

Low Energy Dynamics and Tunneling States in Silica Glass

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We present the results of a simulation study of silica glass which addresses the issue of large-amplitude low energy motions involving reorientations of SiO_4 tetrahedra. Using methods developed for crystalline silicates we find that random networks of linked SiO_4 tetrahedra are as flexible as crystalline phases for infinitesimal displacements. Patches of the networks can also undergo large sudden distortions involving reorientations of the SiO_4 tetrahedra, with little change in energy and an energy barrier of around 0.06 eV. These may act as tunneling states to provide the mechanisms for the anomalous low-temperature thermal properties of glasses. [S0031-9007(98)07382-7]

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The structure of silica glass is well described as an infinite random network of SiO_4 tetrahedra linked together at the corners. Evidence comes from diffraction studies [1], reverse Monte Carlo [2] and molecular dynamics simulations [3], and model building [4]. Over short length scales there are similarities between the structures of amorphous silica and the cristobalite and tridymite crystalline phases of silica [5], and the quantitative extent of these similarities and the associated length scale has recently been deduced [6]. A description of the vibrational dynamics of silica glass is less developed [7–10].

In this Letter we address the issue of the excitations between 0–5 meV, which will include those believed to be responsible for two-level tunneling states [11] and associated with the anomalous thermal behavior at low temperatures [12]. We find here, rather surprisingly, that silica glass has the same degree of flexibility as dynamically disordered [13] crystalline phases. We also find that it is able to undergo large sudden rotational rearrangements of the structure with little energy cost, which may be identified with the tunneling states of [11]. Earlier difficulties in clearly pinpointing these states have led to some doubt about their existence [14]. In addition to visualizing these tunneling states we also answer the natural question concerning the extent of the part of glass structure which flops from one state to another, whether it involves one atom or tetrahedron, or whether it is spatially more extended.

Any low energy vibrational modes will necessarily involve only minimal distortions of the SiO_4 tetrahedra [15]. Whether an infinite framework of corner-linked SiO_4 tetrahedra can vibrate without the tetrahedra distorting is actually a very subtle issue (and for a long time it was not certain that such an infinite framework could even be constructed). It is conventional to refer to the vibrational modes in glasses which do not involve distortions of the interatomic bonds as “floppy modes” [16], and if the only forces are those associated with stretching of these bonds, the floppy modes will have zero frequency.

The number of floppy modes is equal to the difference between the degrees of freedom and the constraints [16,17]. For silica the number of degrees of freedom equals the number of simple bond constraints [18], so the topology of silica, whether amorphous or crystalline, is neither floppy nor overconstrained but balanced between the two extremes. Thus one cannot easily predict whether the floppy modes envisaged in [15] can exist.

We have recently obtained new insight into this issue by studying the crystalline forms of silica (and other framework aluminosilicates) using our “rigid unit mode” (RUM) model [19], in which we treat the SiO_4 tetrahedra as rigid units and search for phonon modes that can propagate without the tetrahedra distorting [20]. We have found that symmetry can cause some of the bond constraints to be degenerate, allowing for a nonzero number of zero-frequency phonons (“RUMs”). For example, β -cristobalite, like most crystalline framework aluminosilicates, has RUMs on planes of wave vectors [13]. For two phases related by a displacive phase transition there are fewer RUMs in the phase of lower symmetry. At the other extreme, high-symmetry zeolites may have one or more RUMs for each wave vector [21]. RUMs are not always restricted to wave vectors on symmetry points and can have wave vectors on exotic curved surfaces within the Brillouin zone [22]. Since crystalline phases can thus violate the simple bond constraint counting scheme to a greater or lesser extent, it is not possible to predict the number of floppy modes in glasses from simple constraint counting arguments alone.

Although RUMs are important in crystalline phases, when RUMs occur with wave vectors on surfaces in reciprocal space, the relevant fraction of reciprocal space is vanishingly small. In crystalline phases one can hunt for RUMs in a systematic manner because symmetry gives a guide, but in glasses the lack of translational symmetry makes any systematic search impractical. Instead we use a different approach, which uses our split-atom algorithm [20,23] within the formalism of molecular

lattice dynamics to calculate the vibrational density of states $g(\omega)$ by diagonalizing the dynamical matrix for a grid of wave vectors. This method gives $g(\omega) \propto \omega^2$ as $\omega \rightarrow 0$ (the normal Debye result) when there are no RUMs, and $g(\omega) \sim \text{constant}$ as $\omega \rightarrow 0$ when there are RUMs [24]. We have used atomic configurations of silica glass obtained from starting configurations of amorphous silicon formed by the Wooten-Weaire algorithm [25]. Oxygen atoms were incorporated into the configuration along each Si—Si bond, and the structure was relaxed using molecular dynamics simulations, with the potential of [26] to remove the linear Si—O—Si bonds, a point we return to later. The radial distribution functions of our relaxed structures are in excellent agreement with experimental data.

The calculated $g(\omega)$ for silica glass is compared with that of β -cristobalite in Fig. 1. The striking result is the similarity between the two cases for $\omega \rightarrow 0$, which suggests that *glass has the same low energy flexibility as the crystal*. High-precision experimental comparisons of the low energy spectra of glass and crystalline silica are not common, but this result is consistent with recent inelastic neutron scattering data [7]. From the mode eigenvectors we can define the participation ratio \mathcal{P} [9]:

$$\mathcal{P} = \frac{(\sum |\mathbf{u}|^2)^2}{N \sum |\mathbf{u}|^4}, \quad (1)$$

where \mathbf{u} is the displacement of an atom in a vibration, and the sum is over all atoms. Smaller values of \mathcal{P}

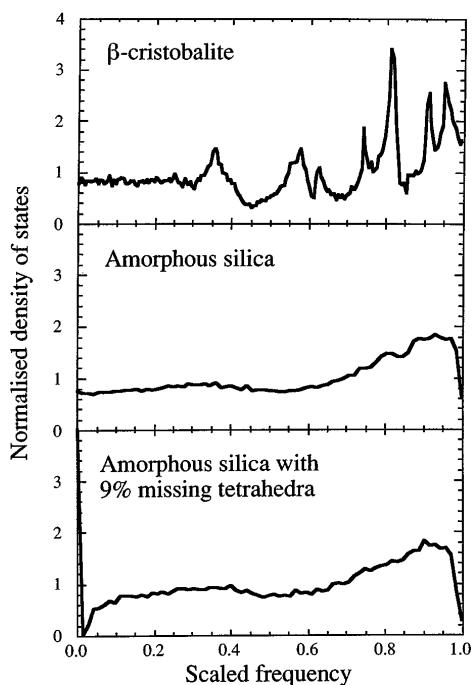


FIG. 1. Vibrational density of states $g(\omega)$, calculated using our split-atom method [20,23], for silica glass, β -cristobalite, and the silica glass configuration with a fraction of missing Si atoms.

for any mode of vibration indicate a high degree of localization, whereas values nearer 1 indicate that the vibration involves all atoms in the sample. For our glass configuration $\mathcal{P} \sim 0.8$ for all ω , which implies that *the low- ω modes involve many tetrahedra and are not localized*.

In Fig. 1 we compare, for interest, the effect of removing a fraction of the Si atoms in order to create nonbridging Si—O bonds—this may resemble the basic topology of tetrahedra in alkali silicates. The result is the formation of real $\omega \sim 0$ modes, which are seen as the peak in $g(\omega)$ at $\omega = 0$. This peak is formed out of low energy modes in $g(\omega)$ for the fully linked silica glass, and by increasing the number of Si vacancies we find that the peak at $\omega = 0$ increases and opens up the low- ω gap in $g(\omega)$. The new $\omega \sim 0$ modes have values of \mathcal{P} ranging uniformly from 0 to ~ 0.8 . This increase in the number of RUMs is consistent with the observation of increased inelastic neutron scattering intensity found in alkali disilicate glasses over silica glass [7].

The existence of low- ω modes indicates a flexibility against infinitesimal atomic displacements, but the picture that has been proposed to explain the anomalous thermal data at low temperatures [12] suggests the existence of large-amplitude reorientational motions of SiO_4 tetrahedra [11]. Figure 2 shows the time dependence of the coordinates x, y, z of one atom that shows a large jump motion, together with other similar events we have identified in other simulation runs for comparison. In Fig. 3 we show snapshot images of the reorientations of the associated group of tetrahedra. For this jump motion the participation ratio indicates that the number of tetrahedra involved in this event is around 30. The largest atomic displacement in these events is typically 0.8 \AA . See Ref. [27].

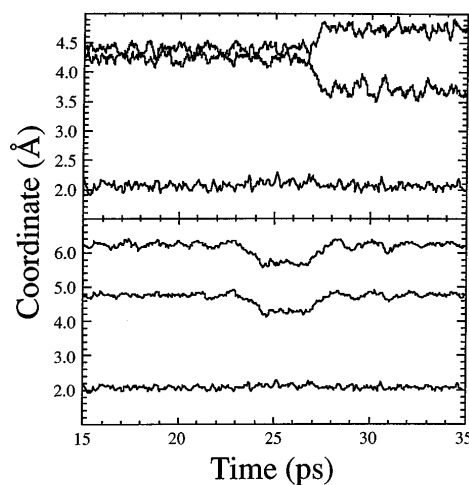


FIG. 2. Time dependence of atomic coordinates x, y, z (in orthogonal \AA units) for an atom undergoing a large jump involving a movement of about 0.5 \AA (top), and an atom in a different simulation run that jumps from one site to another and subsequently jumps back again (bottom).

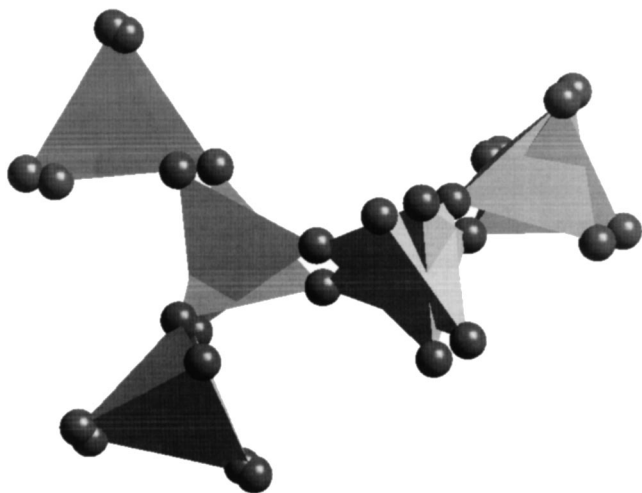


FIG. 3. Snapshot images of the tetrahedra participating in the jump event indicated in Fig. 2. The figure shows superimposed snapshots of the local configuration captured before and after the jump event in order to highlight the large-amplitude reorientational motions.

We consider that *the jump event shown in Figs. 2 and 3 is a candidate event for the jump motions envisaged in the two-level tunneling excitations.* However, it is not possible to detect an energy barrier in the simulations at finite temperature. Figure 4 shows the potential energy of the (constant total energy) simulation through this jump event, and any energy changes are clearly substantially lower than the normal energy fluctuations. To extract values of the energy barrier and change in energy as the system flips from one state to another we have relaxed the structures either side of the jump event and halfway through the jump event (i.e., the transition state) using the molecular dynamics code at 0 K. For the configuration in the transition state we pinned the position of the atom that moves the most in order to prevent the state from relaxing to either of the states either side of the transition state.

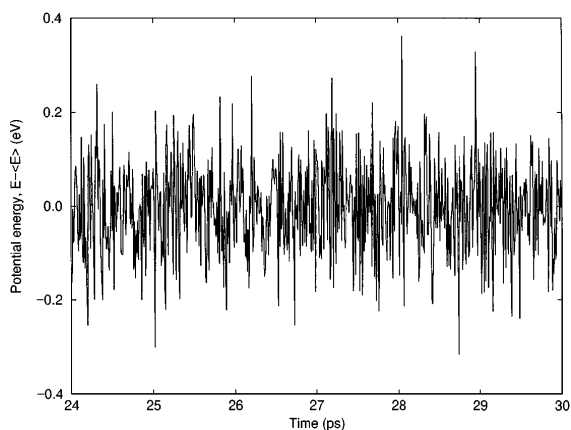


FIG. 4. Time dependence of the potential energy of the simulation sample (with its average value subtracted) through the jump event shown in Figs. 2 and 3.

This procedure gave an energy barrier of 0.06 ± 0.02 eV (for about 30 tetrahedra; see above), and the change in energy of the sample on flipping from one state to another is less than 0.01 eV. The uncertainties arise from numerical errors in the simulations that are hard to control to greater precision because of their small size relative to the total system energy. Our estimates of the size of the energy barrier and the energy difference are within the ranges proposed by [11]. Our simulations show that jump events in a sample of 216 tetrahedra occur at intervals of around 20 ps.

What is clear is that the system can remain in one state for times corresponding to many periods of oscillation of SiO_4 tetrahedra before jumping to another state, which means that the system has a local free energy minimum in this state, without being able to oscillate back and forth into the second state. This means that the jump can occur only when all of the tetrahedra associated with the jump are aligned in a particular way. In effect, for most configurations of the tetrahedra the energy barrier against the system jumping from one state to another is usually very large, much larger than the normal energy fluctuations at 50 K. But as the system evolves through the cooperative small-amplitude oscillations of the tetrahedra, eventually *the potential energy barriers collapse* to the small value we have measured. This is in contrast to the idea of the system jumping across a fixed energy barrier. There is therefore a range of barrier heights, with a small neck in the system phase space that allows the sample to go from one configuration to the other with little cost in energy. Of course, for quantum tunneling it will be possible for jump events to sample more of the energy barriers than the one given by this neck in phase space. This is one of the new insights into the operation of these tunneling states that emerges from this work.

Further insight into the issue of large-amplitude reorientational motions can be obtained by returning to the initial topology of the glass configuration with linear $\text{Si}-\text{O}-\text{Si}$ bonds. Recall that this structure was relaxed using molecular dynamics simulations, which allowed the tetrahedra to rotate to give $\text{Si}-\text{O}-\text{Si}$ bond angles of around 145° . For our initial configuration we have produced a number of different relaxed structures by using different initial atomic velocities and have then compared the different structures using the method employed for comparing configurations before and after jump events. From calculations of the participation numbers we find that the changes between different relaxed configurations involve around 100 tetrahedra and that in each case it is a subset of this group of tetrahedra that is involved in the large-amplitude displacements described above. This clearly suggests that our network contains islands of floppy regions (in the sense of being able to support large-amplitude reorientational motions) within a more rigid framework (albeit one that can sustain floppy modes with infinitesimal displacements).

Finally, it should be noted that large amplitude atomic motions and potential tunneling states have been studied in metallic and other glasses [28], but in each case their identification has always required some initial stimulation of the system. Here we have for the first time identified potential tunneling states naturally by allowing the system to evolve in its own phase space.

To conclude, we have shown that (i) silica glass networks have a flexibility for infinitesimal displacements that is similar to that of crystalline networks and (ii) there exist regions within the glass network in which the tetrahedra are able to undergo large-amplitude reorientations with little energy cost and with low energy barriers for cooperative motions. These may be responsible for the anomalous low-temperature thermal properties of glasses, although it is not possible to calculate these within our classical simulations.

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