Local events and stretched-exponential relaxation in glasses

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We discuss the relaxation in glasses in terms of local relaxation events (LRE) which glass uses to adjust to external perturbations. The dynamics of LRE is governed by a differential equation with a solution that fits well to the stretched-exponential relaxation. We discuss how this picture gives rise to the observed correlations of nonexponentiality with temperature, relaxation time, and structure of glass or fragility of a glass-forming system.

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Relaxation phenomena in many structural and electronic glasses follow the remarkably universal stretched-exponential law.[1–3] Relaxing quantity, $q(t)$, decays as

$$q(t) \propto \exp(-(t/\tau)^{\beta}), \qquad (1)$$

where $0 < \beta < 1$.

Several derivations of the form of stretched-exponential relaxation (SER) have been proposed. For example, dependence (1) can be derived by averaging the usual exponential with a certain distribution of relaxation times.[4,5] Another phenomenological way of deriving SER is to assume that microscopic relaxation processes terminate in randomly distributed static traps, resulting in the reduction of the space dimensionality for relaxation relative to the geometric dimensionality.[3] Similar ideas were discussed by other workers,[6] and used to construct simulation models,[7] although in the simulations SER has been often assigned to different mechanisms.[7–9] SER has also been related to the distribution of relaxation rates that depend on sizes of relaxing units.[10]

A ubiquitous character of SER[1–3,11] suggests that the underlying physical process should be quite general in different glassy systems. The challenge has been formulated recently that in order to understand the relaxation process, one needs to relate β, τ, and the structure of glass.[2] This calls for the microscopic description of relaxation. Such a description has been elusive since the discovery of SER by Kohlrausch,[12] prompting the suggestion that the origin of SER remains "one of nature's best kept secrets."[3] In our view, microscopic description of relaxation in glasses should begin with recognizing atomistic processes involved, and discuss the dynamics of these processes as relaxation proceeds.

In this paper, we propose that SER can be derived from the differential equation that describes the dynamics of local relaxation events, and discuss the relationships of β and τ with temperature and structure of glass or type of glass former.

We begin by identifying local relaxation events (LRE), by which glass adjusts to a given set of temperature T and pressure p. A LRE was identified in the molecular dynamics (MD) simulation as a rebonding event that involves a sudden jump of an atom across the ring of connected tetrahedra.[13] This involves breaking old bond(s), forming new one(s), and subsequent relaxation of the local structure (the animation of a typical LRE can be found in the electronic form of Ref.

13), resulting in the irreversibility of structural changes introduced by LRE. LRE are spatially heterogeneous events, in that relaxation times are different for events in different locations of glass structure.[14] On the basis of LRE dynamics, we have predicted[15] that temperature-induced densification takes place in the pressure window, centered around the rigidity percolation point. This nontrivial effect has been recently confirmed experimentally, with a high degree of accuracy.[16] The agreement suggests that LRE, identified in the MD simulations, indeed serve as elementary relaxation "quanta," by which glass adjusts to a given set of (p, T), and we can use modeling results to discuss how the activation barriers change with the number of LRE.

Each LRE carries a microscopic change of relaxing quantity. For example, in SiO_2 glass under pressures above 5 GPa, each LRE is accompanied by the average relative volume change $\Delta V/V_0$:[14]

$$\Delta V/V_0 = \nu n, \qquad (2)$$

where ν is the volume change per one LRE ($\nu < 0$ for positive pressure), and n is the number of LRE, quantified by the number of new and broken bonds per atom.

The probability to induce a LRE, $f = \exp(-U/kT)$, where U is the activation barrier. Because under a given set of external conditions, a relaxing quantity approaches constant value,[2,3,17] it is natural to assume that the number of LRE, n, that glass uses to adjust to a given set of (p, T), is finite. Then the rate equation for n is

$$\frac{dn}{dt} = \frac{1}{\tau_0}\exp(-U(n)/kT) - Cn, \qquad (3)$$

where the second term on the right-hand side of the equation describes saturation, such that $dn/dt = 0$ as $t \to \infty$. $U(n)$ is the effective value of activation barrier that changes as relaxation proceeds by LRE. In this picture, the relaxation is complete after a certain number of LRE is induced, bringing glass into the equilibrium with external conditions. It should be noted that glass is a nonequilibrium system by preparation; we use term "equilibrium" in a sense that relaxation time under the change of external perturbations is much shorter than that arising from the nonequilibrium nature of originally prepared glass,[2,3] so that at equilibrium no change

of relaxing quantity can be detected at the experimental time scale.

Equation (3) can be solved if dependence $U(n)$ is known. Some time ago, Goldstein considered how local stresses redistribute in glass under external stress. He argued that atoms in the region of a local relaxation event support less stress after the relaxation than before, and therefore atoms elsewhere support more stress after a local relaxation than before.[18] One can speculate that loading more stress on the region of next LRE increases its activation barrier. A reaction path of a thermally induced LRE is set by the minimal energy barrier defined by the local and medium-range structure. In SiO_2 glass, for example, reaction paths are defined by the constraints needed to maintain connected tetrahedral (or higher-coordinated) structure, with the energy barrier minimized along rotations and displacements of tetrahedra (polyhedra).[19,20] The additional stress, that acts on the local region due to the redistribution of local stresses,[18] also depends on the direction of externally applied force, and is generally applied at random relative to the discrete set of the minimal energy reaction paths. This blocks minimal energy paths and increases $U(n)$. For example, in SiO_2 glass, we have observed that the local environments of late LRE are changed substantially by structural changes introduced by preceding LRE,[13] resulting in the increase of the waiting times needed to induce late LRE.[14,21] To the first order,

$$U(n) = U_0 + \alpha(U_m - U_0)n, \qquad (4)$$

where α is the coupling constant and U_0 and U_m are the lower and the largest values of activation barrier, $U_m \gg U_0$.[14] In network glasses, U_0 is associated with atomic motion involving only rotation and displacement of rigid constituent units,[19,20] and U_m is on the order of energy required to break a bond. Generally, U_m is associated with the maximal barrier needed to be overcome to force a particle out of its local environment.

By combining Eq. (4) with Eq. (3) (without the saturation term on the right part which is small for parameters at which the logarithmic part of SER becomes approximately constant, see Ref. 24), one gets

$$n(t) = \frac{kT}{\alpha U_m} \ln\left(1 + \frac{\alpha \gamma U_m}{kT} \frac{t}{\tau_0}\right). \qquad (5)$$

Experimentally, the volume of silica glass indeed depends logarithmically on time,[22] and it turns out that the slope of logarithmic relaxation of volume, given by combining Eqs. (2) and (5), yields a good quantitative agreement with the experimental value.[14] This supports the validity of expansion (4).

We now relate the dynamics of LRE to SER. LRE are induced during both the fast "preparation" phase when the external conditions are changed, and during the relaxation phase. The total number of LRE, n_t, is

$$n_t = n_0 + n_r(t), \qquad (6)$$

where n_0 and $n_r(t)$ is the number of LRE induced during the preparatory and relaxational phases, respectively. The SER under consideration is due to the "tail" of LRE that are in-
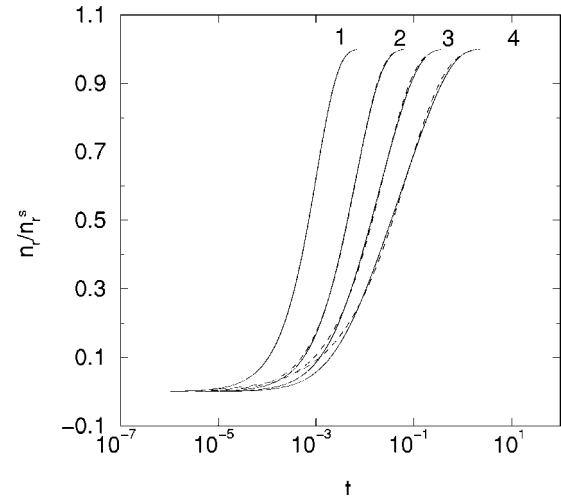

FIG. 1. Normalized number of LRE, n_r/n_r^s, as a function of time. Solid lines are the solutions of Eq. (7), and dashed lines are fits to the SER form of $n_r/n_r^s = 1 - \exp - (t/\tau)^\beta$. Curves labeled 1, 2, 3 and 4 correspond to the solution of Eq. (7) for $n_r^s = 0.001, 0.005, 0.01$, and 0.015, respectively, and $A \approx 330$. Fits of curves 1–4 to the SER give the following parameters for (β, τ): (0.99, 0.001), (0.86, 0.007), (0.68, 0.02), and (0.55, 0.07), respectively.

duced during the slow relaxational phase, while most of the events are usually induced during the fast preparation phase. In this picture, slow relaxation is due to the fact that glass has not relaxed to a new set of external conditions during the fast preparation phase. If, for example, this phase is sufficiently long in time, and the external conditions are applied at such small increments as to induce one LRE at a time, $n_r = 0$. We introduce parameter n_r^s which is the saturated number of LRE in the relaxation phase, such that $n_r(t) \to n_r^s$ as $t \to \infty$. Then from Eqs. (3), (4), and (6) follows

$$\frac{dn_r}{dt} = \exp(-An_r) - \frac{n_r}{n_r^s}\exp(-An_r^s), \qquad (7)$$

where $A = \alpha U_m/kT$, t is redefined as t/τ_0, and the coefficient in the saturation term is chosen such that $dn_r/dt = 0$ when $n_r \to n_r^s$.

Equation (7) has two parameters, n_r^s and A. When $An_r^s \ll 1$ (and hence $An_r \ll 1$ since $n_r < n_r^s$), the right part of Eq. (7) becomes $[1 - (n_r/n_r^s)]$, giving the Debye-type exponential solution. This takes place when the number of LRE in the relaxation phase is too small, or (and) when the temperature is too large and results in the fast activation of events. Hence this model sets the scale for the temperature, T_n, at which the nonexponentiality of solution of Eq. (7) sets in, corresponding to glassy relaxation. From $A(T_n)n_r^s \approx 1$, $kT_n \approx \alpha U_m n_r^s$. Below we show that for $T \approx T_n$, the solution of Eq. (7) describes SER.

In Fig. 1 we show the results of numerical integration of Eq. (7) for n_r, normalized by n_r^s, for various values of n_r^s. The range of n_r^s is defined by the condition of interest $An_r^s \approx 1$, and for definitiveness we used $U_m = 6$ eV, giving $A \approx 330$. To compare the solutions with SER, we recall that n_r^s was de-
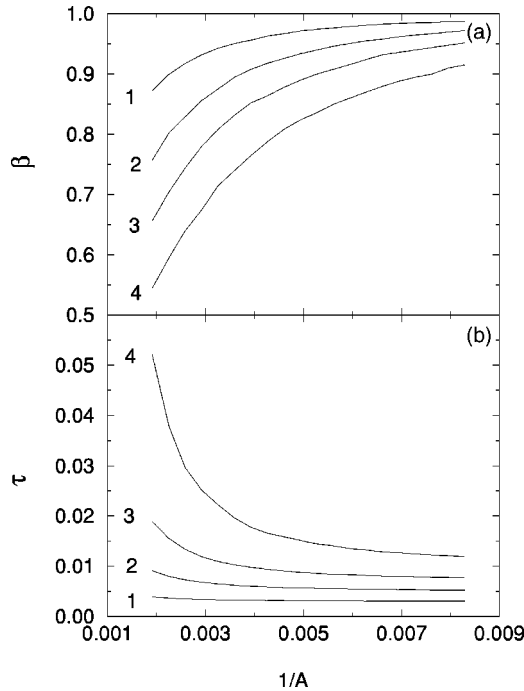
FIG. 2. β (a) and τ (b) as a function of $1/A = kT/\alpha U_m$ for (1) $n_r^s = 0.003$, (2) 0.005, (3) 0.007, and (4) 0.01.

fined such that $n_r/n_r^s \to 1$ as $t \to \infty$, corresponding to a relaxing quantity [defined, for example, by Eq. (2)] reaching a constant value at $n_r = n_r^s$. Therefore we fit the solution of Eq. (7) to the SER of the form $n_r/n_r^s = 1 - \exp - (t/\tau)^\beta$. The fit is done using the least-squares method. Note that Eq. (7) and the form of SER have only two parameters each. This makes an existence of a good fit nonaccidental, but characteristic of the physical process under consideration. If the fit exists, the family of parameters (A, n_r^s) should unambiguously map onto (β, τ), without any extra tuning parameters.

Figure 1 shows very good fits to SER over about eight decades, especially in the intermediate logarithmic[24] and long-tail time range. As n_r^s increases, the fit in the short waiting time range becomes less perfect, but we note that this is also the case experimentally.[3,23] It has been a very good fit in the range of intermediate and long waiting times that made SER such a ubiquitous function for many glassy systems.[1–3,11]

We can now discuss the physical meaning of model parameters and their relation to the nonexponentiality of relaxation. The first important point to note is that β decreases with n_r^s (see the legend in Fig.1). This will be discussed in more detail below.

In Fig. 2 we plot the solutions of Eq. (7) for β and τ at different values of temperature and n_r^s. First, it follows from Fig. 2 that for a given n_r^s, β increases with $T \propto 1/A$ [see Fig. 2(a)]. This is consistent with a wide set of experimental observations that show that the degree of nonexponentiality decreases with T.[2,3,17] Second, we find that τ increases as β decreases [see the legend in Fig. 1 and Figs. 2(a) and 2(b)], consistent with experimental and modeling results.[25]

How is the nonexponentiality related to the structure of glass or type of supercooled liquid at different temperatures?

Recall that n_r^s is defined by the degree of retardation of the system after the fast preparation phase. According to Fig. 1, the more the system is lagged behind the equilibrium in terms of the required number of local events in the relaxation phase n_r^s, the more nonexponential the relaxation is. One would expect that the retardation is reduced in glasses with higher average coordination number $\langle r \rangle$. Given all other conditions equal, glass with increased cross-linking responds to stress more efficiently, since more local stress-transferring interactions are available. Hence a larger number of LRE partition into n_0 [see Eq. (6)], reducing n_r^s in the relaxation phase. According to our model, this increases β (see Figs. 1 and 2), and is in agreement with experimental results that show consistent increase of β with average coordination number $\langle r \rangle$.[17]

This effect can also be discussed in terms of system "fragility" and "strength,"[26] often used to describe relaxation in glasses. Experimental data show that larger values of $\langle r \rangle$ correspond to stronger glasses and larger values of β.[17] The strong glass-forming system is characterized by the in-built resistance to structural change caused by temperature, while fragile system easily rearranges to alternative structures by particle reorientations.[26] Consequently, one expects a smaller number of local events, n_r^s, to be induced in a stronger system at a given set of external conditions, which corresponding to larger β in our picture [see Figs. 1 and 2(a)], consistent with experimental results.

It is interesting that experimentally, the sensitivity of β to temperature is reduced in strong glass-forming systems[17]. In network glasses, this is accompanied by the increase of $\langle r \rangle$.[17] As discussed above, stronger glass corresponds to a smaller value of n_r^s. Plotted in Fig. 2(a) is β as a function of T for different values of n_r^s. It is indeed seen that as n_r^s decreases (glass becomes stronger), variations of β over the same temperature range decrease.[27,28] Hence the sensitivity of β to temperature for various glass types is correctly predicted in this model.

The proposed model also allows one to discuss the relaxation of glass-forming systems near glass transition temperature. It has been shown that the macroscopic relaxation of supercooled liquids is due to a superposition of the contributions from dynamically distinguishable subensembles.[29] Hence, similarly to network glasses, the proposed model can relate parameters of SER of glass-forming systems with their fragility. Experimentally, the broad correlation has been found between the fragility of more than 70 glass-forming systems and β, with β increasing from about 0.2 to unity as the system becomes stronger.[11] The same trend is seen in network glasses.[17] As discussed above, one expects a smaller number of local events, n_r^s, to be induced in a stronger system at a given set of external conditions. This corresponds to larger values of β in our picture [see Figs. 1 and 2(a)], consistent with experimental results.

Finally, one could speculate whether Eq. (7) can describe glass transition. When a glass former is cooled down, it can be viewed as retarded relative to the new temperature and volume, with each LRE relaxing the system towards changing external conditions. The only assumption behind Eq. (7) is the increase of barriers as relaxation proceeds by LRE, Eq.

(4), and it has been shown that activation barriers in a glass-forming system indeed increase as T decreases.[8] This gives Eq. (7). A more detailed consideration of this process can be the subject of future studies.

In summary, we have proposed that SER naturally follows from the dynamics of local events by which glass adjusts to the change of external conditions. The nonexponentiality of relaxation depends on the degree of the system retardation during the fast change of conditions. This model allows one to discuss variations of nonexponentiality with temperature and glass structure or fragility of a glass-forming system.

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