complete representation of the behaviour of tridymite. However, unlike other models, it did give a disordered high-temperature phase in agreement with experiment, and an ordered low-temperature phase. Some models did not give a disordered phase, and others did not give ordering at low temperatures; a detailed comparison of the performance of different models is given elsewhere (Pryde and Dove, 1998). This model has a shell model for oxygen anions, a specific O–Si–O bond-bending potential, Buckingham Si...O and O...O interactions, and formal charges. All parameters in the model were obtained by empirical fitting to the structure and properties of quartz.

For simulations of glass we used the model potential of Tsuneyuki *et al.* (1988). This potential has given results for some crystalline phases of silica that reproduced experimental

results. This model has Buckingham Si...Si, Si...O and O...O interactions, and non-formal ion charges. All parameters in this model were obtained by fitting to quantum mechanical energy surfaces of atomic clusters.

### Animations

Central to our work has been the ability to visualize the results of our molecular dynamics simulations. The images were produced from the time-sequence of atomic configurations generated by the molecular dynamics simulations using an in-house customization of the MSI Cerius package, and converted into Quicktime movies using Silicon Graphics MovieMaker package.

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