

Simulation of two-level tunneling states and floppy modes in silica glass

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ABSTRACT

We present the results of a computational study of the low-energy dynamics of silica glass. Molecular dynamics simulation results show that parts of the glass structure can undergo large cooperative reorientations of SiO₄ tetrahedra. These motions involve reorientations of about 30 tetrahedra with an energy barrier of about 0.06 eV. We relate these motions to the presence of double-well potentials which give rise to two-level tunneling states, thereby providing the mechanism for the anomalous low-temperature thermal properties of glasses. In addition to studying the flexibility of silica glass in terms of the large tetrahedral rearrangements, we also address the flexibility of silica glass in terms of its ability to sustain Rigid Unit Modes, or modes that propagate without distortion of SiO₄ tetrahedra. We find that silica glass is surprisingly similar to its corresponding crystalline phases in its ability to support RUMs. We relate this similarity to the structural similarity of silica glass and its crystalline phase over short length scales.

Keywords: silica glass, molecular dynamics, low-energy dynamics, two-level states, rigid unit modes

1 Introduction

The study of silica glass attracted a lot of attention in the past decades. Silica glass is technologically and geologically important and is one of the principal network glass-forming systems. A special attention has been paid recently to the study of low-energy dynamics of silica glass, including two-level tunneling states, Rigid Unit Modes, Boson peak and other features. We present the results of computational study of silica glass dynamics, in relation with the issue of existence of two-level tunneling states and low- ω floppy modes in silica glass.

We start this paper with the description of the method to produce defect-free models of silica glass. We then proceed to addressing the issue of presence of double-well potentials in silica glass structure. According to the main assumption of the phenomenological theory [1] which explains anomalous thermal properties of glasses at low temperature [2], double-well potentials exist in

the glass structure acting at certain objects (atoms or groups of atoms). Tunneling in the double-well potentials gives rise to two-level tunneling states in the energy spectrum. The contribution of the latter to the low-energy dynamics results in aforementioned anomalous thermal properties that are not seen in crystalline solids, including the linear behaviour of heat capacity with temperature and other interesting features. However, it has been difficult to pinpoint double-well potentials in glasses which led to the growth of literature doubting their existence. Using the MDS technique, we demonstrate that silica glass structure is able to support large-amplitude atomic jumps of up to 0.8Å. The jumps are seen as collective rearrangements of several tens of connected SiO₄ tetrahedra. We relate this motion to the presence of double-well potentials, envisaged in [1], in the structure of silica glass. Finally, we address the ability of silica glass structure to sustain Rigid Unit Modes (RUMs), or modes that can propagate in the structure without distortions of SiO₄ tetrahedra. We find that silica glass is very similar to its crystalline phase in its ability to support RUMs and relate this similarity to the structural similarity of silica glass and β -cristobalite over short length scale.

2 Silica glass configurations

Silica glass, one of the principal network glass-forming systems is well described as the continuous random network of vertex-connected SiO₄ tetrahedra. In computer simulations, the use of periodic boundary conditions impose tight constraints on the formation of the network, and many “liquid quench” algorithms suffer from difficulties in produced models that are completely free of defects. Our approach to generate models of silica glass for this work is to start with defect-free models of amorphous silicon which have periodic boundary conditions. These structures, kindly provided to us by Prof. Thorpe, were generated by randomizing the ideal diamond structure with further relaxing it to the lowest metastable state to get the configuration which correlation functions fit the experimental data [3]. To convert these configurations to silica we inserted oxygen atoms in the middle of each pair of silicon atoms, to create a network of vertex-connected SiO₄ tetrahe-

dra. Our prototype silica glass structures were then relaxed using the molecular dynamics simulation method DLPOLY [4], in particular to allow the linear Si–O–Si bonds to relax to the usual bent state. In the molecular dynamics simulations, both to relax the structure and then to perform subsequent analysis calculations, we used the Tsuneyuki interatomic potential [5]. Using this procedure, we derived a number of silica glass structures with different topology, with and without four-membered rings of tetrahedra, and containing 216, 512 and 4096 SiO₄ tetrahedra each. The calculated radial distribution functions and structure factors were found to be in a very good agreement with experiments (see [6], [7] for more detail).

3 Large tetrahedral reorientations in silica glass structures

It was proposed in [1] that atomic motions in double-well potentials in silica glass involve rigid rotations or displacements of SiO₄ tetrahedra. We naturally assumed that the corresponding displacements of atoms in these types of motions significantly exceed those caused by the thermal vibrations around equilibrium positions at low temperature. To select those atoms which may participate in motion in double-well potentials, we constructed the distribution of average square displacements of all atoms. Using the data from molecular dynamics simulation production runs at low temperature, we calculated $\sigma = \langle |\mathbf{r}|^2 \rangle - |\langle \mathbf{r} \rangle|^2$ for each atom, where \mathbf{r} is the position of the atom within the sample, and formed the probability distribution function $P(\sigma)$. For the atoms with the largest values of σ from two different simulations we show the time dependence of their coordinates x, y, z in Figure 1.

The event seen in Figure 1a involves the atom jumping between one metastable position to another, and then subsequently jumping back to the original position. Similar changes in coordinates are found for other atoms involved in this event with large values of σ . On the other hand, the event shown in Figure 1b from a different simulation run has the atom jumping from one position to another but without the atom subsequently returning to its original position. The largest value of atomic displacements in the observed events is typically around 1 Å. Events which involve more frequent jumps between equilibrium positions can be observed in the simulation runs of the structures of larger size, a point to which we return later. Using various techniques (see [6], [7]), we established that the number of SiO₄ tetrahedra participating in one jump is around 30. In Figure 2 we show the superposition of the group of tetrahedra before and after the jump. Animations of the molecular dynamics simulations showing sudden tetrahedral rearrangements of silica glass structure are available at <http://www.esc.cam.ac.uk/movies>.

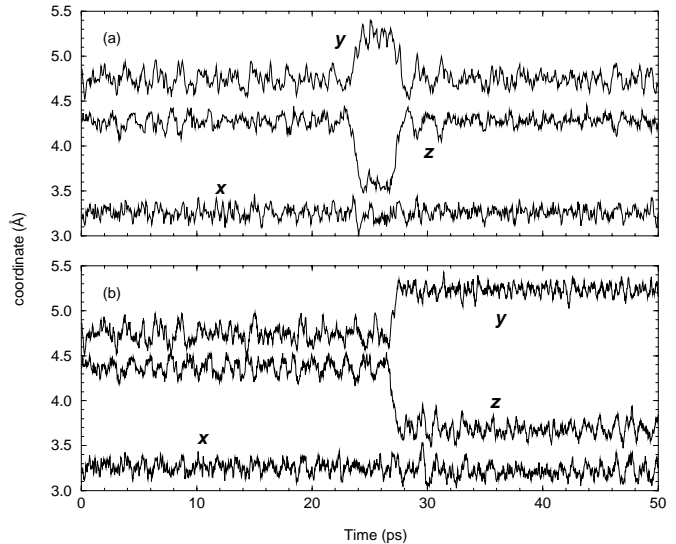


Figure 1: Time dependence of atomic coordinates x, y, z (in orthogonal Å units) showing an atom undergoing a large jump involving a movement of about 0.8 Å and subsequent jump back (a) and atom in a different simulation run which oscillates around the new equilibrium after the jump (b).

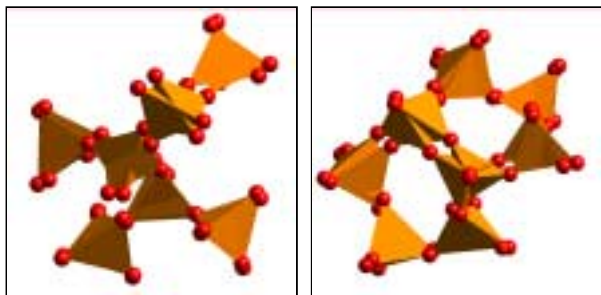


Figure 2: Snapshot images of the tetrahedra participating in the jump events indicated in Figure 1. The figure shows superimposed snapshots of the local configuration captured before and after the jump event in order to highlight the large-amplitude reorientational motions. Animations of the jump events, showing whole tetrahedra reorientations, can be viewed from <http://www.esc.cam.ac.uk/movies>.

We estimated the parameters of the double-well potentials basing on the MD results, giving the an energy barrier of 0.06 ± 0.02 eV and the energy difference between the potential minima is less than 0.01 eV (see [6], [7]). We found that as the system evolves through the cooperative small-amplitude oscillations of the tetrahedra, it finds the path in the phase space with the energy barrier small enough (around 0.06 eV in our measurement) to allow it to jump in another potential minimum with little energy cost and thus to avoid crossing barrier separating equilibrium states which would be inaccessible otherwise. Of course, for quantum tunneling it will be possible for jump events to sample more of the energy barriers than the one determined by this path in phase space.

Simulation of larger structures (512 and 4096 tetrahedra) shows that the jump events become more frequent and uncorrelated with each other. This can make a noticeable contribution to the low-energy dynamics of silica glass, particularly if quantum effects are incorporated in the simulation. The development of path integral molecular dynamics simulation technique to simulate the low-energy dynamics of silica glass is currently undergoing.

We note that pressure-induced transformations have been studied recently in silica glass and have been related to the double-well potentials [8]. By analyzing the atomic trajectories from MD simulation, we see that large atomic jumps may disappear in a certain region of the sample as external pressure increases and new jumps start to take place in the regions where no jumps were seen before applying the pressure. This study will be carried in more detail in the future, including the response of double-well potentials to decompression.

4 Rigid Unit Modes in silica glass

In addition to two-level tunneling states, we also address the ability of silica glass to support Rigid Unit Modes (RUMs), or modes that can propagate without SiO_4 tetrahedra having to distort. In studying the low-energy vibrational modes of silica glass, it is assumed that any low-energy distortion of a silicate structure will have a minimal deformation of the constituent SiO_4 tetrahedra [9], since these units are fairly stiff and any significant deformation will be accompanied by high-frequency modes. Whether an infinite framework of corner-linked SiO_4 tetrahedra can vibrate without the tetrahedra distorting is actually a very subtle issue. The vibrational modes that do not involve distortions of the interatomic bonds are usually referred as “floppy modes” in the context of network glasses [10] or Rigid Unit Modes in the context of crystalline framework structures [11]. The usual approach to analysing the flexibility of a structure is to use the procedure of “Maxwell counting”. In an atomic system, such as the chalcogenide

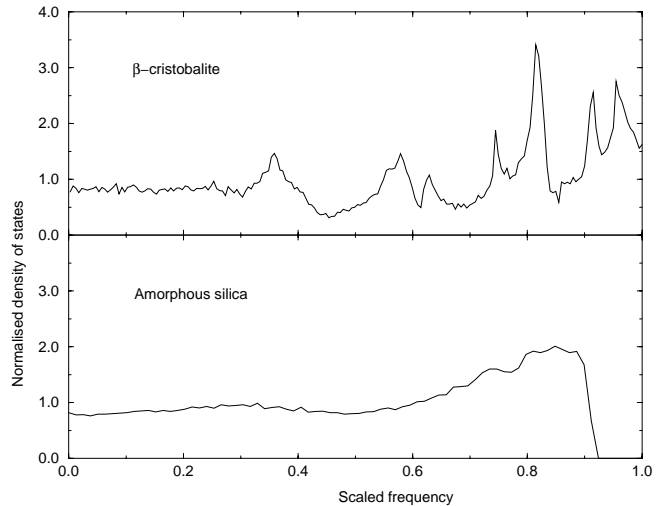


Figure 3: Density of states, $g(\omega)$, calculated using our split-atom method, for (a) β -cristobalite and (b) silica glass. The values of the frequencies have been scaled against the maximum frequency in this figure.

glasses, it is taken that each atom has 3 degrees of freedom, and each bond gives one constraint to the system. The number of RUMs/floppy modes is equal to the difference between the number of degrees of freedom and the number of constraints [10]. The Maxwell counting procedure gives an interesting result when applied to silica. For a network of vertex-connected tetrahedra the total number of degrees of freedom equals the total number of constraints, so that the structure of silica, both amorphous and crystalline, is neither floppy nor over-constrained, but balanced between the two extremes (see [6], [7]). Thus one cannot easily predict whether the floppy modes can exist in silica glass.

We have recently developed this approach in detailed application of the RUM model to framework crystalline structures of silicates, originally in 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 [11]. The RUM approach has turned out to be more of more general use than the initial search for mechanisms of displacive phase transitions, and has encompassed phenomena such as negative thermal expansion [12] and zeolite activity [13], as well as providing more detailed quantitative insights into the thermodynamic properties of phase transitions [14]. In crystalline silicates, it was often found that the RUMs lie on special planes of wave vectors, determined by the symmetry [11]. There are no corresponding sheets of wave vectors in silica glass, so the same type of search method will not be appropriate. Instead we use a density-of-states search method for the determination of the RUM flexibility of silica glass.

We have calculated $g(\omega)$ for our silica glass configurations, and the results are given in 3. There the $g(\omega)$

for silica glass is compared with $g(\omega)$ of β -cristobalite. The similarity of $g(\omega)$ for the two systems for $\omega \rightarrow 0$ is striking – in fact, one can view the overall form of $g(\omega)$ of silica glass simply as a lower-resolution version of $g(\omega)$ of β -cristobalite. This comparison implies that silica glass has the same RUM flexibility as β -cristobalite, which is actually an astonishing result given that the RUM flexibility of β -cristobalite had previously been interpreted as being due to the effects of the high symmetry of its crystal structure [11]. The calculated participation ratio indicates that the low- ω RUM-like vibrations involve all tetrahedra in the glass, and are not localised to particularly flexible segments of the glass structure.

The same RUM flexibility of silica glass and β -cristobalite can give an insight into their structural similarities. As was shown in [15], [16], over short length scales there are strong similarities between the structures of amorphous silica and the crystalline tridymite and cristobalite phases of silica. Using Reverse Monte Carlo modelling, these similarities were found to extend over the length scale 0–10 Å [16]. Common RUM flexibility, which includes the flexibility of the rings of connected SiO₄ tetrahedra, gives the possibility for the glass structure to employ structural elements of its high-temperature crystalline phase in producing a disordered yet fully linked network. Thus the structural similarities between the silica glass and its high temperature crystalline phase may be related to the inherent RUM flexibility of these structures. This point has been discussed in detail by Keen and Dove [16].

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