Intermediate state in pressurized silica glass: Reversibility window analogue

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We propose that silica glass exists in a special intermediate state for pressures between ~ 3 and 5 GPa, which can be identified as an analogue of the "reversibility window" observed in chalcogenide glasses. In this state there is a gradual reduction of the degree of low-energy flexibility of the structure, which matches a gradual change in the average coordination number. At lower pressures ($P < \sim 3$ GPa) the structure can accommodate buckling of the structure network without any deformations of the SiO_4 polyhedra, and at higher pressures ($P > \sim 5$ GPa) the structure is rigid and deforms through rearrangements of the bonding on a local scale. For pressures within the 3-5-GPa window, there is balance between the two mechanisms, with the flexibility assisting in the global rebonding processes. The most dramatic manifestation of the window is seen at high temperature, where there is a much greater relative volume decrease on heating at pressures within the window than for other pressures, with the window widening at higher temperatures.

One of the recent ideas in our understanding of the physics of amorphous materials is that of the "reversibility window." This idea has arisen from studies of the effects of rigidity on properties in chalcogenide glasses. Phillips[1] and Thorpe and co-workers[2,3] showed that when the average coordination number exceeds $\langle r \rangle = 2.4$ the structure will be rigid, and when the average coordination number is lower than this the structure will support floppy modes. By changing the chemical composition of chalcogenide glasses it is possible to tune the average coordination number in a continuous fashion, and there has been a search for measurable changes in macroscopic properties on changing $\langle r \rangle$[3]. Recently Boolchand and co-workers[4–6] observed dramatic changes in properties for a small range of $\langle r \rangle$ between 2.4 and 2.54 in Si_xSe_{1-x}, and with a somewhat tighter window in $Ge_{0.25}Si_{0.75-x}I_x$. These are accompanied by a loss of irreversibility of the heat flow on cycling through the glass transition temperatures for this range of compositions, a phenomenon that has led to the range of glasses being called the been called the "reversibility window." Phillips[7] has described this as "the most striking discovering in glass science in many decades." There may or may not be some degree of overstatement in this view, but there are, nevertheless, some important generic implications that govern the properties of several classes of other actively studied materials, including high-temperature superconductors[7] and proteins.[8–10] Thorpe and co-workers[8–10] has recently argued that the same rigidity arguments can be applied to our understanding of protein folding, and the possible existence of a reversibility window in this case may provide proteins with the very functionality they need for their important role in life itself.

It has been suggested that the key to understanding the reversibility window in the chalcogenide glasses is the possibility that the rigidity that sets in for $\langle r \rangle \geqslant 2.4$ only affects part of the glass structure, with some clusters of the structure retaining some degree of flexibility until $\langle r \rangle \geqslant 2.4 + \delta$ ($\delta = 0.14$ in Si_xSe_{1-x}).[4] The reversibility window will exist when the system is in this state of partial rigidity. Because of the significance of the idea of the reversibility, it is essential to look for similar effects in other cases where some degree of partial rigidity can be tuned and controlled. In this paper we argue that silica glass held under pressure gives such an example, and we correlate the changes in coordination number under pressure with changes in the degree of flexibility of the structure. In the course of developing this idea, we believe that we are now able to shed light on a range of anomalous properties of silica glass under modest (0–10 GPa) pressures. The most prominent manifestation of the intermediate state is the temperature-induced densification in the window of pressures that bound the intermediate state.

We have performed extensive molecular dynamics simulations on samples of silica glass under various pressures.[11,12] Details of the method (preparation of the starting configuration, validation of the starting configuration, interatomic potentials, simulation program, simulation methodology, etc.) were given in earlier publications.[11–15]

We found the following behavior. For $0 < P < \sim 3$ GPa, the structure topology retains its integrity. We have seen earlier[15] that in this pressure range the volume is lowered as a result of buckling of the network through rotations of quasirigid SiO_4 tetrahedra of the form illustrated in Fig. 1 (note that our initial network is perfect; all silicon atoms are bonded to four oxygen atoms, and there are no nonbridging oxygen atoms). There are a significant number of floppy modes [otherwise called "rigid unit modes" (Refs. 13 and 14)] in this configuration, and their number does not change on increasing pressure to ~ 3 GPa. Floppy modes are vibrational modes, and hence by definition their atomic motions are reversible (unlike the rigid unit deformations of Fig. 1, which give rise to the buckling of the network on increasing pressure).

For $P \geqslant \sim 3$ GPa we see the onset of deformations of the SiO_4 tetrahedra, leading to increased average coordination number for the silicon atoms, (Fig. 2), and hence the number of local constraints.[11] This is a gradual process, and as a result it does not immediately destroy the flexibility of the network. We find that the number of floppy modes[16] decreases gradually on increasing pressure over the range $\sim 3 < P < \sim 5$ GPa, until the structure becomes rigid for $P \geqslant$
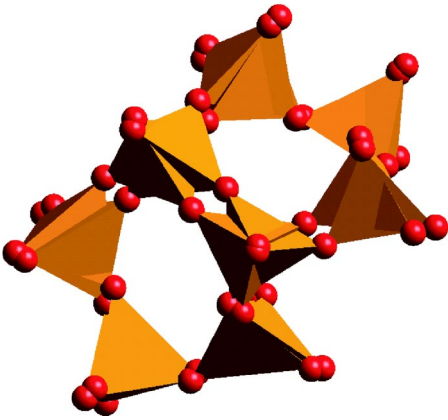
FIG. 1. Buckling of the structure due to large amplitude rotations of groups of SiO4 tetrahedra. The picture shows two superimposed structures to highlight the magnitude of tetrahedral reorientations.

~5 GPa (this was partially documented in Ref. 11, but we have recently extended the analysis with a finer variation of pressure to enable us to see the gradual decline in the inherent flexibility clearly[15]).

On increasing pressure beyond ~5 GPa there is a much greater degree of rebonding, as seen in Fig. 2. At this point, the structure has lost its flexibility, and further compression is necessarily accompanied by the breakdown of the medium-range structure.[15] One of the interesting consequences is the change of structure compressibility: our simulation results also suggest that dV/dP is lower for $P \gtrsim \sim 5$ GPa. This is consistent with the compressibility anomaly seen in high-quality experimental data for the pressure dependence of the volume of amorphous silica.[17,18]
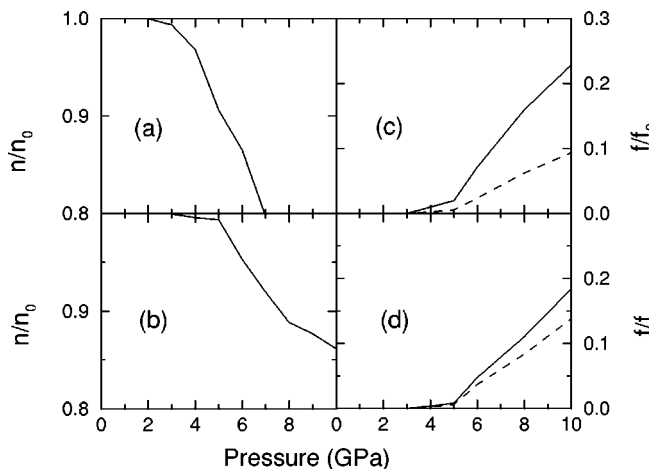
Thus we can define three regimes for the pressure depen-

FIG. 2. Fraction of four fold coordinated Si atoms as a function of pressure P in glass structures compressed to pressure P (a) and decompressed from P (b), together with the fraction of new (solid line) and broken (dashed line) bonds calculated by comparing the initial structure and the structure at pressure P (c), and by comparing the initial structure and the structure decompressed from pressure P (d). The coordination numbers are calculated by using 0 cutoff radius of 2 Å.

dence of silica glass, namely, the floppy region for ~0–3 GPa, the partially floppy region for ~3–5 GPa, and the rigid region for $P > \sim 5$ GPa.

We now add the proposal, which is the key point of this letter, that the intermediate pressure regime, ~3–5 GPa, can be described as defining an effect analogous to the one that gives rise to the reversibility window in chalcogenide glasses. We present two main pieces of evidence for the existence of this window in pressurized silica glass.

Our *first* piece of evidence for this comes from simulations in which we equilibrate at different pressures, and in which we increase pressure to a fixed pressure and then release the pressure, both at a fixed temperature of 300 K. Figure 2 shows how the number of tetrahedrally coordinated silicon atoms changes in both cases. We noted above the onset of small changes at ~3 GPa and the much larger changes at ~5 GPa; this is even more apparent in the decompression curve. Figure 2 also shows the fractions of new and broken bonds[12] as a function of pressure and as a function of the pressure reached before decompression. In both cases the two pressures of ~3 and 5 GPa mark critical points in the data; in Fig. 2(d), we note that between ~3–5 GPa there is a high degree of reversibility in rebonding. We interpret the ability of the system to reinstate its topology reversibly in the pressure range 3–5 GPa is due to the extra flexibility compared to the system for $P > \sim 5$ GPa; this flexibility allows the structure to deform without significant rebonding.

Our *second* piece of evidence for the existence of a reversibility window analogue for the pressure range ~3–5 GPa comes from simulations taken to a given pressure at 300 K, and then heated for a fixed period of time (5 ns; a long time compared with the dynamical atomic processes, after which no further density changes are seen) at various temperatures up to 1200 K. After heating, the volume is compared with the volume at that pressure before heating, Fig. 3. The "window" shape of this graph is in striking resemblance to the reversibility window seen in chalcogenide glasses[4]. The first point to make is that temperature increase leads to densification between between ~3 GPa ~5 GPa. The values of densification of 7-8% at high temperature in Fig. 3 are in a very good agreement with recent *in situ* experiments[19,20]. In our model the negative thermal effect takes place because silica glass is flexible to allow for rebonding processes to take place globally in the structure, allowing it to densify better in response to external pressure. The second important point is that pressure has two competing effects: it brings SiO_4 tetrahedra close together, assisting in global rebonding processes, and at the same time it reduces the structure flexibility, inhibiting global rebonding. The interplay of these two effects leads to the pressure window between ~3 GPa and ~5 GPa, in which the tetrahedra are close enough for the rebonding processes to take place, *and* at the same time the structure is still flexible enough to allow for these rebonding processes to take place globally.

Figure 3 shows that the left edge of the window has a strong dependence on temperature, with the window being wider at higher temperature. Since the structure's flexibility is lost for $P > \sim 5$ GPa, the upper pressure of the window is
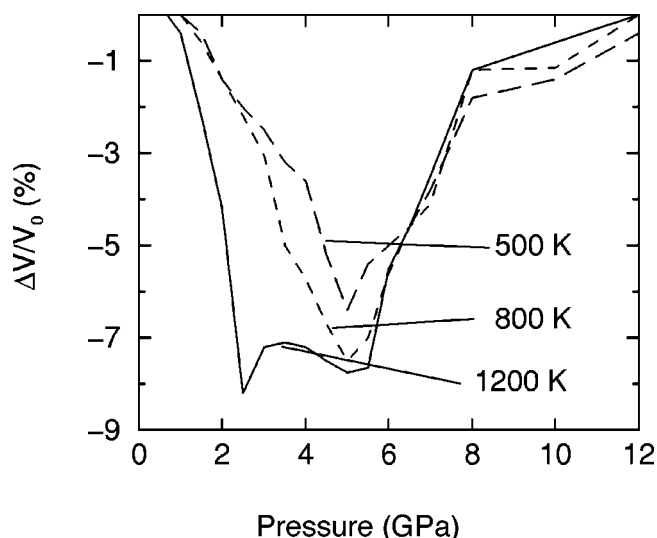
FIG. 3. Thermally induced densification in glass structure at various temperatures. The structure is pressurised to pressure P, annealed for 5 ns at temperatures of 500 K (long-dashed line), 800 K (dashed line), and 1200 K (solid line). The resulting volume is compared with the corresponding volume at pressure P before heating (V_0).

defined for all temperatures. The lower end of the window is defined at the pressure at which the structure can flex without rebonding. At higher temperatures, the vibrations have higher amplitude, allowing SiO_4 tetrahedra to come close enough together to allow a rebonding process and accompanying densification. The lower-pressure edge of the window

is therefore reduced at lower temperatures. For $P < \sim 3$ GPa, tetrahedra are too far away from each other for rebonding processes to occur and cause volume decrease.

This identification of a special window of pressures between $\sim 3–5$ GPa is important for the interpretation of experimental data. For example, Mukherjee et al.[21] interpreted densification taking place on heating at 3.6 GPa (within the identified pressure window) as evidence of a phase transition. The results of this work suggest that the observed densification in this and other experiments[19,20] is related to the existence of the intermediate state in pressurised silica glass that gives rise to the temperature-induced densification.

In conclusion, we have shown that the intermediate state between floppy and rigid, recently recognized to exist in chalcogenide glasses, also exists in silica glass under pressure. Whereas in chalcogenide glasses, the intermediate state gives rise to the reversibility window of heat flow, in pressurised silica glass it results in a temperature-induced densification in the pressure window that bounds the intermediate state, through the coupling between the structural flexibility and rebonding processes. The challenge now is to seek further experimental confirmation of this window by measuring densification over a wide range of temperatures and pressures.

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