A simple nonlinear equation for structural relaxation in glasses

Itamar Kolvin\textsuperscript{1} and Eran Bouchbinder\textsuperscript{2}
\textsuperscript{1} Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem 91904, Israel
\textsuperscript{2} Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

A wide range of glassy and disordered materials exhibit complex, non-exponential, structural relaxation (aging). We propose a simple nonlinear rate equation \( \dot{\delta} = a [1 - \exp(b \delta)] \), where \( \delta \) 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 non-equilibrium variable. Relaxation rates extracted from the data imply the existence of cooperative rearrangements on a super-molecular scale.

Glass-forming materials exhibit rapid increase in relaxation timescales when going through their glass temperature \( T_g \). 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 characterized by a non-exponential 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,\textsuperscript{2,3} crumpling of thin sheets,\textsuperscript{4,5} aging of contact area in dry friction,\textsuperscript{6} aging of conductivity in electron glasses,\textsuperscript{7,8} and mechanical relaxation of star polymers in gels.\textsuperscript{9,10} This behavior is paralleled in a broad range of disordered systems: compaction of granular materials,\textsuperscript{2,3} crumpling of thin sheets,\textsuperscript{4,5} aging of contact area in dry friction,\textsuperscript{6} aging of conductivity in electron glasses,\textsuperscript{7,8} and mechanical relaxation of star polymers in gels.\textsuperscript{9,10} This apparently wide-spread behavior might suggest a generic origin of slow glassy relaxations (aging).

Glassy relaxation is typically probed by tracking the time evolution of a macroscopic quantity, e.g. the volume or the enthalpy of a sample, in response to an abrupt change in an externally controlled variable, e.g. the temperature. In the latter case, when an initial 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 the new temperature \( T \). 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 a new equilibrium at \( T \) that is at the heart of “structural relaxation”.

Structural relaxation is conventionally interpreted in terms of the Tool-Narayanaswamy-Moynihan (TNM)\textsuperscript{11}, or its equivalent KAHR\textsuperscript{12}, phenomenological 4-parameter models. The main assumption in these models is that during relaxation, a single dynamical variable is sufficient for describing the non-equilibrium 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 property, e.g. volume.

However, it is known that these models do not describe experimental data accurately\textsuperscript{11}, and actually fail to account for thermal history dependence\textsuperscript{13}. In addition, while it has been recognized that non-monotonic relaxation (i.e. the Kovacs memory effect\textsuperscript{14}) cannot be described by a single non-equilibrium state variable\textsuperscript{15,16}, some recent works have suggested that this might be possible for monotonic relaxations of the type considered here\textsuperscript{17,18,19}.

In spite of the seemingly universal nature of structural relaxation in glasses, as well as its great scientific and technological importance, a theoretical understanding of it is still missing. In this Letter, we propose a simple, analytically solvable, nonlinear rate equation for describing structural relaxation (aging) in glasses. The proposed equation is shown to quantitatively capture extensive experimental measurements on volume relaxation, yet it explicitly demonstrates the inadequacy of a single non-equilibrium description of glassy relaxation. This analysis allows us to shed light on some basic properties of structural relaxation in these systems, including estimates of activation energy barriers and volumes.

Volume relaxation of glassy materials is usually studied using mercury dilatometry.\textsuperscript{12} The classical experiments in volume relaxation were performed by Kovacs more than five decades ago.\textsuperscript{14} These measurements, which in extreme cases reached months, are routinely used and provide a standard testing ground for models. In these so-called down-jump experiments, a glass sample is rapidly quenched from equilibrium at \( T_0 \) to a lower temperature \( T \). Measurements begin at \( t_i \), the characteristic time it takes for the vibrational degrees of freedom to thermalize.

The first question we raise is whether structural relaxation can be properly described by a single non-equilibrium variable model. 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 the instantaneous value of the variable, i.e. \( \dot{\delta}(t) = r[\delta(t)] \), where \( r[\cdot] \) is a functional. Therefore, in the framework of 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 a set of measurements which differ only in initial condition could be time-shifted in such a way that all curves would collapse on a single master curve. An example of
such a set is shown in Fig. 1(a) with measurements digitized from Kovacs’ original work [14], given in terms of $\delta = (V - V_\infty)/V_\infty$, the normalized deviation of the volume from its asymptotically stable value $V_\infty$. Here the temperature $T = 30^\circ C$ is the same for all measurements, and only the initial state of the system 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 $60^\circ C \rightarrow 30^\circ C$ curve. The failure of the time-shifted curves to collapse on a master curve implies that using a single non-equilibrium variable (here the deviation of the volume from its equilibrium value) would be inadequate for constructing a predictive model of structural relaxation.

There are two basic approaches for understanding logarithmic relaxations. The first approach sees the relaxation as a linear response, i.e. relaxation rates are independent of the state of the system. A logarithmic response can then be obtained by summing over a spectrum of exponential relaxation modes. This approach was suggested in [14], pursued in [22], and was recently also invoked in the context of electron glasses [3]. 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 the 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 [4]), describes logarithmic relaxation as a result of the dependence of rate on instantaneous state, e.g. slowing-down due to compaction. A nonlinear equation of the form $\delta \propto \exp(b\delta)$ is then proposed to yield $\delta \propto -\log(t)/b$.

We follow the latter approach and propose to describe structural relaxation by the following equation

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

(1)

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

$$\delta(t) = -\frac{1}{b} \log \left[1 - \left(1 - e^{-b\delta_0}\right) e^{-abt}\right],$$

(2)

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

To test the model we present in Fig. 2 fits of Eq. (2) to a significant portion of Kovacs’ original data [14]. For each curve the parameters $\delta_0, a, b$ were independently varied. Note, however, that $\delta_0$ is essentially determined by the first data point and hence is not a real fitting parameter. Down-jumps in PVAc with fixed target temperature $T$ (panel (a)) and fixed initial condition $T_0$ (panel (b)) are satisfactorily captured by Eq. (2). We checked the equation also against data for glucose (panel (c)) which appears in [13]. Panels (d-e) show fits to up-jumps - experiments where the initial temperature $T_0$ is lower than $T$, making the initial condition $\delta_0 < 0$. Panel (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 suggest that this asymmetry can be understood to
emerge from the nonlinearity of the response. Additional data were shown to be consistent 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, we argue that the variation of the parameters and with experimental condition may be physically meaningful and provide us with physical insight into structural relaxation. Indeed, Fig. 3 shows that and do show systematic variations with and . Panel (a) shows for PVAc and glucose under a fixed initial temperature (in each experiment, both down and up-jumps). The first observation is that is a function, i.e. it exhibits a smooth variation with . The same is true for (bottom to top). (c) Down-jumps in glucose from a fixed initial temperature to (top to bottom). (d) Up-jumps in PVAc. Note the linear scale. Here 30, 37.5°C (bottom to top) to 40°C. The measurement starts at \( t_i = 36 \text{ sec.} \) (e) Up-jumps in glucose where \( T_0 = 25\text{°C} \) is fixed while \( T = 30, \ldots, 37.4\text{°C} \) (bottom to top). The measurement starts at \( t_i = 36 \text{ sec.} \)

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In the present context, the observation that the structural state of a glass cannot be described by a single non-equilibrium variable implies that and should depend on the initial temperature . Indeed panel (b) demonstrates that depends on . Here the parameter in PVAc and glucose is plotted against the jump size for both down-jumps and up-jumps and a wide range of variation of both and . This shows that is in fact a function of both and , which strikingly implies that a relaxing glass carries memory of its original state at for very long times, sometimes for days! The dependence of on initial (not shown here) is the opposite of that of . In spite of this fact, we have not found any simple connection between the two. We also verified (not shown) that the final exponential relaxation rate, which is controlled by the product , depends on as well.

Another interesting feature of panel (b) is the approximate collapse of all measurements on a single curve as a function of for both down-jumps and up-jumps and a wide range of variation of both and . This shows that is in fact a function of both and , which strikingly implies that a relaxing glass carries memory of its original state at for very long times, sometimes for days! The dependence of on initial (not shown here) is the opposite of that of . In spite of this fact, we have not found any simple connection between the two. We also verified (not shown) that the final exponential relaxation rate, which is controlled by the product , depends on as well.

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properties of glasses do not necessarily equilibrate simultaneously (see section B.1.8).

Equation (1), with its parameters $a$ and $b$, does seem to contain meaningful physical information about the process of structural relaxation. In order to quantify this information, we propose to rationalize the equation using a simple two-state model. A common way to motivate such an equation is to assume that an Arrhenius-like expansion. Equation (1) then emerges as a special case of the experiments summarized in Fig. 3(a). The activation barrier turns out to be on a 1eV scale, which might be indicative of cooperative rearrangements of tens of monomers. 

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

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

where $n$ is the fraction of elements in the $+$ state. A key assumption here is that the activation energies are volume dependent, i.e. $k_\pm \propto \exp(-E_\pm(n)/k_BT)$. $E_\pm(n)$ are energy barriers for expansion and contraction. They are assumed to grow with density – it is harder to move in a denser system. Taking into account the fact that $\delta V/k$ is small, of the order of $10^{-3}$, we approximate $n \simeq n_T + \delta n$, where $n_T$ is the equilibrium value of $n$ at temperature $T$. By neglecting terms of order $\delta n$, using the equilibrium condition $k_-(n_T)n_T = k_+(n_T)(1-n_T)$ and writing $\delta n = \delta n/n_T$, we find that

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

where $a$ are expected to be non-negative, as barriers should become smaller with expansion. Equation (1) then emerges as a special case when $a(T) = k_-(n_T)$, $A_+ = 0$ and $b(T) = A_-$. 

This model allows us to extract an energy barrier scale from $a = k_0 \exp(-E_-(V_T)/k_BT)$, where $V_T$ is the equilibrium volume at $T$. Since $k_0$ is a pre-exponential factor, its exact value is not important. We take $k_0 \sim 10^{12}$ sec$^{-1}$, which is the typical scale of molecular vibration. In Fig. 4 we extract values of the energy barrier $E_-$ from the experiments summarized in Fig. 3(a). The activation barrier turns out to be on a 1eV scale, which might be indicative of cooperative rearrangements of tens of monomers. 

![Graph showing variation of the parameters in Eq. (1) with initial temperature $T_0$ and target temperature $T$.](image1)

![Graph showing variation of relaxation rate $a$ with $T$ for experiments of fixed initial condition. The dashed line is an exponent $e^{T/T}$ with $T = 1^\circ K$. The error bars are smaller than the symbols.](image2)

![Graph showing volume dependent energy barrier $E_-(V_T)$ for the parameter $a$ in Fig. 3 panel (a). Here $k_0 = 10^{12}$ sec$^{-1}$. Solid lines are linear fits.](image3)
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 $\partial E_c / \partial T \sim -0.02$ eV/K. Taking for PVAc $\alpha \approx 7 \times 10^{-4}$ K$^{-1}$ and $\kappa \approx 0.42$ GPa$^{-1}$ [14] we find $v \sim 2$ nm$^3$. A similar estimate for glucose also results in a cubic nanometer scale. These estimates imply that structural rearrangements involve tens of basic units (e.g. monomers in a polymer), which seems consistent with the typical size of dynamical heterogeneities reported in the literature [29]. 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 to describe structural relaxation in glasses. Our analysis clearly demonstrates that the structural state of a relaxing glass cannot be fully accounted for using a single non-equilibrium variable. In fact, we explicitly showed that a glass may carry information about its thermal history for extremely long timescales. Furthermore, the simple analysis allows the estimation of typical energy and volume scales associated with thermally-activated structural relaxation processes. Theses estimates indicate the existence of cooperative rearrangements on a super-molecular scale.

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[1] C.A. Angell, K.L. Ngai, G.B. McKenna, P.F. McMillan, and S.W. Martin, J. Appl. Phys. 88, 3113 (2000).
[2] H.M. Jaeger, C.-h Liu, and S. R. Nagel, Phys. Rev. Lett. 62, 40 (1989).
[3] J.B. Knight, C.G. Fundrich, C.N. Lau, H.M. Jaeger, and S.R. Nagel, Phys. Rev. E 51 3957 (1995).
[4] K. Matan, R.B. Williams, T.A. Witten, and S.R. Nagel, Phys. Rev. Lett. 88, 076101 (2002).
[5] B. Thiria and M. Adda-Bedia, Phys. Rev. Lett. 107, 025506 (2011).
[6] O. Ben-David, S.M. Rubinstein and J. Fineberg, Nature (London) 463, 76 (2010).
[7] Z. Ovadyahu and M. Pollak, Phys. Rev. B 68, 184204 (2003).
[8] A. Amir, Y. Oreg and Y. Imry, Ann. Rev. Cond. Matt. Phys. 2, 235 (2011).
[9] P.G. de Gennes, J. Phys. France 36, 1199 (1975).
[10] M. Geoghegan, C.J. Clarke, F. Boué, A. Menelle, T. Russ, and D.G. Bucknall, Macromolecules 32, 5106 (1999).
[11] C.T. Moynihan et al., Ann. N.Y. Acad. Sci. 279, 15 (1976).
[12] A.J. Kovacs, J.J. Aklonis, J.M. Hutchinson and A.R. Ramos, J. Polym. Sci. 17, 1097 (1979).
[13] S.L. Simon, P. Bernazzani, J. Non-Cryst. Solids 352, 4763 (2006).
[14] A.J. Kovacs, Adv. Polym. Sci. 3, 394 (1963).
[15] S. Mossa and F. Sciortino, Phys. Rev. Lett. 92, 045504 (2004).
[16] L. Leuzzi, J. Non-Cryst. Solids 335, 686 (2009).
[17] E. Bouchbinder and J.S. Langer, Phys. Rev. E 80, 031132 (2009).
[18] E. Bouchbinder and J.S. Langer, Soft Matter 6, 3065 (2010).
[19] P.C. Hiemenez and T.P. Lodge Polymer Chemistry 2nd Ed., pp. 474-476 (2007) CRC press.
[20] P. Sollich, F. Lequeux, P. Hebraud and M. Cates, Phys. Rev. Lett. 78, 2020 (1997).
[21] E.M. Bertin, J.-P. Bouchaud, J.-M. Drouffe and C. Godrèche, J. Phys. A 36, 10701 (2003).
[22] R.M. Kimmel and D.R. Uhlmann, J. Appl. Phys. 40, 4254 (1969).
[23] We tested our equation against data for PVAc from the group of R. Svoboda [24], from an earlier paper by Koves [20] and unpublished data from Kovacs' lab obtained through G.B. McKenna.
[24] G.B. McKenna et al., Polymer 40, 5183 (1999).
[25] R. Svoboda, P. Pustková and J. Málek, J. Phys. Chem. Solids 68, 850 (2007).
[26] J. Málek, R. Svoboda, P. Pustková and P. Čižmárek, J. Non-Cryst. Solids 355, 264 (2009).
[27] R. Svoboda, P. Pustková and J. Málek, Polymer 49, 3176 (2008).
[28] A.J. Kovacs, J. Polym. Sci., 30, 131 (1958).
[29] M.D. Ediger, Ann. Rev. Phys. Chem. 51, 99 (2000).