Inherent Structure Analysis of the Thermal History Dependence of Yielding in Glasses†

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Molecular simulations and an inherent structure analysis are used to investigate how the response of a glass to stress depends on its thermal history. Although the stress response at low and high strains is independent of the thermal history of the glass, the stress response at intermediate strains depends strongly on the thermal history. Previous experiments and simulations have shown that the peak stress, defined as the maximum stress the system can withstand before flowing, increases as a glass is annealed. The present inherent structure analysis addresses this phenomenon. The present results show that as glasses are strained, more highly annealed glasses remain in their initial metabasin up to larger strains (and thus larger stresses). This greater stress-absorbing capacity of the metabasins that characterize more highly annealed systems allows the more annealed systems to withstand more stress before flowing.

I. Introduction

Ductile glasses, including many polymer and metallic glasses, are characterized by nonlinear mechanical responses. At low strains, the stress increases linearly with strain, the constant of proportionality being the shear modulus. As the strain is increased further, the stress increases more slowly and nonlinearly with strain, until the stress reaches a maximum with respect to strain; this maximum stress defines the peak stress (note that the peak stress is one of several definitions for a yield stress). At high strains, the system is in the plastic flow state, and the stress becomes independent of strain. In some cases, the peak stress is greater than the plastic flow stress—in these cases, a strain softening regime exists where the stress decreases with strain. If experiments are performed by imposing stress rather than strain, the application of a stress less than the peak stress leads to elastic (or nearly elastic) deformation, while a stress greater than the peak stress leads to plastic flow.

Many mechanical response experiments have been carried out on polycarbonate and polystyrene glasses, which are ductile glasses with many applications related to their mechanical properties. These experiments show that yield stresses (based on the present definition of peak stress as well as other definitions) are larger for more highly annealed materials.[1−7]

Molecular simulations have also addressed the thermal history dependence of the peak stress. Utz, Debenedetti, and Stillinger were the first to show in molecular simulations that the peak stress increases with the annealing time of the sample,[8] and subsequent simulations by others have addressed this phenomenon in more detail.[9]

The present paper addresses the origin of the thermal history dependence of the peak stress, using the inherent structure framework. The inherent structure framework developed by Stillinger and Weber considers the dynamics of a system to be decomposed into vibration-like dynamics within an energy minimum and relaxation-like dynamics as the system moves between energy minima.[10] The transition rates between the various minima, which in this picture control the relaxation dynamics, are strongly dependent on the temperature. Furthermore, Sastry, Debenedetti, and Stillinger showed that the system visits different regions of the energy landscape, characterized by different types of energy minima, as conditions change.[11] For example, as the temperature decreases the system visits regions of the energy landscape with deeper (i.e., lower energy) energy minima.

The organization of energy minima on the landscape affects the system properties.[12,13] Recently, Doliwa and Heuer showed that metabasins (groups of proximate energy minima), rather than the energy minima, are the relevant features of the energy landscape in regard to dynamical properties.[14,15] This relevance is due to the fact that often systems repeatedly jump back and forth between energy minima within a single metabasin, indicating that transitions between energy minima within a single metabasin do not lead to correspond to signficant dynamical events. In contrast, a system is unlikely to return to a given metabasin after exiting it, which indicates that transitions between metabasins do correspond to significant dynamical events.

II. Computational Methods

The simulations are carried out on the widely used binary (80%−20%) mixture of Lennard-Jones particles that prevents crystallization. This potential was originally developed by Weber and Stillinger[16] and modified to the Lennard-Jones form by Kob and Andersen.[17] The Lennard-Jones parameters are ϵ_{ij} and σ_{ij} for interactions between particles of type i and type j, where $\epsilon_{22} = 0.5\epsilon_{11}$, $\sigma_{22} = 0.88\sigma_{11}$, $\epsilon_{12} = 1.5\epsilon_{11}$, 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 mass m. The units of energy, density, and temperature are ϵ_{11}, $m\sigma_{11}^{-3}$, and ϵ_{11}/k_B, respectively.

The simulations are carried out for a system of 500 particles in a simulation cell with periodic boundary conditions. The simulation cell is initially cubic, but distorts from the cubic shape as shear strain is imposed. The simulations are carried out the density $\rho = 1.2$.

Glasses at zero temperature are formed here by cooling a liquid infinitely fast. Infinitely fast cooling is used so that the glass is well characterized by the state of the liquid before it

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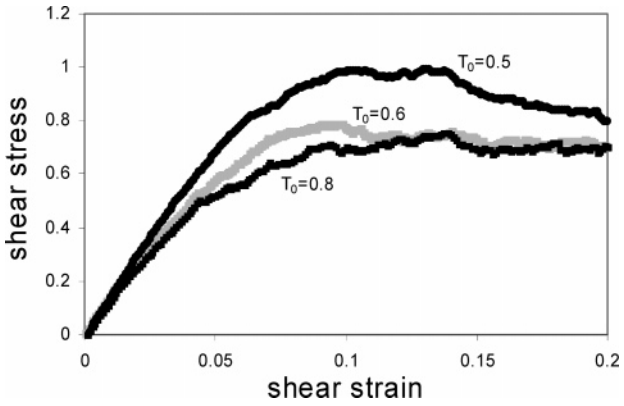

Figure 1. Ensemble-averaged stress in response to imposed strain for glasses at zero temperature. The values for T_0 denote the temperature of the liquids from which the glasses were formed. The plot represents an average over 112 different initial configurations for $T_0 = 0.6$ and $T_0 = 0.8$ and 172 initial configuratations for $T_0 = 0.5$. The calculated stresses for each set of data are shifted by a small constant such that the stress is zero at zero strain for each set of data.

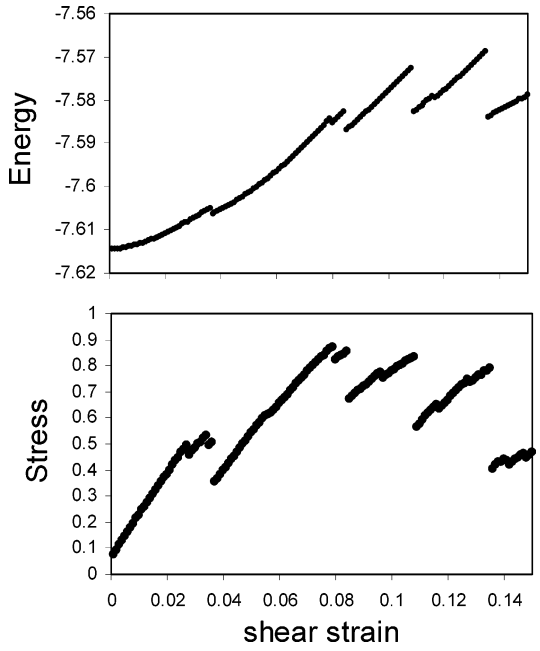

Figure 2. Response to applied strain for a single configuration, at zero temperature. The top plot shows the energy, and the bottom plot shows the stress. This configuration was obtained by quenching from $T = 0.6$.

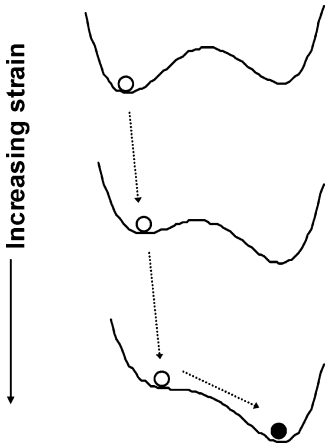

Figure 3. Schematic representation of the changes of the energy landscape upon strain.

was cooled; i.e., no ambiguities exist from the methods and rates of cooling. Molecular dynamics (MD) simulations are used to simulate the liquid at a temperature T. The MD simulations are run under conditions of constant volume (in a cubic simulation cell) and constant temperature, with the temperature controlled by a Gaussian thermostat.[18] Zero-temperature glasses formed by cooling the glass infinitely fast are obtained by carrying out energy minimizations that begin from instantaneous configurations during the MD trajectory; these energy minimizations do not affect the MD trajectory.

To determine the mechanical response of a glass, the glass is sheared in the zero-temperature and zero shear-rate limits. In the zero-temperature and zero-shear-rate limits, the system always remains at an energy minimum. Shearing in these limits is accomplished by incrementing the shear strain, γ, of the simulation cell in very small steps and carrying out an energy minimization after each step. The increments of shear strain are chosen to be small enough to approximate continuous change, and strain increments of 0.001 are used here.

The shear stress, τ, is calculated in the simulations as

$$\tau = \left(\frac{1}{V}\right)\left(\sum_{i=1}^{N}\sum_{j=i+1}^{N} r_{ij} f_{ij} \frac{\partial r_{ij}}{\partial x_i}\frac{\partial r_{ij}}{\partial y_j}\right)$$

where V is the volume and r_{ij} and f_{ij} are the distance and force between particles i and j. Note that since the stress is calculated at zero temperature, velocity contributions to the stress are not relevant.

III. Results

The ensemble averaged stress−strain curves obtained for the glasses quenched from $T = 0.8$, $T = 0.6$ and $T = 0.5$ are shown in Figure 1. At low strains ($\gamma < 0.03$), the stress increases linearly with strain, such that $\tau = G\gamma$ where G is the shear modulus. In this system, the shear modulus G appears to be independent of the thermal history of the glass. At large strains a steady state occurs in which the stress remains constant at the plastic flow value; again, the plastic flow state is independent of the thermal history of the system (note the convergence to the plastic flow state of the glass quenched from $T = 0.5$ occurs at strains greater than those shown in Figure 1).

While the parts of the stress−strain curve at low strains and at high strains are independent of the thermal history of the system, the stress−strain curve at intermediate strains is *strongly* dependent on the thermal history. The value of the peak stress increases as the temperature of the liquid from which the glass is quenched decreases from $T = 0.8$ to $T = 0.6$ to $T = 0.5$. These results show that the peak stress increases with the annealing state of the glass, which concurs with previous experimental[1−5] and simulation[8,9] results.

The nonlinear stress response can be understood in terms of the energy landscape. Figure 2 shows the zero-temperature stress−strain results for a single system (in contrast, the results in Figure 1 represent an ensemble average). The stress and energy usually increase continuously as the system is strained, but occasionally drop discontinuously (energy drops and stress drops always occur together, but in some cases the energy drops are too small to be discernible on this plot). We have previously used studies of the height, position, and curvature of energy minima and energy barriers to show that the discontinuous stress and energy drops arise from strain-induced disappearances of energy minima, as shown schematically in Figure 3.[19] Ensemble

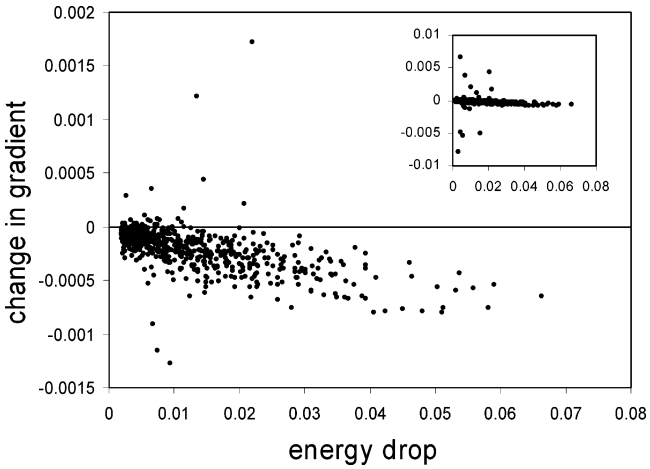

Figure 4. Change in the slope of the energy−strain curve following a discontinuous energy drop, plotted against the magnitude of the energy drop.

averaging (or increasing system size) smooths the discontinuous changes to give the stress−strain curve shown in Figure 1.

The magnitude of the discontinuous energy drops can vary significantly, as seen in Figure 2. The magnitude of the energy drop is related to the extent of the structural rearrangements that correspond to the transition to the other energy minimum; i.e., larger energy drops imply more extensive structural change. Accordingly, if the properties of the system after an energy drop are compared to the properties before the energy drop, the difference will be greater when the magnitude of the energy drop is larger. For example, as shown in Figure 4, the difference between the slopes of the energy−strain curve before and after an energy drop is (on average) greater for larger energy drops.

Based on these observations, we suggest that smaller energy drops are due to transitions to energy minima within the same metabasin, while larger energy drops are due to transitions to different metabasins. A quantitative cutoff between these two regimes is not necessary for the present analysis and, therefore, will not be addressed. While this division is neither rigorous or definitive, we believe that it describes the correct physical behavior.

Figure 2 shows that upon initially straining this system, small energy drops occur before larger energy drops occur. The generality of this result was assessed by determining the ensemble average for the minimum strain at which an energy drop magnitude E_x or higher occurs. As shown in Figure 5, it is a general result that on average small energy drops occur at smaller strains than larger energy drops—this result is shown most clearly in the plot that compares the histograms of the strains necessary to cause energy drops of $E_x = 0.002$ and $E_x = 0.005$, for glasses quenched from $T = 0.5$. In terms of the energy landscape description, this result implies that small strains can cause the disappearance of energy minima that force the system to other minima within the same metabasin, whereas larger strains are necessary to cause the disappearance of energy minima that force the system to other metabasins.

The magnitude of the peak stress is related to the maximum strain for which the system remains in its initial metabasin. This result can be understood in terms of the results in Figure 2. For this particular configuration, the first relatively large energy drop occurs at $\gamma = 0.085$, which can be considered the strain limit for the initial metabasin. As shown in Figure 2, the stress increases when the system remains in its initial metabasin; transitions between energy minima within a megabasin may decrease the stress slightly (e.g., at $\gamma = 0.04$), but then the stress

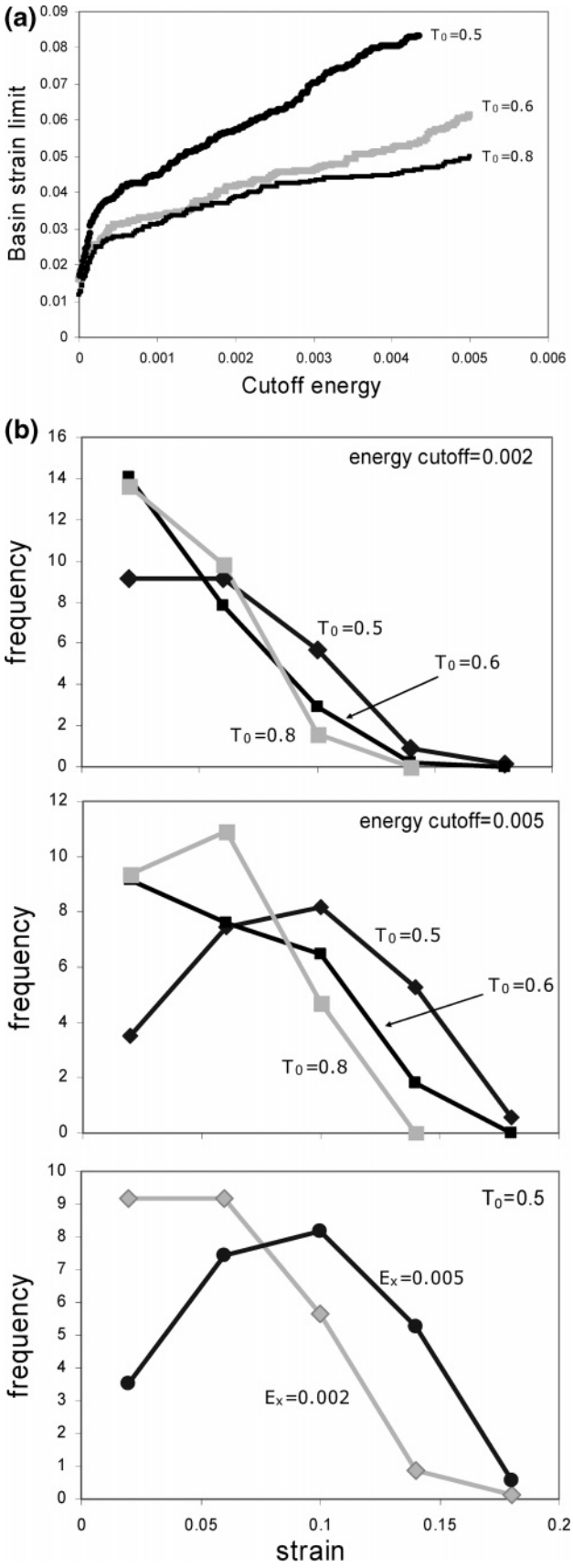

Figure 5. Value of the strain at the first energy drop greater than E_x, plotted against E_x. The values for T_0 denote the temperature of the liquids from which the glasses were formed. The plot represents an average over 112 different initial configurations for $T_0 = 0.6$ and $T_0 = 0.8$ and 172 initial configuratations for $T_0 = 0.5$. (b) Histogram of the frequency distribution of the strains over the same runs, for $E_x = 0.002$ and $E_x = 0.005$.

increases beyond on further straining. However, after the system exits a metabasin(at $\gamma = 0.085$), the stress decreases and does not subsequently return to as high a stress. Thus the higher the strain to which the system stays in its initial metabasin, the higher the stress becomes before decreasing. The relevance of metabasins rather than energy minima in regard to yielding is in line with the results of recent simulations that show that transitions between energy minima within a single megabasin do not lead to significant dynamical events.[14,15]

The effects of thermal history are now addressed. In Figure 5, the minimum strain at which an energy drop magnitude E_x or higher occurs is compared for the glasses quenched from $T = 0.8$, $T = 0.6$, and $T = 0.5$. The strain limits become significantly larger for glasses quenched from lower temperature liquids, especially at higher values of E_x; i.e., these strain limits increase as the temperature of the liquid from which the glass is formed decreases from $T = 0.8$ to $T = 0.6$ to $T = 0.5$. In terms of the energy landscape, this result shows that more highly annealed glasses require larger strains to force the system out of its initial metabasin. For this reason, as discussed in the previous paragraph, the more highly annealed glasses have a larger peak stress.

IV. Discussion

The present results elucidate the thermal history dependence of the peak stress in terms of the energy landscape. Annealing causes a glass to visit different regions of the energy landscape. It has been shown previously that annealing causes the system to visit regions of the energy landscape characterized by deeper (lower energy) energy minima. The present results show that the regions of the landscape obtained by annealing have another difference, in that they are characterized by metabasins that remain stable to larger strains. In other words, the metabasins that the system visits upon annealing have a greater stress-absorbing capacity. This explanation follows the suggestion by Varnik et al. that the increase of the peak stress with annealing time is related the system visiting deeper energy minima as the system anneals.[9]

The phenomenological shear transformation zone (STZ) theory has also been used to address the peak stress.[20] STZs are localized zones within the system that can undergo shear-induced transformations between two states that leads to plastic deformation. STZs are created (and annihilated) by either temperature or a driving force. In the STZ theory, the peak stress is shown to decrease with increasing concentration of STZs in the unstrained system. The thermal history dependence of the peak stress can then rationalized, if it is assumed that annealing reduces the concentration of STZs. The present ideas can be related to the STZ theory by noting that a metabasin *near the point of its strain-induced disappearance* corresponds to an STZ. We have shown here that in more highly annealed systems the metabasins are farther (on average) from their points of strain-induced disappearance; thus, if an STZ is associated with a metabasin near the point of its strain-induced disappearance, the present results show that the concentration of STZs is smaller in more highly annealed systems.

The ideas presented here also have relevance in regard to the strain−rate dependence of the peak stress (at finite temperature). As discussed above, the magnitude of the peak stress is related to the maximum strain for which the system remains in the initial metabasin. For lower strain rates, longer time is necessary for a given strain to be reached; thus the system has a greater chance of escaping the initial metabasin by thermally activated transitions. Thus, the peak stress would be expected to decrease with decreasing strain rate, which concurs with the results of experiments[3,5] and simulations.[9]

V. Conclusions

The inherent structure formalism developed by Stillinger and co-workers has been used to explain the origins of a wide range of phenomena occurring in liquids and glasses.[13] The present paper uses the inherent structure formalism to show how the thermal history affects the yielding of a glass. As a glass is annealed, the system moves to different regions of the energy landscape. In addition to having deeper energy minima, these regions of the energy landscape that the system moves to are characterized by metabasins that remain stable to higher values of strain. The higher the strain to which the system stays in its initial metabasin, the higher the stress becomes before yielding occurs. In this way, annealing leads to the increase of the peak stress.

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