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Simple nonlinear equation for structural relaxation in glasses

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A wide range of glassy and disordered materials exhibit complex, nonexponential, structural relaxation (aging). We propose a simple nonlinear rate equation $\dot{\delta} = a[1 - \exp(b\,\delta)]$, where δ is the normalized deviation of a macroscopic variable from its equilibrium value, to describe glassy relaxation. Analysis of extensive experimental data shows that this equation quantitatively captures structural relaxation, where a and b are both temperature- and, more importantly, history-dependent parameters. This analysis explicitly demonstrates that structural relaxation cannot be accurately described by a single nonequilibrium variable. Relaxation rates extracted from the data imply the existence of cooperative rearrangements on a supermolecular scale.

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Glass-forming materials exhibit a rapid increase in relaxation time scales when going through their glass temperature T_g [1]. When external conditions change abruptly, the observation of the full relaxation to equilibrium becomes exceedingly difficult, except for a narrow range of temperatures near T_g. The relaxation is characteristically nonexponential and spans several orders of magnitude in time. In many cases, the relaxation is logarithmic. This behavior is paralleled in a broad range of disordered systems: compaction of granular materials [2], crumpling of thin sheets [3], aging of conductivity in electron glasses [4,5] and dielectric loss in various glass formers [6,7]. This apparently wide-spread behavior might suggest a generic origin of slow glassy relaxations (aging).

Glassy relaxation is typically probed by tracking the evolution of a macroscopic quantity, e.g., the volume or the enthalpy, in response to an abrupt change in an externally controlled variable, e.g., the temperature. In the latter case, when a temperature T_0 is rapidly changed to T, in the vicinity of the glass temperature T_g, various degrees of freedom of the glass respond differently. The vibrational degrees of freedom quickly equilibrate at T. The structural degrees of freedom, however, carry long-time "memory" of the original state at T_0 and fall out-of-equilibrium with T. It is the out-of-equilibrium dynamics of the structural degrees of freedom towards equilibrium at T that is at the heart of "structural relaxation."

Structural relaxation is conventionally interpreted in terms of the Tool-Narayanaswamy-Moynihan (TNM) [8] or Kovacs-Aklonis-Hutchinson-Ramos [9] phenomenological four-parameter models. The main assumption in these models is that during relaxation, a single dynamical variable is sufficient for describing the nonequilibrium state of the glass. In the case of the TNM model this variable is a "fictive temperature," defined to be a linear function of the probed quantity. It is known, however, that these models do not describe experimental data accurately [1] and actually fail to account for thermal history dependence [10]. In addition, while it has been recognized that nonmonotonic relaxation (i.e., the Kovacs memory effect [11]) cannot be described by a single nonequilibrium state variable [12,13], some recent works have suggested that this might be possible for monotonic relaxations of the type considered here [12,14,15].

In spite of the seemingly universal nature of glassy relaxation, as well as its great scientific and technological importance, a theoretical understanding of it is still lacking. In this Rapid Communication, we propose a simple, analytically solvable, nonlinear rate equation for describing structural relaxation (aging) in glasses. The equation is shown to quantitatively capture extensive experimental data on volume relaxation, yet it explicitly demonstrates the inadequacy of a single-variable nonequilibrium description of glassy relaxation. This analysis sheds light on some basic properties of structural relaxation in these systems, including estimates of activation energies and volumes.

Volume relaxation of glassy materials is usually studied by mercury dilatometry [16]. Classical experiments were performed by Kovacs in the 1960s [11]. These measurements are routinely used since then and provide a standard testing ground for models. In the so-called down-jump experiments, a glass is rapidly quenched from equilibrium at T_0 to a lower temperature T. Measurements begin at t_i, the characteristic time at which the vibrational degrees of freedom thermalize.

The first question we raise is whether structural relaxation can be properly described by a single nonequilibrium variable. To address this question, we denote such a variable by $\delta(t)$ and note that a single variable description means that the rate of relaxation is uniquely determined by its instantaneous value, $\dot{\delta}(t) = r[\delta(t)]$, where $r[\cdot]$ is some functional. Therefore, in such models there exists a function $g(t)$ such that $\delta(t) = g[t + g^{-1}(\delta_0)]$, where $\delta_0 = \delta(0)$ is the initial condition, and hence measurements differing *only* in initial conditions would collapse on a single master curve upon proper time shift. An example is shown in Fig. 1(a) with measurements digitized from Kovacs' original work [11], given in terms of $\delta = (V - V_\infty)/V_\infty$, the normalized deviation of the volume from its asymptotic value V_∞. Here the temperature $T = 30\,^\circ\mathrm{C}$ is the *same* for all measurements, and only the initial state is changed by quenching from different initial temperatures T_0. In Fig. 1(b) we time shift each one of the curves such that their initial values would sit on the $60\,^\circ\mathrm{C} \to 30\,^\circ\mathrm{C}$ curve. The failure of the time-shifted data to collapse on a master curve implies that using a single nonequilibrium variable would be inadequate for constructing a predictive model of structural relaxation.

This observation seems to be in line with the common knowledge that glassy relaxation is characterized by a broad spectrum of relaxation times. A fundamental modeling

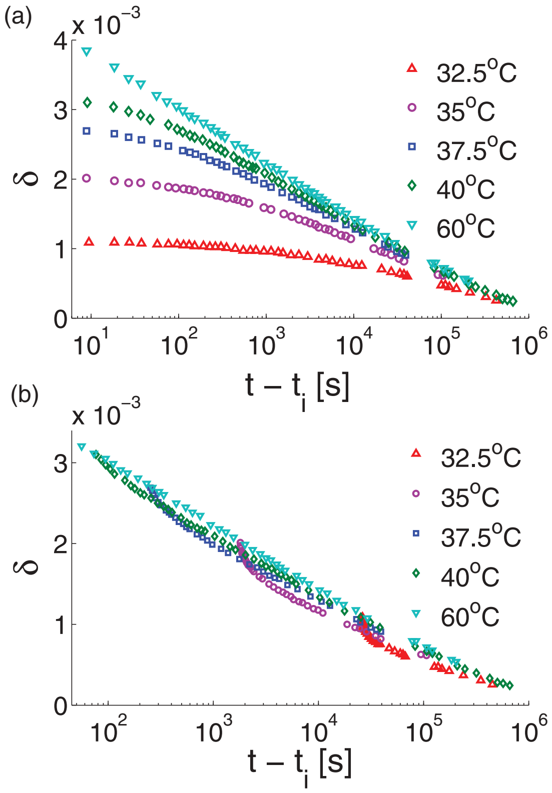

FIG. 1. (Color online) (a) Down-jumps with a fixed target temperature $T = 30\,^{\circ}\mathrm{C}$ in PVAc. Data digitized from Fig. 16 in Ref. [11]. (b) The above measurements time-shifted onto the $60\,^{\circ}\mathrm{C} \to 30\,^{\circ}\mathrm{C}$ curve.

approach would incorporate these various time scales into the evolution of the probability distribution function of the volume v of mesoscopic material elements $f(v,t)$, as it approaches the equilibrium distribution $f_T^{\mathrm{eq}}(v)$ at T during structural relaxation. This is a daunting task that has been pursued only in simple models [17,18]. Our goal here is to show that while models that use only the macroscopic volume $V(t) = N\int_0^\infty v f(v,t)dv$ (where N is the number of elements) cannot be complete, they can still teach us something and might serve as a starting point for constructing an adequate phenomenological model.

There are two basic approaches for rationalizing logarithmic relaxations. The first views the relaxation as a linear response; i.e., relaxation rates are independent of the state of the system. A logarithmic response is then obtained by summing over a spectrum of exponential relaxation modes. This approach was suggested in Ref. [11], was pursued in Ref. [19], and was recently invoked in the context of electron glasses [5]. Essentially, the evolution of the deviation from equilibrium is assumed to take the form $\delta(t) \propto \int_0^\infty p(\lambda)\exp(-\lambda\, t)d\lambda$, where $p(\lambda)$ is a distribution of relaxation rates. When $p(\lambda) \sim \lambda^{-1}$ in a certain range, logarithmic behavior emerges. The second approach, suggested in many contexts (e.g., in Ref. [3]), describes logarithmic relaxation as a result of the dependence of rate on the instantaneous state. A nonlinear equation of the form $\dot\delta \propto -\exp(b\,\delta)$ is then proposed to yield $\delta \propto -\log(t)/b$.

We follow the latter approach and propose to describe structural relaxation using

$$\dot\delta = a(1 - e^{b\,\delta}). \tag{1}$$

Here a is a basic relaxation rate and b is a constant. The 1 added in the parentheses ensures that $\dot\delta$ vanishes with δ. Equation (1) admits the analytic solution

$$\delta(t) = -\frac{1}{b}\log[1 - (1 - e^{-b\,\delta_0})\,e^{-ab\,t}], \tag{2}$$

where δ_0 is the initial condition. For large enough initial amplitudes, for which $\exp(-b\,\delta_0) \ll 1$, and short times $ab\,t \ll 1$, we have $\delta(t) \simeq -\log(ab\,t)/b$. The final stage of the relaxation is exponential, $\delta(t) \propto \exp(-ab\,t)$. For large negative initial amplitudes, for which $\exp(-b\,\delta_0) \gg 1$, and short times $a\,t \ll -\delta_0$, the relaxation is linear $\delta \simeq \delta_0 + a\,t$. Again, the final stage of relaxation is exponential, $\delta(t) \propto -\exp(-ab\,t)$. This marked asymmetry between $\delta > 0$ and $\delta < 0$ relaxations naturally emerges from the exponential $\delta \to -\delta$ asymmetry in Eq. (1).

We note that the dependence of the relaxation rate on the instantaneous state, which is represented by the nonlinearity in Eq. (1), suggests a coupling between different relaxation events, which is absent in the linear response approach. In fact, an equation similar to Eq. (1), in which this coupling is mediated by long range elastic interactions, has recently been proposed [20,21].

To test Eq. (1) we present in Fig. 2 fits of Eq. (2) to a significant portion of Kovacs' original data [11]. For each curve the parameters δ_0, a, b were independently varied. Note, however, that δ_0 is determined by the first data point and hence is not a fitting parameter. Down-jumps in polyvinyl acetate (PVAc) with a fixed target temperature T [Fig. 2(a)] and fixed initial condition T_0 [Fig. 2(b)] are satisfactorily captured by Eq. (2). We checked the equation also against data for glucose [Fig. 2(c)] which appear in Ref. [11]. Figures 2(d) and 2(e) show fits to up-jumps, experiments where the initial temperature T_0 is lower than T, making the initial condition $\delta_0 < 0$. Figure 2(d) is plotted in a *linear* scale to show the manifestly linear portion of the relaxation. Usually, both up-jumps and down-jumps are plotted using a logarithmic time scale to show the asymmetry between the two responses. Here we assign this asymmetry to the nonlinearity of the response. Additional data were shown to agree with Eq. (1) [22].

Is it a mere curve fitting? Equation (1) provides an excellent description of the data, at a price of independently varying the model parameters for each set of experimental conditions. In addition, we already know that a single variable approach as in Eq. (1) cannot constitute a predictive model. Nevertheless, the variation of the parameters a and b with the experimental condition may be physically meaningful and may offer insight into structural relaxation. Indeed, Fig. 3 shows that a and b vary systematically with T_0 and T. Figure 3(a) shows $a(T)$ for PVAc and glucose for a fixed initial temperature T_0 (in each experiment, both down and up-jumps). The first observation is that $a(T)$ is a function; i.e., it varies smoothly with T. The same holds for $b(T)$; see Fig. 3(b) for measurements with fixed T_0. Actually, a exhibits a strong exponential dependence on T, which is a manifestation of the dramatic slowing down associated with the glass transition. The possible origin of this

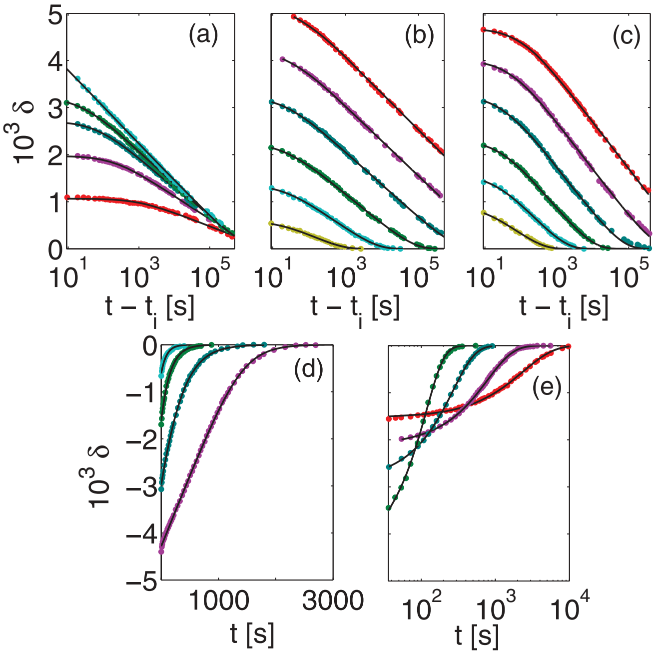

FIG. 2. (Color online) Fits of Eq. (2) to Kovacs' data [11]. The solid black curves are three-parameter fits. (a) Down-jumps in PVAc with fixed $T = 30\,^\circ\mathrm{C}$. See Fig. 1. (b) Down-jumps in PVAc from the same initial condition $T_0 = 40\,^\circ\mathrm{C}$ to $T = 25,\ldots,37.5\,^\circ\mathrm{C}$ (top to bottom). (c) Down-jumps in glucose from a fixed initial temperature $T_0 = 40\,^\circ\mathrm{C}$ to $T = 19.8,\ldots,32.5\,^\circ\mathrm{C}$ (top to bottom). (d) Up-jumps in PVAc. Note the linear scale. Here $T_0 = 30,\ldots,37.5\,^\circ\mathrm{C}$ (bottom to top) to $T = 40\,^\circ\mathrm{C}$. The measurement starts at $t_i = 36$s. (e) Up-jumps in glucose where $T_0 = 25\,^\circ\mathrm{C}$ is fixed while $T = 30,\ldots,37.4\,^\circ\mathrm{C}$ (bottom to top). The measurement starts at $t_i = 36$ s.

dependence in thermally activated processes will be discussed below.

In the present context, the observation that the structural state of a glass cannot be described by a single nonequilibrium variable implies that a and b should depend on the initial temperature T_0. Indeed, Fig. 3(b) demonstrates that b depends on T_0. Here the parameter b in PVAc and glucose is plotted against the jump size $T_0 - T$ for both down-jumps and up-jumps and a wide variation of T and T_0. This shows that b is a function of both T and T_0, which strikingly implies that a relaxing glass carries the memory of its original state at T_0 for very long times. The dependence of a on T_0 (not shown) is the opposite of that of b. Nevertheless, we could not simply connect the two. We also verified (not shown) that the final exponential relaxation rate, controlled by the product $a(T,T_0)\,b(T,T_0)$, also depends on T_0.

Another interesting feature of Fig. 3(b) is the approximate collapse of all measurements on a single curve as a function of $T_0 - T$. This implies that b has a physical meaning. We also note the apparent discontinuity of b when passing from up-jumps to down-jumps, which is known in the literature as the τ_{eff} paradox [23]. We take it to mean that as the asymptotic volume at T is approached from above or from below, the system explores disparate regions in phase space. This indicates that the volume alone cannot tell the whole story about glassy relaxation. This might also imply that the volume and other thermomechanical properties of glasses do not necessarily equilibrate simultaneously (see [1], Sec. B.1.8).

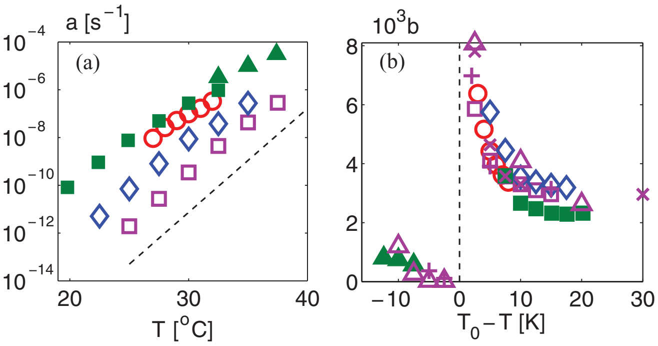

FIG. 3. (Color online) Variation of the parameters in Eq. (1) with initial temperature T_0 and target temperature T. Magenta squares, PVAc down-jumps from $T_0 = 40\,^\circ\mathrm{C}$ [11]; crosses, PVAc down-jumps to $T = 30\,^\circ\mathrm{C}$ [11]; magenta triangles, PVAc T jumps to $T = 40\,^\circ\mathrm{C}$ [11]; pluses, PVAc T jumps to $T = 35\,^\circ\mathrm{C}$ [11,23]; circles, PVAc down-jumps from $T_0 = 35\,^\circ\mathrm{C}$ [24]; diamonds, PVAc down-jumps from $T_0 = 40\,^\circ\mathrm{C}$ [25]; green solid squares, glucose down-jumps from $T_0 = 40\,^\circ\mathrm{C}$ [11]; green solid triangles, glucose up-jumps from $T_0 = 25\,^\circ\mathrm{C}$ [11]. (a) Variation of relaxation rate a with T for experiments of fixed initial condition. The dashed line is an exponent $e^{T/\tilde{T}}$ with $\tilde{T} = 1$ K. The error bars are smaller than the symbols. (b) For PVAc and glucose b shows a consistent dependence on jump magnitude $T_0 - T$.

As is clear from the discussion following Eq. (2), the product $b\,\delta_0$ quantifies the degree of nonexponentiality in the response, similar to the stretching exponent in stretched-exponential representations of glassy relaxation [20]. We expect $b\,\delta_0$ to become small at high temperatures and small temperature jumps, giving rise to a linear response characterized by a purely exponential relaxation, though this regime has not been probed in the data analyzed here. In this context, it is interesting to note that b is in fact growing as $T_0 - T > 0$ becomes smaller in Fig. 3(b). Together with the apparent discontinuous behavior of b mentioned above, this observation calls for further investigation.

Equation (1) seems to contain physical information about structural relaxation. To quantify this, we rationalize the equation using a two-state model. A common way to motivate such an equation is to assume that an Arrhenius-like process depends on an observable. Assume then that the volume evolves through activated jumps of volume elements between a contracted "− state" and an expanded "+ state." Therefore,

$$\dot{n} = -k_- n + k_+(1-n)\,, \tag{3}$$

where n is the fraction of elements in the + state. A key assumption here is that the activation energies are volume dependent, $k_\pm \propto \exp[-E_\pm(n)/k_B T]$. $E_\pm(n)$ are energy barriers for expansion and contraction. They are assumed to grow with density; it is harder to move in a denser system. Recalling that $\delta V/V \sim 10^{-3}$, we approximate $n \simeq n_T + \delta n$, where n_T is the equilibrium value of n at temperature T. Neglecting terms of order δn, using the equilibrium condition $k_-(n_T)n_T = k_+(n_T)(1-n_T)$, and writing $\delta_n = \delta n/n_T$, we obtain

$$\dot{\delta}_n = k_-(n_T)\left(e^{A_+\delta_n} - e^{A_-\delta_n}\right), \tag{4}$$

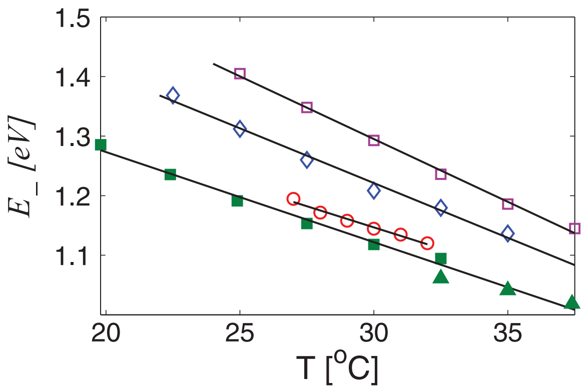

FIG. 4. (Color online) The volume-dependent energy barrier $E_-(V_T) = -k_B T \log(a/k_0)$ for parameter a in Fig. 3(a). Here $k_0 = 10^{12}$ s^{-1}. Solid lines are linear fits.

where $A_\pm = -(n_T/k_B T)\partial E_\pm(n_T)/\partial n$ are non-negative, as barriers become smaller with expansion. Equation (1) then emerges as a special case when $a(T) = k_-(n_T)$, $A_+ = 0$, and $b(T) = A_- \propto \partial E_-(V_T)/\partial V$.

We can then extract an energy barrier scale from $a = k_0 \exp[-E_-(V_T)/k_B T]$, where V_T is the equilibrium volume at T. We set $k_0 \sim 10^{12}$ s^{-1}, which is the typical scale of molecular vibration. In Fig. 4 E_- is calculated for the experiments summarized in Fig. 3(a). The activation barrier is on a 1-eV scale, which might imply cooperative rearrangements of tens of monomers. It is interesting to note that the temperature variation of E_- is rather mild in the vicinity of the glass transition, yet it is enough to produce the strong variation in the relaxation times seen in Fig. 3(a)

To further test the latter, we estimate the size of rearranging regions by a dimensional argument using the measured derivative $\partial E_-(V_T)/\partial T$. Define a volume scale v as

$$v \sim \kappa V \frac{\partial E_-}{\partial V} \sim -\frac{\kappa}{\alpha}\frac{\partial E_-}{\partial T}, \tag{5}$$

where $\kappa = V^{-1}\partial V/\partial P$ is the isothermal compressibility and $\alpha = V^{-1}\partial V/\partial T$ is the thermal expansion coefficient. Linear regressions shown in Fig. 4 yield $\partial E_-/\partial T \sim -0.02$ eV/K. Taking for PVAc $\alpha \simeq 7 \times 10^{-4}$ K^{-1} and $\kappa \simeq 0.42$ GPa^{-1} [11], we find $v \sim 2$ nm^3. A similar estimate for glucose also results in a cubic nanometer scale. These estimates possibly suggest that structural rearrangements involve tens of basic units (e.g., monomers in a polymer), which might be related to other cooperative length scales discussed in the literature [26]. Therefore, while the model cannot explain the dependence of the parameters on the initial temperature T_0, it does seem to be sensitive to the dominant scales of the underlying relaxation processes.

In summary, we proposed a simple mean-field equation for glassy relaxation. Our analysis demonstrates that the structural state of a relaxing glass cannot be fully described by a single nonequilibrium variable. In fact, a glass may carry information about its history for extremely long time scales. Finally, estimates of typical energies and volumes associated with thermally activated relaxation indicate the existence of cooperative rearrangements on a supermolecular scale.

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