INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) L743–L748 PII: S0953-8984(03)69706-7

LETTER TO THE EDITOR

Rigidity and logarithmic relaxation in network glasses

K Trachenko[1], M T Dove[1], V V Brazhkin[2] and J C Phillips[3]

[1] Department of Earth Sciences, University of Cambridge, Downing Street,
Cambridge CB2 3EQ, UK
[2] Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk,
Moscow Region 142110, Russia
[3] Department of Physics and Astronomy, Rutgers University, Piscataway,
NJ 08854-8019, USA

Received 29 September 2003
Published 25 November 2003
Online at stacks.iop.org/JPhysCM/15/L743

Abstract

We propose a microscopic theory of relaxation of glass under pressure. We show how increased rigidity of the glass structure under pressure couples to local densification events to yield slow logarithmic relaxation and relate the microscopic parameters of the theory to the experimental densification data. We discuss two regimes of slow relaxation, one of which is the relaxation in the structure where rigidity percolates. Finally, we suggest that coupling of local densification events to structural rigidity can describe a wider range of relaxations in disordered media.

Slow relaxation is a distinct feature present in several types of disordered media, including structural glasses [1], granular media [2], spin glasses [3] and powders [4]. It is striking that the relaxation of many glasses follows a universal time dependence, usually seen as logarithmic or stretched-exponential relaxation [3, 5, 6], and can span from microscopic times up to astronomical ages [3]. External perturbations accelerate relaxation and one example of this is the relaxation of network glasses under pressure [1]. This and similar studies have been performed recently in the context of studies of new types of transitions between amorphous polymorphs [7]. In order to explain slow relaxation, several phenomenological models have been proposed, including those postulating the presence of sinks and traps [5] and a hierarchy of relaxation times [3, 6]. The question remains as to what is the microscopic mechanism of slow relaxation. What gives rise to the appearance of a wide distribution of relaxation times?

In this letter we propose a microscopic theory of relaxation in glass under pressure. By considering silica glass as a case study, we show that the increase of structural rigidity under pressure slows down the rate of local densification events, leading to the logarithmic time dependence of the volume of the glass and relate the experimental slope of logarithmic relaxation to the microscopic parameters of the theory. The description of glasses in terms of network rigidity is not new and was initiated by Phillips [8]. We have used these ideas to connect network rigidity to glass dynamics [9, 10] and, more recently, to the pressure-induced transformation and its kinetics [11–13]. Here we provide yet another link that has been missing: the link between structural rigidity and slow relaxation in glass.

We start by using insights from the modelling that identified relaxations responsible for glass densification [11]. Unlike in crystals, these take the form of local densification events (lde). As rings distort under pressure and increased coordinations start to appear, an O atom breaks the bond(s) with the native Si atom and forms bond(s) with an Si atom across the ring. LDE are universal, in that different events involved similar local rearrangements of the structure and we have called these events 'coordinons' [11], since they are accompanied by the transfer of local coordination numbers. Here we propose that lde are elementary excitations by which the amorphous structure adjusts to pressure, serving as 'quanta' of local stress relief and densification. In the formalism of constraints and degrees of freedom [8], lde are microscopic rearrangements that accompany the relaxation in a frustrated pressurized covalent network, with an excess in the number of constraints over the degrees of freedom.

To illustrate how lde are related to volume change, we have performed a molecular dynamics (MD) simulation of glass under various pressures for times up to 10 ns. Modelling of silica glass has the advantage of the existence of a successful force field, derived from quantum mechanical calculations for tetrahedral SiO_4 clusters, which has been shown to reproduce the high-pressure phase well [14]. This force field has frequently been used in MD simulations to simulate high-pressure properties of silica and recently it has been shown that microscopic processes of densification using this empirical model are the same as those found in the full quantum-mechanical treatment of glass structure [15]. We have used glass structures with 512–4096 tetrahedra. Other details of the method (preparation of the starting configuration, its validation, simulation methodology, etc) are given in our earlier publications [9–13, 16].

Since, on average, a single lde is accompanied by essentially the same number of new and broken bonds, we can introduce the measure of lde number n, defined as

$$n = (p_\mathrm{n} + p_\mathrm{b})/N \tag{1}$$

where p_n and p_b are the numbers of newly formed and broken bonds, defined as the numbers of nearest O neighbours that are introduced into, and expelled from, the first Si coordination shell and N is the number of atoms in the structure. We have calculated p_n and p_b in compression runs at various pressures. In figure 1 we show p_n/N and p_b/N, together with the relative volume decrease, as a function of time for compression at $P = 5$ GPa. Note that the excess of newly formed bonds over the broken ones corresponds to the appearance of increased coordinations. We observe that lde take place as cooperative rebonding events, involving the cascade of lde (see the 'steps' in figure 1(a) at about 2 and 4 ps). The number of lde slows down in time (see figure 1) as the structure becomes progressively more rigid due to the appearance of increased coordination. This will be discussed in more detail below. The important point here is that cascades of lde are accompanied by sharp step-like volume decreases. This is most clearly seen by comparing figures 1(a) and (b), where two distinct jumps of the relative volume decrease correspond to two cascades of lde at 2 and 4 ns, respectively. We find that the change in volume is correlated with lde throughout the compression run and we have observed this correlation for more than ten values of pressure up to 25 GPa.

In what follows we calculate the relationship between a macroscopic relaxing quantity, the volume decrease $\Delta V/V_0$, and n. Knowing the microscopic volume change per one lde will allow us to reduce the problem to the dynamics of lde.

It is useful to first note the relationship between lde and accompanying volume changes in the experiment and simulation. First, the timescales involved in the compression phase in the simulation and experiment are remarkably different, being typically nanoseconds and minutes, respectively. On the other hand, the compression rate is much faster in the simulation. As a result, we find that the values of densification at a given pressure and temperature are the same in the simulation and experiment [11–13]. This suggests that, for a given amount of

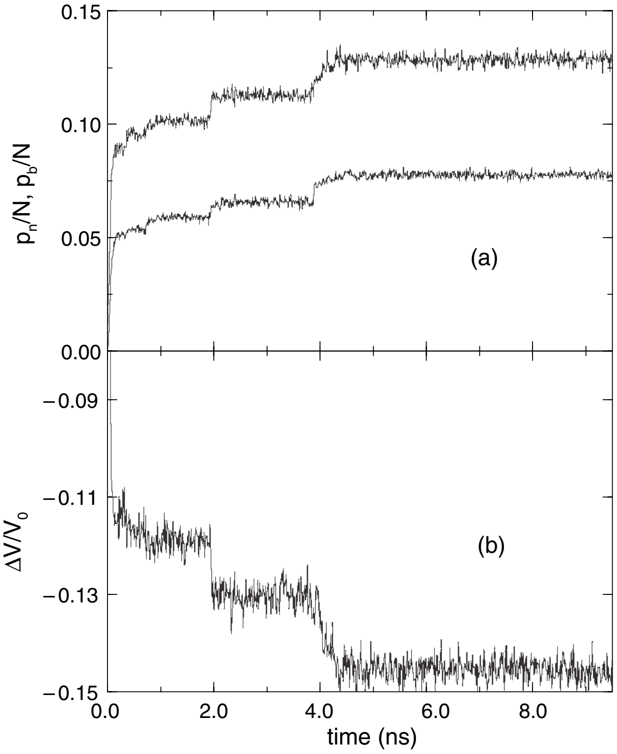

Figure 1. (a) Normalized number of new (top) and broken (bottom) bonds as a function of time, (b) relative volume change during the compression run at 5 GPa as a function of time.

structural change, the number of lde (per unit volume) induced in the simulation matches that in the experiment. Second, in the experiment the densification goes through the compression phase, during which the system arrives at the target pressure, followed by slow logarithmic relaxation [1, 7]. In our theory, this slow relaxation is due to the macroscopic number of lde that persist in compressed glass for a long time. In the simulation, essentially all lde are induced during several nanoseconds, including the slower 'tail' of lde, shown in figure 1. This tail is not logarithmic due to the small (non-macroscopic) number of lde induced in the simulation, but we can use the simulation to calculate the specific volume change per one lde.

We have calculated n at various pressures[4] and have plotted the volume as a function of n in figure 2. It can be seen that densification proceeds without lde up to 3 GPa, followed by their appearance between 3 and 5 GPa and a linear correlation between $\Delta V/V_0$ and n for $P > 5$ GPa. In order to understand these three features, we invoke rigidity concepts. First, in the range $P < 3$ GPa, the glass structure is floppy in the sense that it is able to maintain Rigid Unit Modes (RUMs), the macroscopically extended vibrational modes that do not involve distortions of SiO_4 tetrahedra [9, 10]. We have seen that, under pressure, the structure densifies by static RUM-type distortions [12] and hence without the need to induce lde. Second, in the 3–5 GPa range, glass exists in the intermediate state between floppy and rigid [13]. In this state, the ability of the structure to support RUMs decreases, since increased coordinations serve as additional local constraints [12, 13, 16]. LDE start to be induced at

---

[4] N was calculated at the end of each compression run, including both the fast compression phase and the slower relaxation 'tail'. The advantage of this approach is that microscopic volume change due to one lde, calculated in this way, is averaged over many events, making the calculation more reliable than if we calculated the volume change due to the relatively small number of lde in the 'tail' of slow relaxation. We find that defining the microscopic volume change due to one lde from the slow relaxation 'tail' (shown in figure 1) gives a similar value.

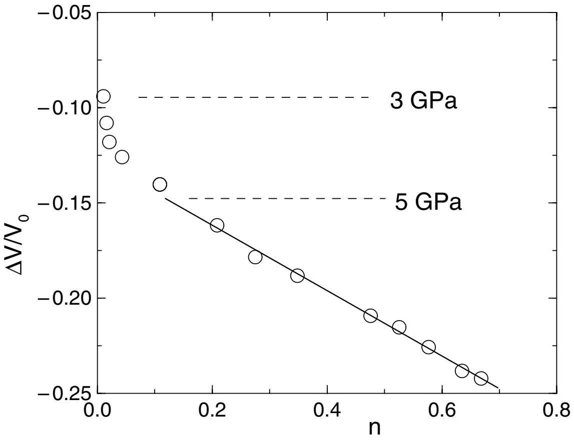

Figure 2. Volume of pressurized glass structure as a function of n. LDE start to appear at 3 GPa. The linear regime for $P >$ 5 GPa is shown. The full line is a guide for the eyes.

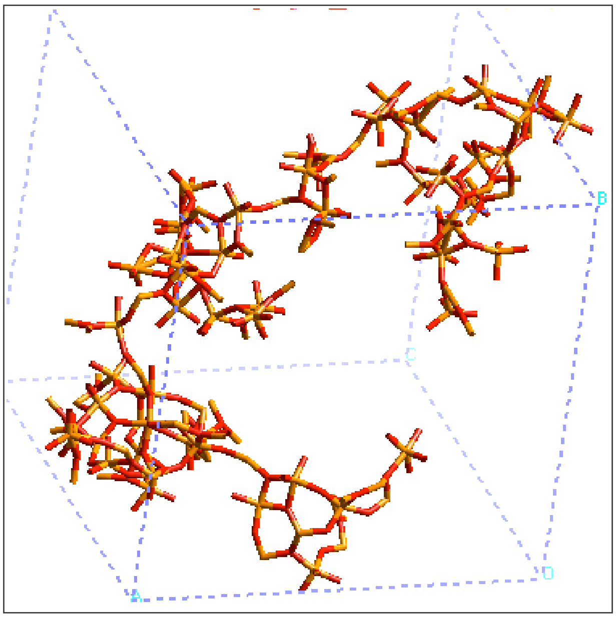

Figure 3. Percolating cluster of the rigid high-pressure phase at 5 GPa.
(This figure is in colour only in the electronic version)

3–5 GPa pressure, but the deformation of the structure is assisted by the remaining, although decreasing, RUM flexibility. Finally, at 5 GPa, the structure becomes rigid against RUMs and further densification takes place exclusively by lde. We note that the arrest of low-frequency modes in densified silica glass has recently been measured experimentally [17]. In our picture, the disappearance of extended RUMs at 5 GPa is related to the percolation of a rigid high-pressure phase in the structure. The tetrahedral glass structure is flexible against RUMs and we can define the elements of the rigid high-pressure phase as Si atoms with more than four O neighbours and O atoms with more than two Si neighbours. In figure 3 we show the percolating cluster of the high-pressure phase at 5 GPa.

From figure 2 it follows that, in the rigidity percolation regime at $P > 5$ GPa, the structure densifies ‘regularly’: since no RUM-type distortions are available in the structure, any further distortion is accompanied exclusively by lde, with an approximately constant value of volume change per n. Therefore, in the regular densification regime we can write

$$\Delta V/V_0 = \upsilon n \tag{2}$$

where υ is the average microscopic volume change due to one lde.

We can now link the relaxation of the structure and its rigidity by noting that the activation barrier for lde increases as the structure becomes progressively more rigid. Indeed, a lde is induced when the ring of SiO_4 tetrahedra is distorted enough for rebonding of O atoms between different Si atoms in the ring to take place. The energy barrier U_i that needs to be overcome depends on how flexible the structure is locally. The probability to induce lde i is

$$p_\mathrm{i} \propto \exp(-U_\mathrm{i}/kT) \tag{3}$$

where U_i is bound by its minimal U_0 and maximal U_m values in an ideal and maximally densified rigid structure (topologically analogous to six-fold coordinated stishovite), respectively. U_0 is related to the small energy needed to excite the RUM motion and its upper value can be taken as 5 meV, since we showed previously that RUMs spread from zero energy to the 5 meV boson peak [10].

After a rigid high-pressure phase percolates in the structure, RUMs become localized to finite clusters, as is seen from the calculation of participation numbers [16]. LDE are confined to the local floppy clusters and U_i progressively increases as the size of the floppy regions decreases with n. U_i is maximal when no RUM-type distortions are available locally and the only way to induce a lde is to break a Si–O bond, with an accompanying energy barrier of $U_\mathrm{m} = 6$ eV [18].

To derive the dependence of n on time, we substitute the local activation barrier U_i by its effective 'mean-field' value U, dependent only on n. In this approximation the local rigidity around a given lde, and hence its activation barrier, is defined by the concentration of the high-pressure phase, which is proportional to n, since each lde introduces an element of the high-pressure phase. To first order, U can be partitioned as

$$U(n) = U_0 + \alpha(U_\mathrm{m} - U_0)n \tag{4}$$

where U increases from U_0 to U_m and $\alpha = 1.5$, since the shortest path during the transition from floppy tetrahedral to completely rigid octahedral stishovite-type structure involves two new Si–O bonds per Si atom, giving per atom $n = 2/3$ (which corresponds to $U = U_\mathrm{m}$ if $\alpha = 1.5$).

The neglect of higher-order terms in (4), corresponding to interactions between lde, is justified in silica glass, since the four-fold coordinated Si cations and the five-fold (or higher) coordinated 'defect' lde centres are separated by intervening oxygen anions. Chemical bonding in silica is more strongly ionic than covalent, resulting in bond-bending constraints that are intact for Si cations but are broken for oxygen anions, a recognized fact in the theory of the structure of vitreous silica [19]. These intervening non-directional oxygen links are extremely flexible and so have the effect of lde decoupling, so long as the density of the latter is low enough that cross-linking of percolating clusters (see figure 3) occurs only rarely.

We can now close the system of equations by writing the rate equation for n. Assuming the relaxation to be far from the exponential saturation regime, we write

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{1}{\tau}\exp(-U(n)/kT) \tag{5}$$

where τ is related to the microscopic relaxation time and is the function of external pressure. By combining equations (2), (4) and (5), and noting $U_\mathrm{m} \gg U_0$, we obtain

$$\Delta V/V_0 = \frac{kT\upsilon}{\alpha U_\mathrm{m}}\ln\left(1 + \frac{\alpha\gamma U_\mathrm{m}}{kT}\frac{t}{\tau}\right) \tag{6}$$

where $\gamma = \exp(-U_0/kT)$ is of the order of unity and we used the initial condition $n = 0$ at $t = 0$.

Hence we have shown that coupling of lde to the structure's rigidity yields logarithmic relaxation of the volume under external pressure. We can compare the logarithmic pre-factor $C = (kT\upsilon)/(\alpha U_\mathrm{m})$ in (6) with experimental data. By taking $\upsilon = 0.18$ from the linear slope in figure 2, $T = 300\ K$ and $U_\mathrm{m} = 6$ eV, we obtain $C = 5.2 \times 10^{-4}$. From the experimental plot of relaxation at 9 GPa [1] (note that this pressure corresponds to the 'regular' densification regime, for which relations (2) and (6) hold), $C = 4.3 \times 10^{-4}$, which agrees well with the estimate from theory, given the approximations involved in the mean-field approach and the estimation of parameters.

In summary, we have shown that coupling of lde to structural rigidity results in the experimentally observed logarithmic volume relaxation in glasses. By extracting the microscopic parameters from realistic simulations, we have linked them to the experimental slope of logarithmic relaxation.

In addition to logarithmic relaxation under pressure, coupling of lde to structural rigidity results in another interesting phenomenon. We have predicted that such a coupling would result in the temperature-induced densification in the pressure window [13]. This effect can only be explained by assuming that pressure-induced lde are essentially the same events as temperature-induced lde. Recently, this pressure window has been confirmed experimentally and we have found similar effects in amorphous GeO_2 [20]. This suggests the universality of lde, in the sense that they are mostly defined by the property of a given network and not by the driving process. Therefore we propose that coupling of lde to structural rigidity can be used to describe a wider range of relaxation phenomena in network glasses, including glass ageing, crystallization [20] or relaxation in response to any external perturbation. The proposed theory is readily generalized to describe relaxation in other disordered media, including powders and granular materials, where corresponding lde can couple to a similarly defined structural rigidity.

We are grateful for support from EPSRC, CMI and Darwin College, Cambridge.

References

[1] Tsiok O B, Brazhkin V V, Lyapin A G and Khvostantsev L G 1998 *Phys. Rev. Lett.* **80** 999

[2] Knight J B, Fandrich C G, Lau C N, Jaeger H M and Nagel S R 1995 *Phys. Rev.* E **51** 3957

[3] Ginzburg S L 1989 Irreversible phenomena in spin glasses *Modern Problems in Physics* (Moscow: Nauka)

[4] Tsiok O B *et al* 1995 *Phys. Rev.* B **51** 12127

[5] For a review, see Phillips J C 1996 *Rep. Prog. Phys.* **59** 1133

[6] Palmer R G, Stein D L, Abrahams E and Anderson P W 1984 *Phys. Rev. Lett.* **53** 958

[7] Brazhkin V V, Lyapin A G, Popova S V and Voloshin R N 2002 *New Kinds of Phase Transitions: Transformations in Disordered Substances* ed V V Brazhkin *et al* (Dordrecht: Kluwer)

[8] Phillips J C 1979 *J. Non-Cryst. Solids* **34** 153
Phillips J C 1981 *J. Non-Cryst. Solids* **43** 37

[9] Trachenko K, Dove M T, Hammonds K D, Harris M J and Heine V 1998 *Phys. Rev. Lett.* **81** 3431

[10] Trachenko K, Dove M T, Harris M J and Heine V 2000 *J. Phys.: Condens. Matter* **12** 8041

[11] Trachenko K and Dove M T 2002 *J. Phys.: Condens. Matter* **14** 7449

[12] Trachenko K and Dove M T 2003 *Phys. Rev.* B **67** 064107

[13] Trachenko K and Dove M T 2003 *Phys. Rev.* B **67** 212203

[14] Tsuneyuki S, Tsukada M, Aoki H and Matsui Y 1998 *Phys. Rev. Lett.* **61** 869

[15] Ekunwe N S O and Lacks D J 2002 *Phys. Rev.* B **66** 212101

[16] Trachenko K and Dove M T 2002 *J. Phys.: Condens. Matter* **14** 1143

[17] Courtens E, Fouret M, Hehlen B, Ruffle B and Vacher R 2003 *J. Phys.: Condens. Matter* **15** S1279

[18] Barrat J L, Badro J and Gillet P 1997 *J. Comput. Simul.* **20** 17

[19] Mozzi R L and Warren B E 1969 *J. Appl. Crystallogr.* **2** 164

[20] Trachenko K, Dove M T, Brazhkin V V and El'kin F S 2003 in preparation