Energy Landscape Picture of Overaging and Rejuvenation in a Sheared Glass

Daniel J. Lacks and Mark J. Osborne

Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106, USA

(Received 5 May 2004; published 13 December 2004)

Molecular simulations and an energy landscape analysis are used to investigate the effects of shear on aging in a glass. Shear beyond the yield point is shown to change the state of a glass such that it resembles (but is not identical to) a different stage in the aging process. A cycle of large strain rejuvenates the glass by relocating the system to shallower energy minima, while a cycle of small strain overages the glass by relocating the system to deeper energy minima. The balance between overaging and rejuvenation is controlled by how well the glass was initially annealed.

DOI: 10.1103/PhysRevLett.93.255501 PACS numbers: 61.43.Fs, 62.20.Fe

Experiments show that stress (or strain) can alter the characteristic relaxation times and related properties of a glass [1–4]. Since relaxation times generally increase as a glass ages, a common interpretation of these experimental results is that stress changes the extent of aging of the glass. Stress usually reduces relaxation times, which has been interpreted as a reversal of aging or “rejuvenation” of the glass [1–4], but recent experiments have shown that stress can alternatively increase relaxation times, which has been interpreted as an acceleration of aging or “overaging” of the glass [4] (other experimental evidence suggesting overaging has also been reported [5]). Although these interpretations are common, results of detailed experimental studies suggest that the stress-induced changes in relaxation times do not represent changes in the extent of aging of the glass [6–8]. Molecular simulations are used here to address these issues, with an emphasis on determining how stress can cause the different, and apparently opposite, rejuvenation and overaging behaviors, and whether these stress-induced changes can, in fact, be related to changes in the extent of aging of the glass.

The present analysis is based on the energy landscape, which provides a framework to describe the properties of disordered systems [9,10]. At equilibrium, the average energy of the energy minima visited \( \langle e \rangle \) is a well-defined property of the system that decreases with decreasing temperature [11]. For out-of-equilibrium systems the value of \( \langle e \rangle \) changes with time until equilibrium is reached. In this way \( \langle e \rangle \) can monitor the extent of aging [12]; for example, following a decrease in temperature \( \langle e \rangle \) decreases with time as the system ages, until equilibrium is reached at the new temperature. A more physically suggestive parameter, which characterizes the same information as \( \langle e \rangle \), is an effective temperature \( T_{\text{eff}} \) defined such that \( T_{\text{eff}} \) for a system with a particular value of \( \langle e \rangle \) is equal to the temperature at which the equilibrium liquid has the same value of \( \langle e \rangle \) [12]. This definition for \( T_{\text{eff}} \) is somewhat similar to earlier ideas of fictive temperatures [13].

The investigation is carried out on the widely used binary (80%–20%) mixture of Lennard-Jones particles that prevents crystallization [14]. The Lennard-Jones parameters are \( \varepsilon_{ij} \) and \( \sigma_{ij} \) for interactions between particles of type \( i \) and type \( j \), where \( \varepsilon_{22} = 0.5\varepsilon_{11} \), \( \sigma_{22} = 0.88\sigma_{11} \), \( \varepsilon_{12} = 1.5\varepsilon_{11} \), and \( \sigma_{12} = 0.8\sigma_{11} \); the interactions are truncated at the distance of \( 2.5\sigma_{ij} \), and shifted with respect to energy such that the energy is a continuous function. All of the particles have the mass \( m \). The units of energy, density, temperature, and normal mode frequency are \( \varepsilon_{11}, m\sigma_{11}^{-3}, \varepsilon_{11}/k_B \), and \( \varepsilon_{11}^{-1/2} m^{-1/2} \sigma_{11}^{-1} \), respectively. The simulation cell has periodic boundary conditions and contains 500 particles at the density \( \rho = 1.2 \).

First, molecular dynamics (MD) simulations are carried out to determine the equilibrium properties of the system, including a sampling of energy minima visited by the system. The MD simulations are run at constant volume and constant temperature, with the temperature controlled by a Gaussian thermostat [15]. Energy minima that the system visits are found by carrying out energy minimizations that begin from instantaneous configurations during the MD trajectory (note that these energy minimizations do not affect the MD trajectory). The equilibrium results for \( \langle e \rangle \) are shown in Fig. 1. Below a glass transition temperature \( \sim 0.45 \), equilibrated results cannot be obtained be-

![FIG. 1 (color online). Average energy of energy minima visited, \( \langle e \rangle \), as a function of temperature for an equilibrium liquid. The line represents a cubic spline interpolation based on the data points.](image-url)
cause aging occurs on time scales longer than the simulation. The results in Fig. 1 are essentially the same as in Ref. [12], but differ slightly because the density $\rho = 1000/9.4^3 \approx 1.204$ is used here, whereas $\rho = 1000/9.4^3 \approx 1.204$ is used in Ref. [12].

The glasses are studied at zero temperature, in order to preclude thermal contributions to aging and thus focus solely on the effects of strain. Infinitely fast cooling is used to form the glass so that the glass is well characterized (i.e., not ambiguous due to methods and rates of cooling). The infinitely fast cooling is carried out with an energy minimization beginning from a configuration of the equilibrium liquid during the MD trajectory. Because of the infinitely fast cooling, the initial effective temperature of the glass (before the system is sheared), $T_{\text{eff}}^{\text{i}}$, is equal to the temperature of the equilibrium liquid from which the glass was formed.

The glasses are studied at zero temperature, in order to preclude thermal contributions to aging and thus focus solely on the effects of strain. Infinitely fast cooling is used to form the glass so that the glass is well characterized (i.e., not ambiguous due to methods and rates of cooling). The infinitely fast cooling is carried out with an energy minimization beginning from a configuration of the equilibrium liquid during the MD trajectory. Because of the infinitely fast cooling, the initial effective temperature of the glass (before the system is sheared), $T_{\text{eff}}^{\text{i}}$, is equal to the temperature of the equilibrium liquid from which the glass was formed.

The glass is sheared in the zero-temperature and zero-shear-rate limits by incrementing the shear strain on the simulation cell in very small steps and carrying out an energy minimization after each step. Shear strain is imposed through the Lees-Edwards boundary conditions [15]. Note that, in the zero-temperature and zero-shear-rate limits, the system always remains at an energy minimum. The increments of shear strain are chosen to be small enough to approximate continuous change; strain increments of 0.001 are used here.

The consequences of a cycle of increasing and decreasing shear strain, for a single glass configuration, are shown in Fig. 2. As the shear strain on the glass increases, the energy of the glass usually increases continuously with strain. However, the energy drops discontinuously at some strains. These discontinuous energy drops also occur as the strain is decreased. After a cycle of an increase and then a decrease of strain, the final energy of the glass is not the same as the initial energy.

The discontinuous energy drops arise from relaxation events that follow strain-induced disappearances of energy minima, as shown schematically in Fig. 3. Strain-induced disappearances of energy minima have been demonstrated elsewhere through studies of the changes in the height, position, and curvature of the energy minimum and the relevant energy barrier [16]. If the system is in an energy minimum that disappears, the system relaxes to an alternate energy minimum, which gives rise to the discontinuous energy drops seen in Fig. 2. These relaxations to alternate energy minima are irreversible, and give rise to the irreversibility of the strain cycle (see Fig. 2).

Ensemble-averaged results for the energy of the glass as a function of shear strain are shown in Fig. 4. These results are obtained for glasses with $T_{\text{eff}}^{\text{i}} = 0.6$ and 0.8, and represent the average of 114 glass configurations. Results are obtained for glasses in which strain is increased to a maximum strain, $\gamma_{\text{max}}$, of 5%, 15%, and 30%, before the strain is decreased back to zero.

The results for $\gamma_{\text{max}} = 30\%$ are considered first. The energy increases with increasing strain, and ultimately reaches a steady-state (plastic-flow) value that is independent of the initial thermal state of the glass. After the strain decreases to zero, the energy of the final glass at zero strain is higher than that of the initial glass. The nonmonotonic energy changes that occur upon decreasing strain are understood as follows: decreasing the strain initially reduces the stress (see inset of Fig. 4) and thus reduces the strain energy, but after the stress decreases to zero further decreases in strain increase the magnitude of the stress (but in the opposite direction), and thus increase the strain energy. The effective temperature of the final glass state, $T_{\text{eff}}^{\text{f}}$, was determined with a cubic spline interpolation from the final $\langle \epsilon_{\text{r}} \rangle$ of the glass and the equilibrium liquid results for $\langle \epsilon_{\text{r}} \rangle$ as a function of $T$; for both the $T_{\text{eff}}^{\text{i}} = 0.6$ and 0.8 glasses, the effective temperature after the cycle of strain is $T_{\text{eff}}^{\text{f}} = 0.94$. Thus a large strain cycle (30%) increases the effective temperature of the glass, in agreement with the results of previous simulations [17].

![FIG. 2](color online) Energy as a function of strain for one particular configuration (with $T_{\text{eff}}^{\text{i}} \sim 0.6$). The thin line represents results upon increasing strain, and the thick line represents results upon decreasing strain.

![FIG. 3](Schematic representation of the changes of the energy landscape upon strain.)
energy landscape is a region that the system visits upon aging. We further characterized the region of the energy landscape that the system visits by the average of the first moment of the normal mode frequencies at the energy minima the system visits, \( \langle \nu_s \rangle \). Figure 5 shows \( \langle \nu_s \rangle \) as a function of \( \langle e_s \rangle \) for equilibrium systems. Figure 5 also shows the results for \( \langle \nu_s \rangle \) as a function of \( \langle e_s \rangle \) for the glass with \( T_{\text{eff}} = 0.6 \) during a cycle of shear with \( \gamma_{\text{max}} = 30\% \). The energy minima visited under shear clearly differ from those visited at equilibrium. Also, since as the system ages it visits energy minima that lie on the equilibrium \( \langle e_s \rangle \)-\( \langle \nu_s \rangle \) curve [12], we can conclude that the energy minima visited under shear differ from those that the system visits upon aging.

To assure that our conclusions are not affected by the choice of a cycle of strain rather than stress, we also addressed the behavior upon the cycling of stress. The important difference between the cycling of stress and strain, as is evident in the insets of Fig. 4, is that the final glasses are at zero strain and finite stress in the case of cycled strain, but are at zero stress and finite strain in this case of cycled stress (note the initial glasses are at zero strain and zero stress). The cycled stress results (i.e., with the cycle ending when the system reaches zero stress rather than zero strain) are for the most part similar to the cycled strain results. As shown in the inset of Fig. 5, the zero-stress states reached by cycling the stress differ from the states that the system visits in equilibrium (or by aging). For the \( T_{\text{eff}} = 0.6 \) glass, the behavior upon the cycling of stress is qualitatively the same as that upon the cycling of strain: \( T_{\text{eff}} \) decreases for \( \gamma_{\text{max}} = 5\% \), and \( T_{\text{eff}} \) increases for \( \gamma_{\text{max}} = 30\% \). However, for the \( T_{\text{eff}} = 0.8 \) glass, the behavior upon the cycling of stress differs from that upon the cycling of strain in that \( T_{\text{eff}} \) decreases in all cases.

The results for \( \gamma_{\text{max}} = 5\% \) are now considered. After the increase and subsequent decrease in strain, the values of \( \langle e_s \rangle \) for the final glasses at zero strain are lower than those for the initial glasses. For the glass with \( T_{\text{eff}} = 0.6 \), this cycle of strain leads to \( T_{\text{eff}} = 0.58 \); for the glass with \( T_{\text{eff}} = 0.8 \), this cycle of strain leads to \( T_{\text{eff}} = 0.69 \). Thus a small strain cycle (5%) decreases the effective temperature of the glass.

For the simulations with \( \gamma_{\text{max}} = 15\% \), \( T_{\text{eff}} = 0.63 \) for the glass with \( T_{\text{eff}} = 0.6 \), while \( T_{\text{eff}} = 0.71 \) for the glass with \( T_{\text{eff}} = 0.8 \). Thus a moderate strain cycle (15%) increases the effective temperature for the more highly annealed state, but decreases the effective temperature for the less annealed state.

As shown above, a cycle of strain moves the system to a different region of the energy landscape, as characterized by \( \langle e_s \rangle \)—we now examine whether this region of the

![FIG. 4 (color online). Results for \( \langle e_s \rangle \) of the glass as a function of strain. In each plot the thin lines represent results upon increasing strain, and the thick lines represent results upon decreasing strain. Results are shown for the glasses with \( T_{\text{eff}} = 0.6 \) and 0.8—the results for the \( T_{\text{eff}} = 0.6 \) glasses are the lower energy set of results. Note that in the \( \gamma_{\text{max}} = 30\% \) plot, the decreasing strain results for the \( T_{\text{eff}} = 0.6 \) and 0.8 glasses are nearly identical. The insets show the ensemble-averaged stress-strain results for the glass with \( T_{\text{eff}} = 0.6 \).](image)

![FIG. 5 (color online). \( \langle \nu_s \rangle \) as a function of \( \langle e_s \rangle \). Circles represent equilibrium results, and the line through the circles is a guide to the eye for these data. The squares represent results obtained from a strain cycle with \( \gamma_{\text{max}} = 30\% \), for the glass with \( T_{\text{eff}} = 0.6 \). Inset: The circles are equilibrium results, the squares are the state of the system following a \( \gamma_{\text{max}} = 30\% \) cycle, and the triangles are the state of the system following a \( \gamma_{\text{max}} = 5\% \) cycle.](image)
difference occurs because $T_{\text{eff}} = 0.94$ for the plastic-flow state, but $T_{\text{eff}} = 0.68$ for the zero-stress state obtained by relieving the stress from the plastic-flow state. The implications of the present results are now discussed. First, our results show that stress does not literally alter the extent of aging of the glass—as shown in Fig. 5, stress moves the system to regions of the energy landscape that are distinct from regions that the system visits at equilibrium or during aging. This conclusion supports McKenna’s suggestion based on the results of dilatometric and mechanical experiments [8]. The stress-induced states are characterized by either shallower or deeper energy minima than in the initial state, where the shallower energy minima states resemble less aged states, and the deeper energy minima states resemble more highly aged states. In this way stress can “rejuvenate” or “overage” the glass, where these terms imply that stress moves the glass to states that resemble (in some relevant property such as depth of energy minima or characteristic relaxation time) states from different stages in the aging process.

Second, the results show how the apparently opposite effects of both rejuvenation and overaging can follow from a cycle of stress or strain. Strain causes energy minima to disappear, after which the system relaxes to an energy minimum that is necessarily lower in energy at that strain (but not necessarily at zero strain); if the strain is then reversed, the new energy minimum remains lower in energy for at least some small extent of strain. Thus small strain cycles move the system to a different state at zero strain; the higher the initial energy, the larger the probability that these new states are at a lower energy than the initial state at zero strain (note that this description of overaging is only qualitative). However, large strain cycles cause the system to undergo many relaxations to new minima, which moves the system far from the initial state; since annealing causes the initial state to be lower in energy, the final state is more likely to be higher in energy when the system is initially more highly annealed. Thus small strains lead to overaging while large strains lead to rejuvenation, and the balance between overaging and rejuvenation is affected by how well the system is initially annealed. While this picture for rejuvenation has been presented previously, the present investigation also addresses overaging, as well as the balance between overaging and rejuvenation [17].

Third, the results elucidate the interpretation of subyield experiments that show that relaxation times for creep under an applied stress decrease with the magnitude of the applied stress [1]. This result was initially considered to be evidence for rejuvenation, but McKenna and co-workers have shown in a series of experiments that the thermodynamic state of the system appears to be unchanged by these subyield stresses [6–8]. From the energy landscape perspective, rejuvenation is caused by the strain-induced disappearance of energy minima; we have shown previously that the strain-induced disappearance of energy minima leads to plastic deformation [16], and so rejuvenation occurs only when plastic deformation occurs. Thus our analysis implies that subyield stresses do not cause rejuvenation, in agreement with experimental results [6–8]. We suggest that the decrease in relaxation times for creep observed under subyield stresses can instead be attributed to the stress-induced lowering of energy barriers for relaxations in the direction of the applied stress, as in the Eyring model for viscosity [18].

Finally, we note that the strain-amplitude-dependent balance of overaging and rejuvenation described here is analogous to the compaction process in granular materials. Granular materials can become more compact with time, which is an aging process. This compaction can be accelerated if the material is tapped slightly (analogous to overaging), but the material can become less compact if it is tapped very vigorously (analogous to rejuvenation) [19].

Funding for this project was provided by the National Science Foundation (Grant No. DMR-0402867).