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Floppy modes in silica glass under pressure

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Abstract
We study the effects of pressure on the existence of floppy modes in silica glass. We find that small values of pressure do not alter the ability of silica glass to sustain floppy modes, as long as they are not accompanied by changes in the topology of the glass, and thus do not change the balance between the number of constraints and degrees of freedom of the system. As increased pressure leads to the appearance of increased coordination numbers, this balance is changed, and the structure loses its ability to support floppy modes. We find that while at low values of pressure floppy modes are spatially extended, as they are in uncompressed structures, high pressure leads to the localization of low-ω (albeit non-zero) floppy modes.

1. Introduction

Silica glass has attracted a lot of research for its geological and technological importance, as well being a classical model of a continuous random network of amorphous materials. The low-energy dynamics of silica glass has been the subject of particular attention in recent years. This has included the study of two-level systems and floppy modes, namely modes that can propagate with little energy cost. The existence of the former in glass was postulated in the phenomenological two-level tunnelling state model [1], and allowed us to explain anomalous low-temperature thermal properties of glasses [2]. In our earlier papers [3–5] we have studied two-level systems in silica glass, by searching for the motions in double-well potentials (dwps). Using molecular dynamics (MD) simulation, we have found that patches of silica glass network undergo large-amplitude tetrahedral orientations, involving several tens of connected SiO_4 tetrahedra, and have related them to the motions envisaged in the two-level tunnelling state model [1].

The ability of silica glass to maintain the motion in dwps is, in other words, flexibility against large-amplitude atomic displacements. At the same time, we have found that silica glass is flexible against infinitesimal displacements [3, 4]. Such a flexibility is needed to maintain floppy modes [6, 7], which allow the structure to distort with very little energy cost. The corresponding modes do not involve the distortion of SiO_4 units, and thus we refer to them as rigid unit modes (RUMs) [3, 4]. The RUM model treats the SiO_4 tetrahedra as being completely rigid and loosely connected at corners. We have found that silica glass is essentially floppy in terms of being able to sustain RUMs, and is very similar to its crystalline phases in being able to support them. This similarity has been related to the structural similarity of silica glass and its high-temperature crystalline phases over the medium range [4]. We have studied how floppy modes in silica glass react to certain structural and dynamical modifications. In particular, we found that possible impurities, that lead to non-bridging atoms, significantly increase the flexibility of the structure against floppy modes [4]. We interpreted this effect by noting that the appearance of non-bridging Si–O bonds is accompanied by the reduction of Maxwell constraints compared with the number of degrees of freedom (see below). This effect is consistent with experimental results for silica glass [8] and borate glasses [9]. On the other hand, increased interaction between Si atoms was found to result in the diminished ability of the structure to support RUMs.

The studies mentioned above were carried out at zero pressure. The effects of pressure in silica glass have been studied extensively [10, 11], in the context of existence of high- and low-density polymorphs of silica glass. Silica glass, if compressed beyond 25 GPa, becomes irreversible on decompression, showing about 20% increase in density [10, 11]. MD simulations appeared to be important in understanding the structure of glass at elevated pressures, as well as of decompressed structures [11–13]. It has been shown that the densification of silica glass is accompanied by the increase of coordination numbers [12, 13]. The densification on decompression has been correlated with the increase of coordination numbers [13]. However, the microscopic details of the densification process are not yet fully understood, and to address this, we have recently performed a MD simulation study of the mechanism of densification in silica glass [5]. Among other issues, we studied how the flexibility of the structure against large-amplitude atomic motions, found in [3, 4], is affected by pressure. We found that small changes of pressure up to 3 GPa activate the motion in dwps that are located in different regions of the structure. This suggested that dwps, envisaged in [1], are evenly spread throughout the glass structure, each with a different potential barrier that can be changed with pressure. At higher pressures, the motions in the dwps involve changes of the local topology—local regions of the glass network become unstable and relax, giving rise to large atomic displacements. These motions then lead to changes of local topology, including breaking some of the initial bonds and forming new ones. We found them to be an important element of the irreversible densification [5].

In this work, we study the effects of pressure on the floppy modes in silica glass. We use MD to pressurize glass structures and apply the RUM model to search for modes that can propagate without SiO_4 tetrahedra having to distort. We find that up to 3 GPa, pressure has little effect on the RUM flexibility of the glass structure. On the other hand, for pressures beyond 3 GPa, this ability diminishes and is quickly lost as pressure increases. This effect is shown to be related to the topological changes that occur in the structure of silica glass under pressure. We propose that future scattering experiments on densified silica glass may reveal significant reduction in the inelastic spectrum at low frequency, relative to uncompressed silica.

2. Glass models and simulation methods

To simulate pressure effects in silica glass, the DL_POLY MD simulation package [14] was used. We have used atomic configurations of silica glass obtained from the configurations of amorphous silicon with periodic boundary conditions formed by the Wooten–Weaire algorithm [15]. Oxygen atoms were inserted along each Si–Si bond, and the structures were relaxed using the Tsuneyuki interatomic potential [16]. In this work, we used configurations containing 216 and 512 SiO_4 tetrahedra. The radial distribution functions (rdfs) of the relaxed structures were found to be in excellent agreement with experimental data (see [4] for comparison of calculated and experimental rdfs). The equilibration during compression and decompression was carried out in stages in the constant-pressure ensemble (*npt*). We note that the Tsuneyuki interatomic potential was derived from *ab initio* calculations for small clusters of silica and was shown to reproduce high-pressure silica polymorphs well [16].

Pressurized structures were analysed using the *split-atom method* [17], for their flexibility against RUM distortions. In this method, a RUM is identified by setting up a dynamical matrix in such a way that RUMs are obtained as zero-frequency solutions, since a RUM is a phonon normal mode that can propagate without requiring the distortions of the SiO_4 tetrahedra. In the dynamical matrix the SiO_4 tetrahedra are treated as rigid units within the framework of molecular lattice dynamics, and all the bridging oxygens are replaced by pairs of atoms, called split atoms. The pairs of split atoms are held together by harmonic spring forces of zero equilibrium length, which act to resist any motion that moves them apart.

In crystalline silicates, it has often been found that the RUMs lie on special planes of wavevectors, determined by the symmetry [18, 19]. There are no corresponding sheets of wavevectors in glass, so the same type of search method will not be appropriate. Instead a density-of-states search method is used for the determination of the RUM flexibility of silica glass [19, 20]. In essence, the dynamical matrix is solved within the split-atom method for a set of vectors in reciprocal space and the density of states $g_R(\omega)$ is formed. For crystalline phases, this method gives the usual Debye result, $g_R(\omega) \propto \omega^2$ as $\omega \to 0$, when there are no RUMs, and $g_R(\omega) \sim$ constant or infinity as $\omega \to 0$ when there are RUMs [19, 20]. It should be noted that the $g(\omega)$ produced this way is not to be confused with the $g(\omega)$ of a real material, because in a real material the full set of force constants would give non-zero values of the RUM frequencies and so $g(\omega \to 0) \sim$ constant would not be obtained. Instead, the RUM $g_R(\omega)$ should be seen as a particular diagnostic tool with the purpose of giving a unique quantitative assessment of the RUM flexibility of a framework structure.

3. Results and discussion

3.1. Floppy modes at zero pressure

It should be noted that the question of whether an infinite framework of corner-linked SiO_4 tetrahedra can vibrate without the tetrahedra distorting is actually a very subtle issue. The number of floppy modes is equal to the difference between the number of degrees of freedom and the number of constraints, a procedure known as 'Maxwell counting' [21]. The Maxwell counting procedure gives an interesting result when applied to silica: for a network of vertex-connected tetrahedra the number of degrees of freedom is equal to the 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[3]. In crystalline silicates it has been conjectured that symmetry may be responsible for degenerate constraints [22, 23]. This may

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[3] For a SiO_4 tetrahedron, the integrity of the tetrahedron is fully defined by the fixing the lengths of the six O–O distances and three of the Si–O bonds, thus giving nine constraints. The number of degrees of freedom of a tetrahedron in the SiO_2 network is nine, thus for silica there are nine constraints and nine degrees of freedom associated with each SiO_2. The same result can be obtained by considering the SiO_4 tetrahedra as rigid units with six (translational and rotational) degrees of freedom. Holding the corner of any tetrahedron at the same position as the corner of its neighbouring tetrahedron gives three constraints per corner, and noting that each corner is shared by two tetrahedra, it can be derived that the number of constraints is six ($4 \times 3/2$), or the same as the number of degrees of freedom. Either analysis assumes an infinite system, since the non-bridging bonds at surfaces will reduce the number of constraints per atom [22, 23].

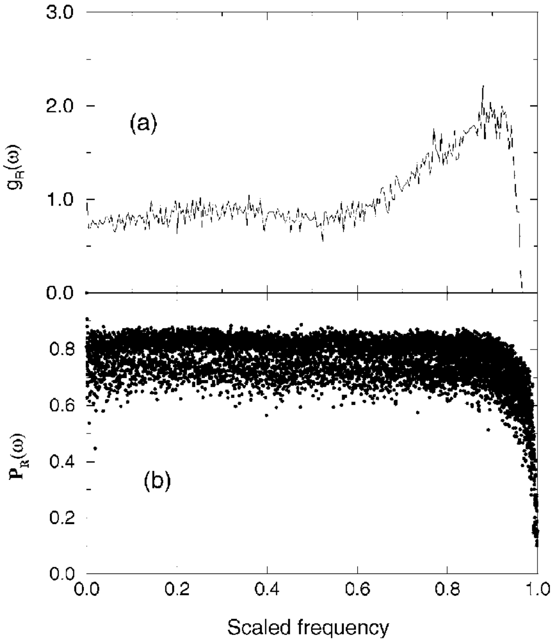

Figure 1. The density of states, $g_R(\omega)$ (a), and the participation ratio, $\mathcal{P}_R$ (b), calculated using the RUM model. The values of the frequencies are determined by the spring force constant in the split-atom method and have been scaled against the maximum frequency in this figure.

lead to the increased ability of the structure to sustain floppy modes. In glass, there may also be degenerate constraints leading to the appearance of floppy modes. However, because of the topological disorder, the speculation about the possible reduction of the number of constraints is not straightforward. Thus one cannot easily predict whether the floppy modes can exist in silica glass.

In figure 1(a) we plot $g_R(\omega)$, calculated for silica glass. It follows from figure 1(a) that $g_R(\omega) \sim$ constant as $\omega \to 0$, indicating that glass structure can sustain RUMs. Previously, we have found that amorphous and crystalline silica are very similar in terms of being able to support RUMs [3,4], which we related to their structural similarity over the medium range [4].

The information about the spatial extent of RUMs can be obtained by calculating the participation ratio $\mathcal{P}_R$, defined as

$$\mathcal{P}_R = \frac{\left(\sum |\boldsymbol{u}_R|^2\right)^2}{N \sum |\boldsymbol{u}_R|^4} \tag{1}$$

where $\boldsymbol{u}_R$ are the atomic displacements associated with the RUM eigenvectors. If the value of $\mathcal{P}_R$ is close to $\sim$1 for a particular vibration, all atoms participate equally in that vibration. The participation ratio is shown in figure 1(b). As can be seen from this figure, $\mathcal{P}_R \sim 0.8$ for all ω, including the low-ω modes. This means that floppy modes involve all tetrahedra in the glass, and are not localized to particularly flexible segments of the glass structure.

3.2. Floppy modes at elevated pressures and in decompressed structures

Application of pressure distorts the glass structure. We find that up to pressures about $P = 3$ GPa, the topology of glass remains tetrahedral, preserving the balance of degrees of freedom and the number of constraints, as in uncompressed structures. One might expect

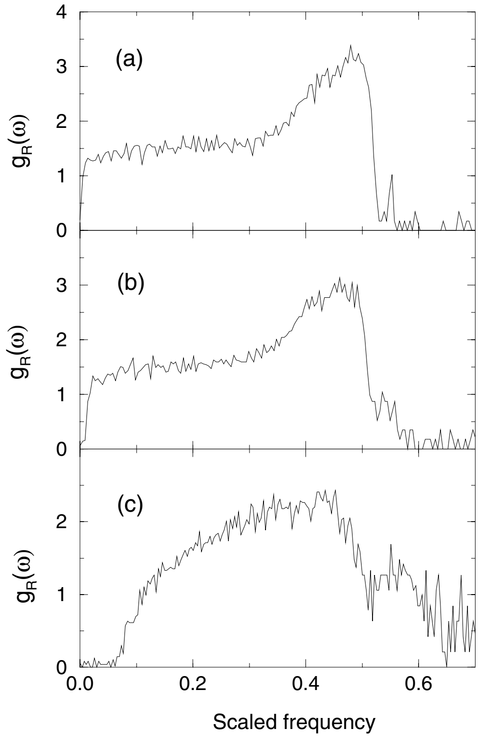

Figure 2. The density of states, $g_R(\omega)$, calculated using the RUM model, for silica glass structures, compressed to 4 GPa (a), 5 GPa (b) and 20 GPa (c). The values of the frequencies are determined by the spring force constant in the split-atom method and have been scaled against the maximum frequency in this figure.

that this would not alter the ability of the structure to support floppy modes in this pressure range. As was noted above, the definite answer to this can only be derived by searching for RUMs in the pressurized structures. We have calculated $g_R(\omega)$ in several structures compressed to pressures up to 3 GPa, and found them to be very similar to the one shown in figure 1. It appears that fully connected amorphous network, even if distorted from its initial configuration at zero pressures remains RUMs floppy, as long as it preserves the tetrahedral structure.

We have calculated $g_R(\omega)$ for higher values of P up to 20 GPa. In figure 2 we plot $g_R(\omega)$ for $P = 4$, 5 and 20 GPa. It follows from figures 2(a), (b) that at 4 GPa, the number of zero-frequency RUMs reduces (compare with figure 1), and at 5 GPa $g_R(\omega) \to 0$ as $\omega \to 0$, indicating that the structure has lost its ability to support RUMs. At $P = 20$ GPa we observe the absence of not only zero-frequency RUMs, but also floppy modes with small non-zero values of ω.

We relate the abrupt loss of the ability of the structure to sustain RUMs to the appearance of increased coordination numbers, noted earlier [12, 13]. Indeed, an increased O coordination around a Si atom increases the number of constraints on the polyhedral unit, but does not change the number of degrees of freedom, thus making the structure stiffer, and less able to support RUMs. In figure 3(a) we plot the number of fourfold-coordinated Si atoms as a function of pressure from our MD simulation of structures containing 512 SiO_4 tetrahedra. As soon as pressure increases beyond ~3 GPa, there appear Si atoms with increased coordinations. This is consistent with the diminished and eventually lost ability of the structure to support RUMs, as is seen in figure 2 [20] for crystals with high coordinations.

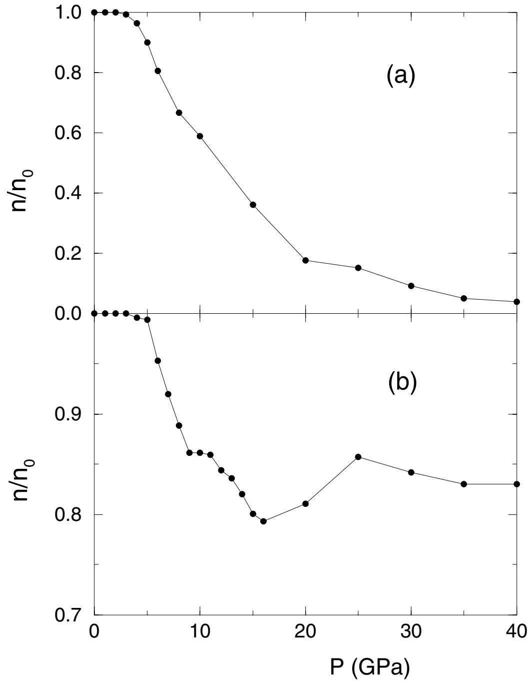

Figure 3. Fraction of fourfold-coordinated Si atoms as a function of applied pressure P in (a) compressed structures, and (b) structures decompressed from pressure P.

At 20 GPa, only about 20% of Si atoms remain fourfold coordinated (see figure 3(a)). Due to the substantial increase of the number of constraints over the degrees of freedom, the structure becomes stiff enough not only to prohibit zero-frequency RUMs, but also floppy modes with small non-zero frequencies, as is seen in figure 2(c). It appears that Maxwell counting, in addition to getting insights about the flexibility of the structure against zero frequency RUMs, can be used to predict the ability to sustain floppy modes with non-zero, yet small-value frequencies.

The interesting feature from figure 2 is that, together with the disappearance of RUMs and reduction of the number of low-ω modes, modes with large frequency start to appear. This reflects the fact that the structure stiffens as pressure increases, resulting in the increase of energy involved in the vibrations.

Another way to look at the change of the degree of the structure's ability to sustain floppy modes is to study structures decompressed from a given pressure. As pressure increases, fewer Si atoms are able to regain fourfold coordinations on decompression, reaching about 85% as pressure increases beyond 20 GPa (see figure 3(b)). We have decompressed the structures from 5 and 20 GPa and have calculated $g_R(\omega)$ for them, shown in figure 4. By comparing figures 4(a) and 2(b), one can see that as the structure achieves more fourfold coordinations on decompression, its ability to support RUMs increases. This is seen as the increase of $g_R(\omega)$ at $\omega \to 0$ in figure 2(b) relative to figure 4(a). The structure decompressed from 20 GPa partially regains the ability to support low-ω floppy modes, as is seen by comparing figures 4(b) and 2(c). However, unlike the structure decompressed from 5 GPa, this structure contains enough increased coordinations to prohibit zero-frequency floppy modes (compare figures 4(a) and (b)).

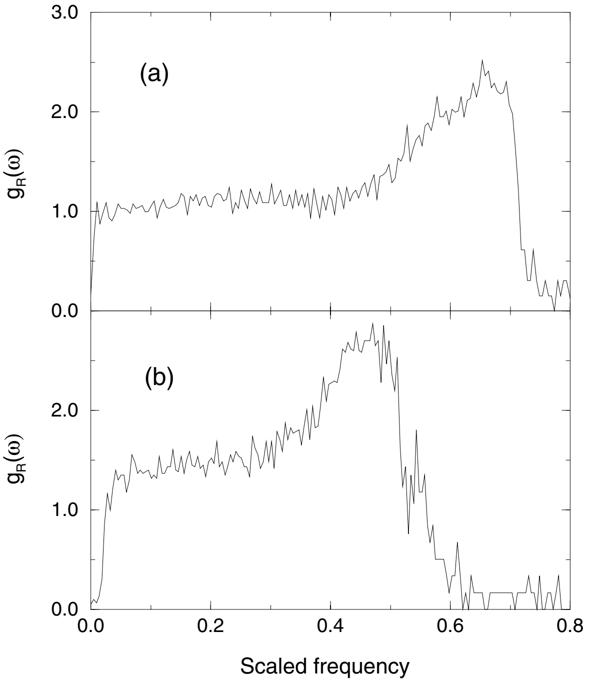

Figure 4. The density of states, $g_R(\omega)$, calculated using the RUM model, for silica glass structures, decompressed from 5 GPa (a) and 20 GPa (b). The values of the frequencies are determined by the spring force constant in the split-atom method and have been scaled against the maximum frequency in this figure.

It should be noted that the topology of atomic bonding in the decompressed structures is the result of forming new bonds and breaking old bonds during both compression and decompression [5]. We have found that forming new bonds and breaking old ones are dominant processes during compression and decompression, respectively, and that the degree of rebonding during compression/decompression is substantial. Therefore parts of the structure that regain tetrahedral topology on decompression may have very different topology than they had in the initial uncompressed structure [5]. The flexibility to support floppy modes, however, is defined by the final balance of the number of constraints and degrees of freedom, and hence is not affected by the process of densification.

To address the spatial extension of RUMs under pressure, we have calculated the participation ratio (1) for structures compressed at $P = 5$ and 20 GPa and plot $\mathcal{P}_R$ in figure 5. At 5 GPa, similar to the case $P = 0$ shown in figure 1(b), the major portion of floppy modes involves all tetrahedra in glass in a wide range of ω, except for modes with $\omega \to 0$, which have disappeared as discussed above. Note that the modes seen in both figures 5(a) and (b) at $\omega \to 0$ and having $\mathcal{P} = 1$ correspond to acoustic modes in the structure.

At $P = 20$ GPa, some localized vibrations have appeared, as follows from the participation ratio reaching small values at $\omega \sim 0$ (see figure 5(b)). By comparing figures 5(b) and 2(c), we see that those localized modes have the smallest frequency that the system can support, since modes with smaller frequency have disappeared. To study this localization, we have analysed the structure at this pressure and found that there are areas that contain connected SiO_4 tetrahedra, with some of them connected to the others at all four corners. These areas are separated from each other by regions that contain SiO_n units with increased

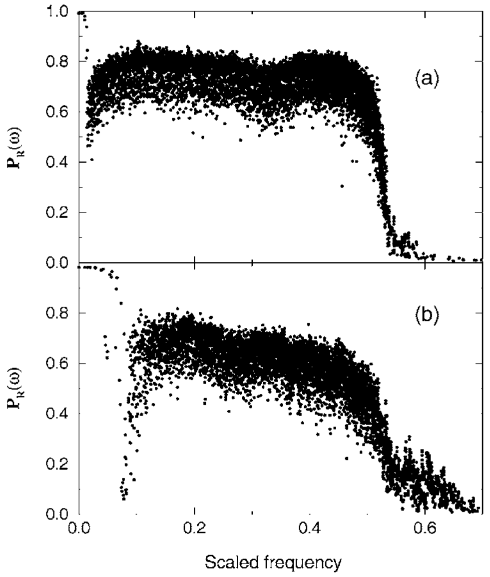

Figure 5. The participation ratio, $\mathcal{P}_R$, calculated using the RUM model, for silica glass structures compressed at (a) 5 GPa and (b) 20 GPa. The values of the frequencies are determined by the spring force constant in the split-atom method and have been scaled against the maximum frequency in this figure.

coordinations, $n > 4$. We argue that the localized low-ω vibrations in such areas may be responsible for the localization observed in figure 5(b).

Consider the system consisting of a tetrahedron, which is connected to four other tetrahedra, which, in turn, are connected to SiO_n units with increased coordinations. Maxwell counting, if applied to the central tetrahedron only, would give it the possibility to move without distortion, provided that the tetrahedra it is connected to are able to move without distortion as well (as it takes place in the tetrahedral network). Since four peripheral tetrahedra are embedded in the structure that is not RUM floppy, any motion of the central tetrahedron as a single unit would require a certain distortion in the surrounding structure. However, the energy cost accompanying such a distortion is smaller than the distortion in the structure consisting of connected SiO_n units, all of them having increased coordinations. We can make such a statement, since we have seen earlier that Maxwell counting, that defines the floppiness of the structure against zero-energy motions (RUMs), can also be used to measure the ability of the structure to distort with small non-zero energy cost. In this sense, if the structure is locally more RUM floppy in certain regions (as judged by Maxwell counting) than elsewhere, it is those regions that will also give rise to small, yet non-zero floppy modes. Therefore we suggest that the localization of low-ω floppy modes, seen in figure 5(b), occurs in parts of the structure where the remaining SiO_4 tetrahedra are connected to each other.

If we assume that increased coordinations are formed at random in a pressurized glass structure, the analogy with percolation is appropriate, since it is the connectivity of SiO_4 tetrahedra that is important for the structure to be locally flexible against both RUMs and low-ω floppy modes. As pressure increases, Si atoms with increased coordinations appear, which we consider as random sites on the cubic lattice. The threshold of site percolation on a cubic lattice is about $p_c = 31\%$ [24]. In our model, when the concentration of Si atoms with increased coordinations increases beyond $1 - p_c = 69\%$, the percolating cluster formed by

SiO_4 tetrahedra breaks. From figure 3(a), the pressure that corresponds to 31% of fourfold Si atoms is about $\tilde{P} \sim 16$ GPa. We may therefore expect to find strong localization of low-ω floppy modes in the pressure range around $\tilde{P}$ (see figure 5(b)). Of course, some localization would occur before the percolation threshold (see figure 5(a)), since the isolated chains of SiO_4 tetrahedra start to appear before the percolating cluster of connected tetrahedra breaks down.

4. Summary

In summary, we have studied how floppy modes in silica glass react to external pressure. We have found that at low values of pressure up to 3 GPa, that do not alter the tetrahedral topology of glass, silica glass remains RUM floppy, as it is at zero pressure. As soon as pressure increases beyond 3 GPa, leading to the appearance of increased local coordinations, RUMs start to disappear. Further pressure increases result in the disapperance of low-ω floppy modes. We have related the disappearance of RUMs and low-ω floppy modes to the changes of topology of glass under pressure, which lead to the increase of the number of constraints over the degrees of freedom of the system, making it stiff in terms of being able to support those modes. We have also seen that at higher pressure low-ω floppy modes become localized, and have suggested that this localization is related to the disconnecting of cluster of SiO_4 tetrahedra.

Recently, using inelastic neutron scattering, we have indentified floppy modes as the broad $\omega \sim 0$ band of the dynamic structure factor [4]. The results of this work suggest that densified silica glass (either under pressure, or decompressed from high pressure) may show decreased, or absent intensity in the $\omega \sim 0$ region. Similar effects may be seen in Raman scattering, thus making them the subject of future scattering experiments.

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