Shear-induced overaging in a polymer glass

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A phenomenon recently coined as “overaging” implies a slowdown in the collective (slow) relaxation modes of a glass when a transient shear strain is imposed. We are able to reproduce this behavior in simulations of a supercooled polymer melt by imposing instantaneous shear deformations. The increases in relaxation times \( \Delta \tau_{1/2} \) rise rapidly with deformation, becoming exponential in the plastic regime. This “overaging” is distinct from standard aging. We find increases in pressure, bond-orientational order and in the average energy of the inherent structures \( < e_{IS} > \) of the system, all dependent on the size of the deformation. The observed change in behavior from elastic to plastic deformation suggests a link to the physics of the “jammed state”.

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In recent years, there has been considerable progress geared towards understanding how glasses respond to shear. Phenomena such as shear thinning and “rejuvenation” are common when shear flow is imposed. Unlike crystals, glasses “age,” meaning that their state depends on their history \[1, 2, 3\]. When a glass falls out of equilibrium, it evolves over very long timescales. It has been found that relaxation in supercooled liquids often depends on cooperative and spatially correlated motion, meaning the dynamics are heterogeneous \[4\]. Much research has also been devoted to developing a wide-reaching, coherent theory which can explain the jammed state \[5, 6\]. It has been found that such a state is characterized by the appearance of a yield shear stress and can be achieved by changing the load, density or temperature of a system. In addition, it has been found that the concept of random close packing is somewhat ill-defined and in the so-called jammed state, one can increase the degree packing at the expense of randomness, or vice-versa, thus allowing for a variety of possible jammed configurations \[7, 8\].

The concept of jammed state also provides insight as to the effect of stress on a glass. When imposing a continuous shear strain, one can rejuvenate the glass, effectively wiping out the memory of the system \[9, 10\]. In this sense, the glassy state is particularly sensitive to shear. In 2002, Viasnoff and Lequeux published experimental results for colloidal suspensions, showing that after imposing transient shear, one obtains simultaneous overaging and rejuvenation, since the relaxation times are altered in a non-trivial manner \[11\]. In this case, overaging means that relaxation times of the system become longer more quickly than is normally the case. Their results are qualitatively explained through Bouchaud’s Trap Model and the related Soft Glassy Rheology (SGR) model \[10, 12\]. In essence, this phenomenological approach relies on the distribution of relaxation times \( \tau \) (or equivalently, of potential wells of different depths) which can be over- or underpopulated when applying a transient shear or a temperature step. Using a similar perspective, Lacks and Osborne have argued, in a zero temperature study, that the so-called “overaging” is different in nature from ordinary aging, in that the minima visited can be similar in both cases, but not identical \[13\]. It has also become clear that it is difficult to induce decreases in energy by strain in well-annealed glasses, since the disappearance of energy minima does not usually lead the system to a lower potential well \[13, 14, 21\].

In this letter, we report on some of the characteristics of this overaging from a more general perspective. We find that overaging is present and easily observed in simulations of a common glass-forming polymer model simply by imposing relatively small, instantaneous shear deformations. After a certain waiting time \( t_w \), one can observe an unambiguous slowing-down in the decorrelation of particle positions, just as was seen experimentally \[11\]. We use the term “overaging” to refer only to the longer relaxation times, not to any decrease in energy of the system (as in the case of ordinary aging). We have identified two distinct regimes of overaging, corresponding to elastic and plastic deformations. There is a rapid increase in relaxation times \( \Delta \tau_{1/2}(\epsilon) \), which contrasts with the associated increase in the average energy of the internal structure of the system \( < e_{IS} > \), as introduced by Stillinger and Weber \[15\]. We concur with the recent study, finding that overaging is quite distinct from aging in its regular sense \[14\]. In our case, we show that it is possible to obtain longer relaxation times without the system’s slow evolution towards more energetically favorable configurations. In addition, the yield shear strain of the material plays a key role in this phenomenon. Finally, we resolve an increase in order in
the system, primarily associated with the elastic energy stored in the system.

The simulations are performed by molecular dynamics, using the velocity Verlet algorithm, combined with velocity-rescaling to achieve constant temperature. We adopt the bead-spring model to simulate the polymeric melt, each chain consisting of 10 monomers linked together through a finitely-extensible nonlinear elastic (FENE) potential of the form

$$U_{\text{FENE}}(r_{ij}) = 0.5kR_0^2\log\left[1 - \left(\frac{r_{ij}}{R_0}\right)^2\right],$$

where $k = 30\varepsilon_{LJ}/\sigma^2$ and $R_0 = 1.5\sigma$. In addition, all particles interact via a truncated and shifted Lennard-Jones (LJ) potential,

$$U_{LJ}(r_{ij}) = 4\varepsilon_{LJ}\left[(\sigma/\sigma_{ij})^12 - (\sigma/\sigma_{ij})^6\right]$$

with the cutoff radius set at 2.5$\sigma$. For simplicity, all data are presented in reduced LJ units based on the mass $m$, the radius of each particle $\sigma$ and the LJ energy scale $\varepsilon_{LJ}$. Each MD step corresponds to 0.005 reduced time units. The samples have 105 chains, so a total of $N = 1050$ particles, and periodic boundary conditions (PBCs) are applied in all directions. We use up to 40 independent samples in order to average the results. The combination of the FENE and LJ potentials causes two competing length scales, thus inhibiting crystallization and producing a typical fragile glass. In a previous paper, we have identified a glass transition (GT) based on the simulation timescales used, as well as a rigidity transition (RT) located just below the GT. We also observed that the shear modulus $\mu$, computed via instantaneous deformations, is highly dependent on the size of the shear deformation $\epsilon$. Specifically, larger values of $\epsilon$ can be characterized as irreversible or plastic deformations which alter the structure (and energy landscape) of the system. In such cases, the residual stress is reduced leading to smaller $\mu$ values. In contrast to the recent work of Lacks and Osborne, we have a well-annealed system, as well as a non-zero temperature. This means that the system has the ability to explore a range of energy wells (as opposed to a single one) through thermal activation.

All samples are set at $T = 0.44$ and are initially at identical pressures in the neighborhood of 0.57 in the rigid phase (near the onset of rigidity which occurs below the GT). They are created via a slow compression of the simulation box, followed by a damping-forced algorithm to realize the NPT ensemble. By definition, these systems are out of equilibrium, but we start with samples that have been allowed to evolve considerably and see no evidence of aging on the timescales of our computer experiments. Starting with a cube of side $L$, an affine shear deformation $\varepsilon_{xy}$ is applied in the $x$ direction, in a plane with its normal along the $y$ direction. An atom initially in position $(x, y, z)$ is displaced to $(x + \varepsilon_{xy}y, y, z)$. The boundaries of the simulation box consequently are shifted for $x_{\text{min}}$ from 0 to $\varepsilon_{xy}y$, and for $x_{\text{max}}$ from $L$ to $\varepsilon_{xy}y + L$. For a given system, the shearing is repeated in the five other directions, substituting $xy$ by $yz, -xy$, etc. Individual samples lack symmetry and therefore the various deformations will not usually give the same stress components. Once the system has been allowed to relax for a fairly long time $t_w$, this process can be repeated on the previously deformed sample, either deforming it further or returning it to its original shape. Both methods yield identical increases in relaxation times.

In order to monitor the relaxation in the system, we compute the two-time, “self” part of the incoherent scattering function,

$$C_q(t_w + \tau, t_w) = \frac{1}{N} \sum_{j=1}^{N} \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t_w + \tau) - \mathbf{r}_j(t_w))]$$

where the wavevector $\mathbf{q}$ is close to the first peak in the structure factor $S(\mathbf{q})$, $t_w$ is the time elapsed since the deformation. This “two-time” correlation function has been proven useful in investigating aging, because of the different timescales in relaxation. We use $\tau_{1/2}$, the time it takes for $C_q$ to decrease to 0.5, in order to gauge the local decorrelation in the system. The effect of the deformations is seen in Fig. As was found in Ref. for large deformations ($\epsilon \gtrsim 0.1$), there is an initial combination of overaging and rejuvenation, as relaxation times corresponding to both high and low-energy states are overpopulated. Eventually, the initial shape of the function is recovered since only the slow relaxations remain overpopulated. Interestingly, one can repeat this process a number of times, achieving the same results after every applied deformation. Our focus is not on the
FIG. 2: Energy of the inherent structure (IS) of the system, calculated for various $\epsilon$ immediately after (squares) and $t_w = 10^3$ (circles) after the deformation. Note that, for large (plastic) deformations, the inherent structure of the system is able to evolve.

FIG. 3: Incremental relaxation times after $t_w = 10^3$ for various $\epsilon$. The line is a guide to the eye and shows an exponential dependence on $\epsilon$ for plastic deformations.

FIG. 4: Evolution of the local bond-orientational order parameter $Q_{6,\text{local}}$ at $t_w = 10^3$ after the deformation. While the statistics are poor, there is a clear increase in $Q_{6,\text{local}}$, at least for $\epsilon \lesssim 0.1$. Data based on 40 samples deformed twice, and treating each deformation as independent.

transient effects, but rather on the behavior after a relatively long $t_w$. As seen in the inset of Fig. 1, small shear also causes overaging but is the result of a simpler physical mechanism.

We start from a well-relaxed system. The strain increases the energy and appears to raise the energy barriers between available energy wells, as evidenced by the increased decorrelation times. For small shear as seen in Fig. 2, there is no major configurational change. The difference between the $<e_{\text{IS}}>$ immediately after and a relatively long time after a given deformation is minimal. This difference increases rapidly as we enter the plastic regime where a large part of the strain energy is relaxed by the configurational changes. Plastic shear maps the system onto a very different energy well, from which the system can escape fairly easily. This is the source of the initial combination of overaging and rejuvenation observed in Fig. 1 and in Ref. [11]. After a reasonable waiting time ($t_w = 10^3$), there is a net increase in $\tau_{1/2}$. The characteristic incremental relaxation time $\Delta \tau_{1/2}(\epsilon)$ is shown for various shear deformations $\epsilon$ in Fig. 3, after subtracting the reference relaxation time $\tau_{1/2}(\epsilon = 0)$, which is a constant on our simulation timescales. In the plastic regime, there is a clear exponential behavior.

To get some inkling of what may be causing the overaging we look at the structural changes occurring. When applying a relatively large deformation, the chains are initially stretched from their equilibrium lengths. But after letting the system relax for approximately $10^3$ time units, the radial distribution function and the average radius of gyration of the chains return to their “undeformed” values. A more sensitive measure of structural change is the local bond-orientational order parameter $Q_{6,\text{local}}$ which uses higher-order spherical harmonics and is defined as [7, 8, 22]

$$Q_{6,\text{local}} \equiv \sum_{j=1}^{N} \frac{4\pi}{13} \sum_{m=-6}^{6} \left| \frac{1}{n_b} \sum_{i=1}^{n_i} Y_{6m}(\theta_i, \phi_i) \right|^2 \right)^{1/2}$$

Indeed, $Q_{6,\text{local}}$ increases slightly as we increase $\epsilon$, while $\epsilon \lesssim 0.1$, followed by a plateau or slight decrease (see Fig. 4), noting that subsequent deformations do not have a large effect on the order parameter. This ordering is most apparent for small shear, indicating that it is directly related to the elastic energy stored in the system. Increased order is usually associated with a lower energy
state. In our polymeric system, however, the potential energy is dominated by the stiff intra-chain bonds. The increased order is at the expense of the potential energy, i.e. that the strain “jams” the system; and in the case of plastic shear, reorganizes the potential wells. The dynamics are also affected. Once again, the two regimes of shear strain are very distinct. Small strains have little or no effect, while large strains reduce the “heterogeneity” in the system (i.e.; there are less deviations from a Gaussian distribution of particle displacements [21]) and more particles become “mobile” [24]. This, in turn, causes a decrease in the shear modulus \( \mu \) of the system, i.e. shear softening [17]. Increased mobility is not incompatible with increased relaxation time. Average waiting times are dominated by the contributions from the largest \( \tau_{1/2} \) of the “metabasins” whereas the mobility is controlled only by the most mobile particles [24, 25].

An interesting aspect of this study is the similarity with “tapping” experiments on granular matter [28] and glassy systems [27], which can produce jammed structures. Common features in the structure and force distributions of granular and “glassy” jamming have also recently become apparent [28]. Just as tapping granular matter can both increase or decrease the density, transient or instantaneous shear can produce a variety of effects on the glassy system, while continuous shear always “unjams” or rejuvenates it. In conclusion, this is not aging in the conventional sense (the system has not aged more quickly); \( < \epsilon_J > \) does not decrease and neither does the mobility. The very similar behavior observed in colloids [10, 11], the present polymer glass [17], and binary Lennard-Jones mixtures [21] suggests a universal behavior and unique origin of the overaging, observed so far in two of these systems. Shear produces changes in the microstructure which lead to increased relaxation times. This may be put to profitable use in some applications. It appears also to be a way to increase ordering. Finally, repeated applications of the deformations yield increasingly larger relaxation times, and may generate a glassy state of practical interest, whose properties are yet to be fully understood.

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