Atomistic Simulation of Aging and Rejuvenation in Glasses

Marcel Utz,[1] Pablo G. Debenedetti,[1] and Frank H. Stillinger[2,3]

[1]*Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544*
[2]*Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544*
[3]*Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*

Slow structural relaxation ("aging") observed in many atomic, molecular, and polymeric glasses substantially alters their stress-strain relations and can produce a distinctive yield point. Using Monte Carlo simulation for a binary Lennard-Jones mixture, we have observed these phenomena and their cooling-rate dependences for the first time in an atomistic model system. We also observe that aging effects can be reversed by plastic deformation ("rejuvenation"), whereby the system is expelled from the vicinity of deep minima in its potential energy surface.

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Glasses are typically not in thermal equilibrium, due to the loss of ergodicity at the glass transition temperature T_g. As a result, slow relaxation processes are often observed to occur at finite temperatures $0 < T < T_g$. This phenomenon is usually referred to as structural relaxation for small molecule glasses. Struik [1] has introduced the term "physical aging" for polymer glasses, in order to distinguish structural relaxation from processes which involve chemical reactions, such as oxidative degradation. In the following, we will refer to the structural relaxation of all glasses as "physical aging."

Because of the gradual changes of material properties associated with physical aging, the phenomenon has great technological interest [1–8]. A strong connection has been demonstrated between physical aging and the mechanical behavior of polymer glasses [1,6,8]. The yield stress upon shear increases with aging time. After yielding, the stress rapidly drops to a value which is independent of aging time. From this fact, it has been concluded that plastic yielding erases the aging history of polymer glasses. This interpretation is corroborated by differential scanning calorimetry measurements [6]: Well annealed glasses typically exhibit a pronounced endothermal peak at the glass transition, which grows in magnitude with aging time. Plastic deformation gradually reduces this peak, eliminating it completely when the stress has decayed to its aging-independent large-strain value [6]. In spite of extensive experimental efforts, theoretical understanding of physical aging and its connection to plastic deformation has been limited up to now [8].

Here, we report results from Monte Carlo simulation of a binary mixture of Lennard-Jones atoms. We find that for this system aging during the limited time scale accessible to atomistic simulation [$O(1$ ns$)$], followed by plastic deformation at $T = 0$ (cf. Fig. 1) is sufficient to reproduce the experimental features of aging and mechanical rejuvenation. Consequently, rejuvenation effects are expected to be observable experimentally in atomic glasses only at very high deformation speeds and/or at very low deformation temperatures. For polymers, due to their much slower

relaxation dynamics, the necessary deformation speeds fall into a range that is readily accessible to experiments. To our knowledge, the present work is the first direct atomistic simulation of physical aging and its reversal by plastic deformation, and we believe that our results provide general insight applicable to a wide range of different glassy systems.

The model consists of an orthorhombic box, subject to periodic continuation conditions, containing $N = 4000$ atoms. The total potential energy of the system is given by the sum over all pair contributions

$$E_{ij} = 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] + c_{ij}r_{ij}^2 + d_{ij}$$

for $r_{ij} < r_c$, where r_{ij} is the distance between atoms i and j, and ϵ_{ij} and σ_{ij} are, respectively, the energy and length parameters. The constants c_{ij} and d_{ij} are chosen such that E_{ij} is continuously differentiable at the cutoff
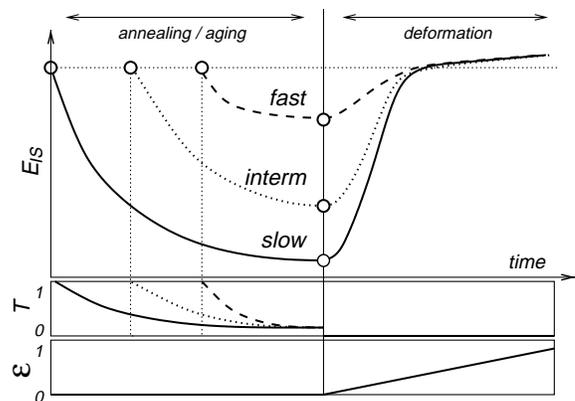
FIG. 1. Schematic representation of the thermomechanical protocol and of the effects of physical aging and plastic deformation on the energy of the inherent structure E_{IS}. First, the system is cooled at different rates from the liquid to $T = 0.1$, followed by energy minimization into amorphous structures with different potential energies. Then, the system is subjected to plastic deformation ε, erasing the effect of annealing on the inherent structure. This reversal of annealing/aging effects has been termed "mechanical rejuvenation" [1].

radius r_c [9]. Two different types of atoms were used in the present simulations, at a composition of $A_{80}B_{20}$, with parameters $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, and $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$ [10]. A cutoff radius of $r_c = 2.5$ was used in all cases. All quantities are in terms of reduced units [9] with respect to σ_{AA} and ϵ_{AA}.

The model studied here is closely related to the one introduced by Weber and Stillinger to simulate the glass former $Ni_{80}P_{20}$ [11]. Its relaxation dynamics in the liquid [10] and in the glassy state [12] have been studied extensively [13].

Here, initial structures have been prepared, starting from an fcc lattice, by equilibration at $T = 1.0$, using the Metropolis Monte Carlo method [9] for 10^4 cycles. All simulations were carried out at a constant number density of $\rho = 1.2$. After equilibration, the structures were cooled by lowering the temperature in steps of $T_{i+1}/T_i = 0.9$ down to $T = 0.12$. At each temperature, the spatial step length was adjusted to give an acceptance ratio between 40% and 60%. Finally, the potential energy of the structures was minimized at constant volume, generating inherent structures (local potential energy minima [14]) by the conjugate-gradient method [15]. Slowly, moderately, and rapidly cooled samples were prepared by holding the systems at each intermediate temperature along the cooling path for 8000, 2000, and 500 Monte Carlo cycles, respectively. The mean square displacement per particle caused by these annealing protocols was 1.99, 0.64, and 0.37, respectively (in units of σ_{AA}^2).

Plastic deformation was imposed on the system by changing the box dimensions by small amounts, while keeping the fractional coordinates of the particles fixed, and reminimizing the potential energy with respect to the fractional coordinates after each deformation step [16–20]. The intermittent minimization steps essentially couple the system to a heat bath of infinite capacity at $T = 0$, completely precluding structural relaxation during deformation. The results of such simulations are therefore comparable to experiments carried out at strain rates $\dot{\varepsilon} \gg \tau^{-1}$, where τ is the structural relaxation time.

A volume-conserving, plane strain deformation was used, with a single step deformation tensor $d\varepsilon_{11} = 0.005$, $d\varepsilon_{22} = -0.005$, and $d\varepsilon_{33} = d\varepsilon_{12} = d\varepsilon_{13} = d\varepsilon_{23} = 0$, where strain is defined as $\varepsilon = \ln(a_t/a_0)$, with a_t the sample dimension at time t, and a_0 the same dimension in the reference state. After each deformation/minimization step, the potential energy of the system, the stress tensor (obtained from the virial), and the coordinates of all atoms were stored.

Similar to the behavior reported for other systems [16–19], individual simulation runs are characterized by periods of continuous elastic loading with only slight atomic movements, separated by occasional relaxation events with pronounced stress and potential energy drops. Results from five different initial structures have been averaged for each cooling rate to produce the
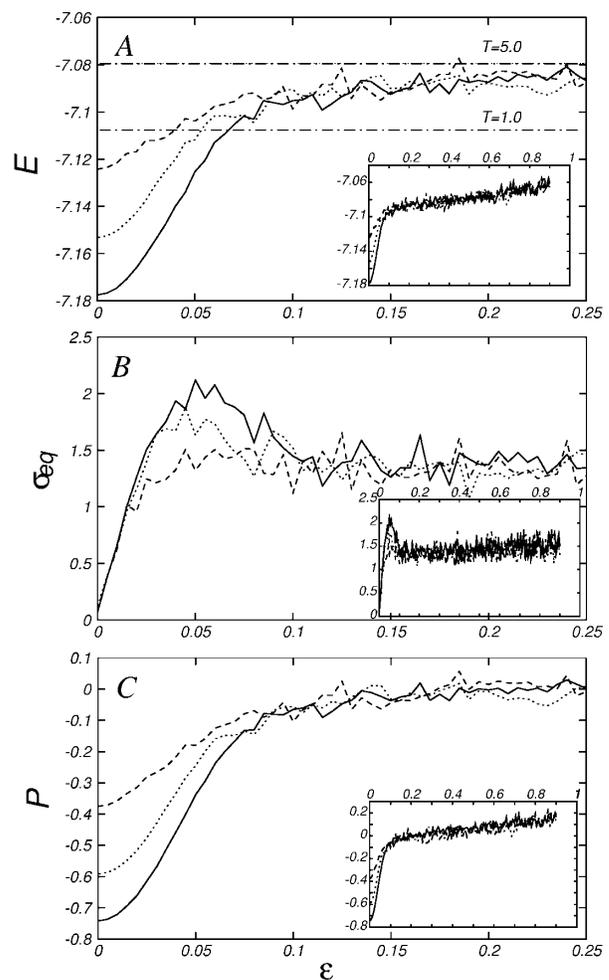
FIG. 2. Potential energy per particle (A), von Mises equivalent stress (B), and pressure (C) as a function of strain. All quantities refer to inherent structures. Each trace represents the superimposed data from five simulation runs with different starting structures. Solid line: slow; dotted line: intermediate; dashed line: fast cooling rate. The dash-dotted lines in panel A represent the mean inherent structure energies obtained from the liquid equilibrated at $T = 1.0$ and $T = 5.0$, as indicated. The insets show the behavior at large strains.

data shown in Fig. 2. The quantities reported (potential energy, von Mises stress, pressure) correspond to inherent structures. The starting potential energy at $\varepsilon = 0$ is substantially lower for the more slowly cooled structures (Fig. 2A). Annealing also leads to more negative pressure in the structures, as shown in Fig. 2C. The von Mises equivalent stress σ_{eq}, shown in Fig. 2B, is defined as the second invariant of the stress tensor $\boldsymbol{\sigma}$: $\sigma_{\text{eq}} = [3/2 \, \text{Tr}(\boldsymbol{\sigma} + P\mathbf{I})^2]^{\frac{1}{2}}$, where $\mathbf{I}$ is the identity tensor and $P = -1/3 \, \text{Tr}(\boldsymbol{\sigma})$ denotes the system pressure.

At small strains, deformation leads to a linear increase in σ_{eq}, and to a corresponding harmonic response in the potential energy. This initial stage ends at $\varepsilon \approx 0.02$, and plastic yield sets in. After the yield point, the von Mises equivalent stress no longer increases. Rather, in the case of the slow and moderate cooling rates, the stress drops

with increasing strain after having reached a maximum at the yield point. This strain softening effect has been observed experimentally in polymer [21] and metallic glasses [22] and represents a major technological concern since it leads to strain concentration and consequently to brittle failure. To our knowledge, this work represents its first direct atomistic simulation. Whereas the strain softening effect is very pronounced in the case of the slowly cooled system, it is less apparent for the intermediate cooling rate and gets almost lost in the noise for the rapidly cooled sample. Indeed, slow annealing leads to a 50% increase in yield stress over the rapidly cooled system.

Beyond deformations of $\varepsilon = 0.1$, the von Mises equivalent stress reaches a constant value of $\sigma_{eq} \approx 1.4$, at which it remains up to very large deformations. At the yield point, the potential energy reaches the value corresponding to the inherent structure obtained from the melt at $T = 1.0$ (cf. Fig. 2A), and then increases slightly with strain, approaching inherent structure energies typical for high-temperature melts. It is important to note that neither the potential energy nor the stress tensor depend on the predeformation history of the system in the high-strain regime. Hence, the system loses memory of its aging state upon plastic yielding [1,6].

The normal stresses that result from plane strain deformation, as represented by the pressure in Fig. 2C, are about 1 order of magnitude smaller than the shear stresses (Fig. 2B). Interestingly, the pressure response closely resembles that of the potential energy, suggesting that the observed changes in energy are mainly due to local compression and expansion of rearranging clusters of atoms as the shear deformation proceeds.

Unlike the present simulations, experiments are usually carried out at constant pressure, rather than constant volume. Substantial density reductions have been observed experimentally in shear bands of metallic glasses [21], in accord with the increase in pressure observed in the present model. Based on experimental evidence from such dilatation measurements [1,21,23] and from positron annihilation experiments [7], physical aging and its reversal by plastic deformation have been explained by the gradual disappearance of free volume in the aging process and its irreversible regeneration at the yield point. While the present results do show a pronounced decrease in system pressure with aging which is erased by plastic yielding, the generation of net free volume and a corresponding reduction in density, absent from our simulations by construction, do not seem to be a prerequisite for aging and mechanical rejuvenation effects.

Of the three pair correlation functions, $g_{AA}(r)$, $g_{AB}(r)$, and $g_{BB}(r)$, the latter is the most sensitive to temperature. Since $\epsilon_{BB} < \epsilon_{AA} < \epsilon_{AB}$, nearest-neighbor contacts between B atoms are progressively avoided by the system at lower temperature [10]. Comparing pair correlation functions for structures cooled at different rates, we found no significant dependence on the cooling rate, ex-

cept for $g_{BB}(r)$, which is shown in Fig. 3 as a function of temperature between $T = 0.9$ and $T = 0.1$ for the fast and the slow cooling rates. The curves have been displaced vertically for clarity. In addition to the structure enhancing effect that lowering the temperature usually has on pair correlation functions, the nearest-neighbor peak decreases, accompanied by a corresponding increase in the second-nearest-neighbor peak. While this reduction of close contacts between B atoms is quite significant in the slow cooling case, it is much less pronounced in the fast cooling regime (dashed line in Fig. 3).

The effect of plastic deformation on $g_{BB}(r)$ is shown in Fig. 4. In the early stages of deformation, the nearest-neighbor peak becomes very pronounced, reaching a height of 1.4. Above strains of $\varepsilon = 0.25$, $g_{BB}(r)$ no longer depends on strain. Differences due to the annealing state of the initial structure vanish at the yield point, around $\varepsilon = 0.1$. The large-strain limiting $g_{BB}(r)$ resembles the one obtained from minimizing, without any annealing process, the potential energy of a structure thermalized at $T = 1.31$, as reported by Weber and Stillinger [11]. Again, this finding confirms that the structural effects of physical aging are erased by plastic deformation.

We have successfully simulated the response of binary Lennard-Jones glasses in different stages of aging on large-strain plastic deformation. Our results confirm the erasure of the aging history by plastic deformation, also known as "rejuvenation." Slow annealing was found to lower the potential energy by replacing energetically unfavorable contacts by more advantageous ones. Plastic yielding reverses these changes, taking the system into a higher energy state which is independent of its aging state. The pronounced increase of the yield stress and the increasing magnitude of the strain-softening effect, which has been established experimentally as a typical feature of the physical aging/rejuvenation phenomenon [1,6,21], is reproduced by our simulations.

Finally, the present results suggest a rather simple explanation of aging and rejuvenation, based on the potential
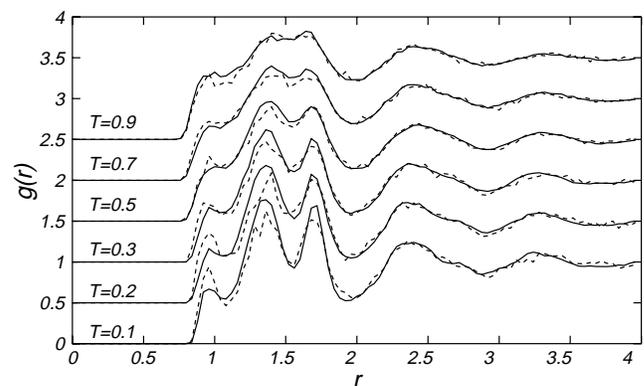
FIG. 3. Inherent structure pair correlation function of B-B atoms $g_{BB}(r)$ as a function of temperature, for slow (solid line) and fast (dashed line) cooling rates.
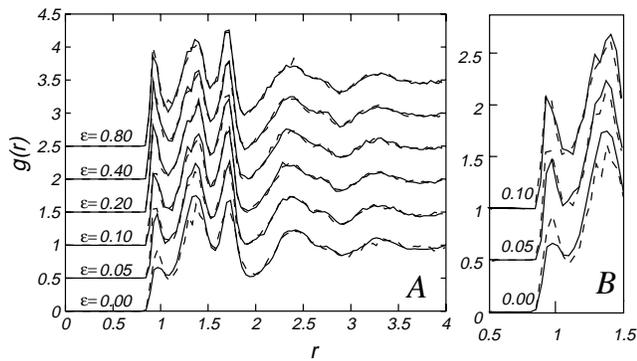
FIG. 4. A: Inherent structure pair correlation function of *B*-*B* atoms $g_{BB}(r)$ as a function of deformation, for slow (solid line) and fast cooling (dashed line) rates. B: enlarged section around the nearest-neighbor peak of $g_{BB}(r)$.

energy landscape viewpoint [24]. In order for a system to exhibit physical aging the distribution of minima on its multidimensional potential energy surface must have a low-abundance, low-energy tail. In such a situation, slow relaxation processes can take the system from one of the abundant high-energy states into deeper energy minima, leading to a slow loss of energy and entropy. It has been shown that the barrier between neighboring minima on the potential energy surface can be caused to vanish by strain [17]. If a system is initially in one of the low-energy minima due to physical aging, it is unlikely that another low-energy minimum is close. Therefore, in the vast majority of cases, plastic deformation must take the system into high-energy regions of the potential energy landscape. This is corroborated by the fact that the potential energy at high strain approaches the high-temperature limit of the inherent structure energy (cf. Fig. 2A).

It is expected that the potential energy of a system will cease to depend on the initial aging stage once all its volume elements have taken part in at least one plastic relaxation event. This point corresponds to the transition from elastic behavior, where $E(\varepsilon)$ is a harmonic function, to plastic flow, where E depends only weakly on ε. In the simulations reported here, this transition occurs at $\varepsilon \approx 0.1$. Since, at $T = 0$, the stress tensor is given by the derivative of the potential energy with respect to strain, it is not surprising that the lower initial energy of an aged system gives rise to a higher maximum stress before the elastic to plastic transition occurs.

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