Network Rigidity and Properties of SiO_2 and GeO_2 Glasses under Pressure

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We report *in situ* studies of SiO_2 glass under pressure and find that temperature-induced densification takes place in a pressure window. To explain this effect, we study how rigidity of glasses changes under pressure, with rigidity percolation affecting the dynamics of local relaxation events. We link rigidity percolation in glasses to other effects, including a large increase of crystallization temperature and logarithmic relaxation under pressure.

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It has been proposed by Phillips [1] that glass can be described as a network defined by the interplay between the number of degrees of freedom and the number of bonding constraints. The case when the two are equal, corresponds to the "ideal" glass with average coordination number $\langle r \rangle = 2.4$. When the coordination number is lower than 2.4, the structure will support floppy modes [2], and when $\langle r \rangle > 2.4$ the structure is overconstrained and hence rigid. There is considerable interest in the properties of network glasses for varying values of $\langle r \rangle$; in chalcogenide glasses such as Si_xSe_{1-x} the value of $\langle r \rangle$ can be tuned by changing the chemical composition x. Recently it was found that for a small range of values of $\langle r \rangle$ around 2.4 there is a dramatic loss of irreversibility of the heat flow on cycling through the glass transition temperatures [3]. This has been called the "reversibility window", and it has been suggested that it arises because of a heterogeneous spatial distribution of rigidity across the sample. It has been argued that the same rigidity arguments can be applied to understanding 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 [4]. Similar ideas have been applied to understand the properties of high-temperature superconductors [5].

In chalcogenide glasses, the reversibility window is seen around $\langle r \rangle = 2.4$, corresponding to the ideal glass state, being located between floppy and rigid state [3]. This is achieved by tuning the chemical composition x of, for example, Si_xSe_{1-x} glass, which changes the balance between higher-coordinated and lower-coordinated atoms. We have argued in an earlier paper, based on molecular dynamics simulations of silica (SiO_2) glass, that pressure serves as a tuning parameter analogous to changing composition. Pressure introduces locally rigid higher-coordinated elements in what is otherwise a relatively floppy tetrahedral network [6–8].

At a particular pressure the network changes from being flexible to rigid; at this point we say that there is a rigidity percolation. We will say more about this below. The molecular dynamics simulations led to the prediction that there is a special range of pressures around the onset of rigidity percolation in which there is an enhanced temperature-induced rapid densification, and that this range of pressures is an analogue to the reversibility window seen in the chalcogenide glasses [9].

The primary purpose of this Letter is to provide the experimental confirmation of this prediction, using both new experimental data and reanalysis of published data. We provide new simulation data to match the conditions of the experiments, and we also use new simulations to predict that a similar pressure window exists in GeO_2 glass. In addition, we also provide the link between changes of glass rigidity and other physical phenomena, including large increase of crystallization temperature at rigidity percolation point and different behavior of logarithmic relaxation of SiO_2 and GeO_2 glasses under pressure.

We start by presenting the experimental measurement of densification in silica glass. New experimental data were obtained using opposed anvil apparatus toroidal devices [10]. Other experimental data were obtained in an earlier study [11], some of which were not reported at the time. The simulation work simply involved changing the pressure of the sample as a first stage, followed by a series of incremental changes in temperature—this is a relatively easy procedure in the simulations. Thus the densification is defined as $\Delta V(P,T) = V(P,T)/V(P,T = 300) - 1$. For the experimental part of this work, the earlier data were obtained by changing pressure at a fixed temperature. We measured the *in situ* densification at a fixed temperature of 730 K, and ΔV was obtained using the definition above. We also obtained estimates of densification from a wider series of *ex situ* measurements on quenched samples obtained by ourselves together with lower-pressure data from [12]. In this case, the formula for ΔV was corrected by a knowledge of bulk modulus and thermal expansion. For both *in situ* and *ex situ* approaches, even where we have used preexisting published data, the analysis of ΔV is new here. For cases where measurements of ΔV were obtained at the same pressure for both methods, we found that there were no systematic differences in the values of ΔV, and so we report here averages of the two methods.

Our earlier simulations were performed at temperatures at 600, 800, and 1200 K. We have repeated these at a temperature of 700 K for better comparison with the experimental data, using the same interatomic potentials [13] and the same starting configurations as in our earlier work. We have performed new simulations on GeO_2 glass using the interatomic potential model developed to handle high-pressure phases of germania [14]. For GeO_2 we used the same starting configuration as for silica glass (1536 atoms in a perfect tetrahedral network) but now relaxed according to the new potential model.

Our first key point is to compare the experimental data with the simulation results for the pressure window, and this is shown in Fig. 1. This shows that at lower pressures and higher pressures ΔV is close to zero, but in a finite range of pressures around 5 GPa there is a significant decrease in ΔV; i.e., ΔV becomes significantly nonzero and negative. This figure immediately makes our main point, namely, that the experimental data confirms the earlier theoretical prediction, thereby showing that the simulation work is properly capturing the experimental situation. Figure 1 also shows our prediction for GeO_2 obtained here using molecular dynamics simulations (details given above). This shows similar behavior except shifted to much lower pressure and over a narrower range of pressures. The existence of window in GeO_2 glass now needs experimental confirmation, although its precise location in Fig. 1 may depend on the ability of the potential model to capture structural changes in the wide range of (P, T).

In our earlier paper we offered a preliminary explanation of this pressure window based on our rigid unit mode (RUM) model [15,16] coupled with changes in the coordination number. The RUM model quantifies the rigidity of the structure in terms of the number of RUMs, which are the modes that can propagate without constituent SiO_4 and GeO_4 tetrahedra having to distort. In a system where the only allowed deformations are those associated with flexing of the joints between connected tetrahedra, which are a zero-valued force constant, the RUMs will be the vibrations with exactly zero frequency. The model introduces a parameter responsible for the "stiffness" of a tetrahedron which sets the scale for high-frequency vibrations associated with deformations of the tetrahedra. Within this model, a structure with no RUMs gives Debye-type dependence of the density of states, $g(\omega_{\mathrm{RUM}}) \propto \omega^2$, whereas RUM-floppy structure gives $g(\omega_{\mathrm{RUM}}) = \text{constant}$ at the origin. We stress here that this is only true within the model; when other force constants are added, such as the interactions between neighboring tetrahedra, the density of states will always fall to zero at $\omega = 0$. As an example of the RUM analysis, we have previously shown that silica glass containing ideal tetrahedra is as flexible against RUMs distortions as β-cristobalite, as judged by the observation that $g(\omega_{\mathrm{RUM}}) = \text{constant}$ for both phases [15,16]. Hence the RUM model serves as a diagnostic tool to analyze the degree of system's flexibility against RUM-type distortions.

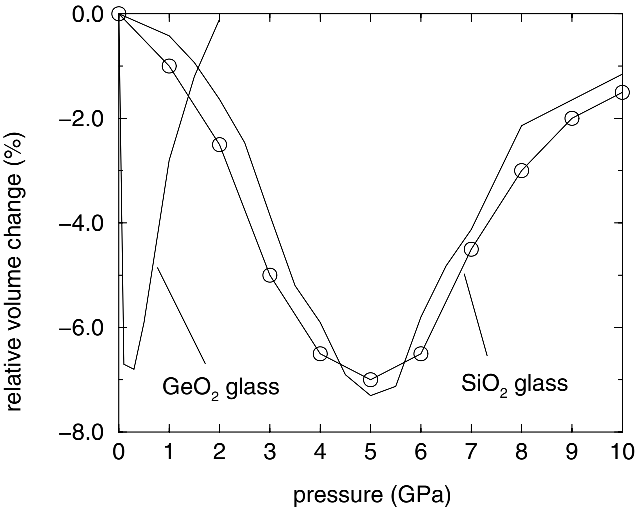

FIG. 1. Temperature-induced densification in the pressure window in SiO_2 and GeO_2 glasses. A circled line is the experimental result; solid lines are the results from MD simulation.

In our earlier paper we concentrated on understanding the origin of the behavior on the low-pressure side of the rigidity percolation point at 5 GPa. On pressurizing above 3 GPa, rebonding events cause an increase in coordination numbers of the atoms, which leads to increased densification. We denote this type of process as a "local relaxation event" (LRE). The existence of any LRE is aided by the RUM flexibility of the network, because the network can more easily adjust to local rebonding. This leads to a lowering of barriers against rebonding events and promotes densification. Moreover, in a RUM-floppy system, increasing the temperature excites low-frequency vibrations with large amplitudes [15,16], which assists in rebonding processes (and hence promotes densification) because atoms across the rings can be brought close together by thermal vibrations. However, the increase in coordination number also gradually increases the rigidity of the network, which in turn leads to a gradual decrease in the number of RUMs. The changes in the RUM density of states with increasing pressure is shown in Fig. 2. An earlier version of this figure was given in our previous paper, but this has been recalculated to a higher precision here and for more pressures in order to look for fine detailed changes around 5 GPa. What can be seen is that $g(\omega_{\mathrm{RUM}})$ at low ω decreases on increasing pressure. We define the rigidity percolation point as the point at which $g(\omega_{\mathrm{RUM}}) \propto \omega$ at 5 GPA (see Fig. 2). At higher pressures, $g(\omega_{\mathrm{RUM}})$ flattens out at the origin and becomes $\propto \omega^2$.

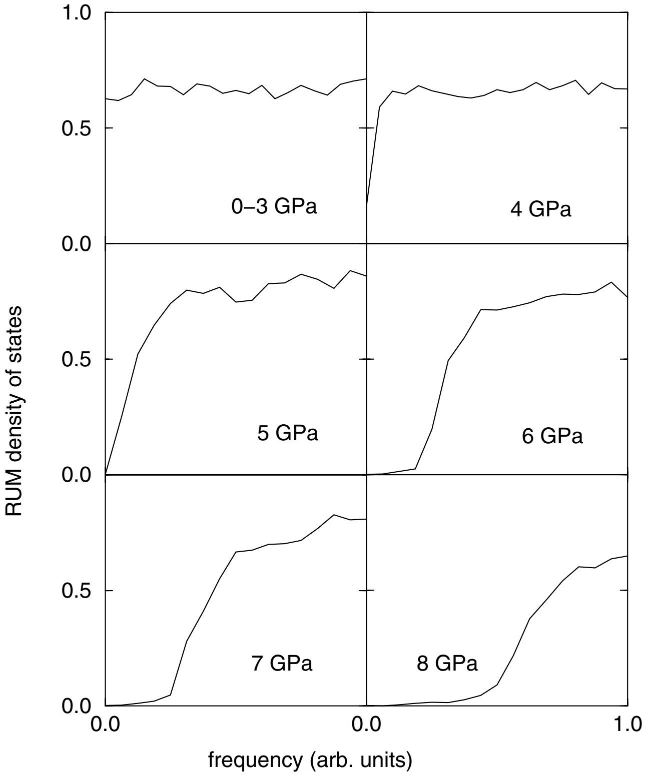

FIG. 2. Normalized RUM density of states of SiO_2 glass under several pressures.

These results are qualitatively consistent with recent experimental studies where the stiffening of the glass network has been seen under pressure [17]. In our previous paper [7], we showed that although the coordination number starts to change around 3 GPa, it is at around 5 GPa that the mean coordination number increases drastically.

We now discuss what happens immediately above 5 GPa. We argue that the number of RUMs does not completely vanish at 5 GPa. Here we argue by analogy to the RUM flexibility of crystalline materials. The case where $g(\omega_{\rm RUM}) =$ constant corresponds in a crystal to where the RUMs lie on two-dimensional surfaces of wave vectors in reciprocal space, and the case where $g(\omega_{\rm RUM}) \propto \omega$ corresponds to one-dimensional lines of wave vectors. There is, of course, no natural analogue of the crystalline reciprocal space in a glass, but the real-space picture is that the correlated RUM motions involve lines of tetrahedra in the former case and planes in the second case. Figure 2 suggests that this is the situation on increasing pressure above 5 GPa. Thus for pressure above 5 GPa there is still some network flexibility, but at a lower level. This residual network flexibility will still enhance rebonding through the same mechanism as below 5 GPa. Hence the curve in Fig. 1 does not have a sudden increase at 5 GPa. However, the reduced number of RUMs means that there are fewer ways in which the network can flex, resulting in a smaller number of induced LRE, and hence there is a gradual change in the densification back towards zero. It is not easy to separate the RUMs from the acoustic modes in Fig. 2, and indeed there is also an additional contribution to $g(\omega) \propto \omega^4$ as discussed in Ref. [18], that will become more prominent in Fig. 2 once the RUM component has decreased.

We find that in GeO_2 glass, increased coordinations appear in the structure at a much lower pressure, around 0.5 GPa (comparable with reliable pressure resolution in the current simulations). This is consistent with a recent study that employed a different interatomic potential [19]. The analysis of $g(\omega_{\rm RUM})$ shows that rigidity percolation sets in almost simultaneously with the onset of increased coordinations. This gives rise to the temperature-induced densification in the pressure window located around 0.5–1 GPa (see Fig. 1). The difference in location of the window with SiO_2 glass can be attributed to a smaller stiffness of tetrahedra in germania glass, which results in their deformation and rigidity percolation setting in at lower pressure and in a more narrow pressure interval than in SiO_2 glass. This result is confirmed by a recent *in situ* study of structural changes of GeO_2 glass, which showed temperature-induced densification taking place around 1 GPa [20].

We have seen that the pressure windows shown in Fig. 1 directly probe the changes of network rigidity of glasses under pressure. We now turn to other effects that can be understood on the basis of network rigidity. These are changes of crystallization temperature under pressure and slow logarithmic relaxation of pressurized glasses.

Recently, the crystallization temperature T_c of SiO_2 glass under pressure has been measured [21]. It has been found that T_c first decreases as pressure increases. This is followed by the sharp large increase of T_c at about 7 GPa [21]. This behavior can be understood if we consider a LRE as an elementary relaxation in the path to crystallization. First, barriers to induce LRE decrease at low pressures, as the tetrahedra are brought closer to each other. Second, the kinetics of LRE is assisted by the RUM flexibility of the pressurized glass, which persists up to the pressure marking rigidity percolation. Therefore one expects initial decrease of the temperature needed to excite LRE and hence decrease of T_c. After rigidity percolates, energy barriers increase from the low values of RUM-type excitations to the considerably higher energies associated with the deformations of tetrahedra. Hence the temperature needed to induce LRE increases sharply after the rigidity percolation point, in good agreement with the experimental value.

We note that computer modelling of crystallization processes is limited by the long times required to observe crystallization, particularly in quantum-mechanical simulations. That the coupling of LRE to structural rigidity affects crystallization process allows one to speculate about the nature of the microscopic processes that accompany crystallization. From the picture above it follows that an elementary event in the path towards crystallization is one LRE, which was identified as the elementary rebonding event during glass densification [6].

We now consider the logarithmic relaxation of volume seen in SiO_2 and GeO_2 glasses under pressure [22]. In these experiments, it is found that for SiO_2 glass, logarithmic relaxation is only seen at pressures starting from about 7 GPa, while in GeO_2 glass it already sets in at about 2 GPa. The origin of this difference can be traced to the different response of network topology of the two glasses to pressure. We have recently suggested that the logarithmic relaxation can be adequately described by the dynamics of LRE and their coupling to structural changes under pressure [23]. If no LRE are induced during pressurizing (which corresponds to the densification by mostly RUM-type distortions), no logarithmic relaxation is expected to take place. We now recall that SiO_2 glass densifies with the aid of RUM-type distortions coupled to a small number of LRE, up to 5 GPa, whereas in GeO_2 glass LRE are already induced at 0.5–1 GPa. Hence in SiO_2 and GeO_2 glasses the logarithmic relaxation is expected to set in only after the corresponding points of rigidity percolation, in good agreement with the experimental observations.

In summary, we performed *in situ* measurements of pressure effects in SiO_2 glass that showed temperature-induced densification in the pressure window. Changes of network rigidity of glass under pressure offer the explanation of this phenomenon, and we have predicted a similar pressure window in GeO_2 glass. We have linked large increase of crystallization temperature of pressurized glass to rigidity percolation. Finally, differences in rigidity of SiO_2 and GeO_2 glasses provide the explanation for a different behavior of logarithmic volume relaxation.

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