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 increase in relaxation times $\Delta\tau_{1/2}$ rises rapidly with deformation, becoming exponential in the plastic regime, and is accompanied by significant changes in the distribution of these relaxation times throughout the system. This overaging is distinct from standard aging. We find increases in pressure, bond-orientational order, and in the average energy of the inherent structures ($\langle e_{\rm IS}\rangle$) 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, considerable effort was 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]. When a glass falls out of equilibrium, it evolves over very long time scales. It has been found that relaxation in supercooled liquids often depends on cooperative and spatially correlated motion, meaning the dynamics are heterogeneous [3]. Much research has also been devoted to developing a wide-reaching, coherent theory which can explain the jammed state [4,5]. 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 of packing at the expense of randomness, or vice versa, thus allowing for a variety of possible jammed configurations [6,7].

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 [8,9]. In this sense, the glassy state is particularly sensitive to shearing. 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 nontrivial manner [10]. 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 model [9,11]. In essence, this phenomenological approach relies on the distribution of relaxation times τ (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 [12]. 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 [12–14].

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 [10]. 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, underlining the key role played by the yield shear strain in this phenomenon. There is a rapid increase in relaxation times $\tau_{1/2}(\epsilon)$, which contrasts with the associated increase in the average energy of the inherent structures of the system ($\langle e_{\rm IS}\rangle$), as introduced by Stillinger and Weber [15]. In our case, we do not observe an evolution towards lower energy configurations. Finally, we resolve an increase in order, associated with elastic deformations, and, in the plastic regime, increased homogeneity in the relaxation dynamics.

The simulations are performed by molecular dynamics (MD), using the velocity Verlet algorithm, combined with velocity rescaling to achieve constant temperature [16]. We adopt the bead-spring model to simulate the polymer melt [17], each chain consisting of 10 monomers linked together through a finitely extensible nonlinear elastic (FENE) potential of the form $U_{\rm FENE}(r_{ij}) = 0.5kR_0^2\log[1-(r_{ij}/R_0)^2]$, where $k = 30\varepsilon_{\rm LJ}/\sigma^2$ and $R_0 = 1.5\sigma$. In addition, all particles interact via a truncated and shifted Lennard-Jones (LJ) potential, $U_{\mathrm{LJ}}(r_{ij}) = 4\varepsilon_{\mathrm{LJ}}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}]$ with the cutoff radius set at 2.5σ. For simplicity, all data are presented in reduced LJ units based on the mass m, the radius of each particle σ, and the LJ energy scale $\varepsilon_{\mathrm{LJ}}$. 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 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 [18–20]. In a previous paper, we have identified a glass transition (GT) based on the simulation time scales used, as well as a rigidity transition located just below the GT [18]. We also observed that the shear modulus μ, computed via instantaneous deformations, decreases with the size of the shear deformation ϵ. Specifically, larger values of ϵ partially relax the system through irreversible or plastic deformations. In contrast to the recent work of Lacks and Osborne [12], we have a well-annealed system, as well as a nonzero 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, calculated using the diagonal elements of the microscopic stress tensor, in the neighborhood of 0.57 in the rigid phase (near the onset of rigidity which occurs below the GT [18]). More precisely, we are dealing with what is called a "collectively jammed" system (in the case of hard spheres [21]), since all groups of particles cannot freely move (creating a nonzero shear modulus). However, we must stress that it is difficult to precisely define the degree of jamming in soft-sphere systems due to the lack of any nonoverlap conditions. The samples are created via a slow compression of the simulation box, followed by a damped-force algorithm such that all are at identical imposed pressures and temperatures [16]. The system is then allowed to evolve at constant volume and temperature. Deformations are applied to systems that no longer show evidence of aging on the time scales of our computer experiments. Starting with a cube of side L, an affine shear deformation ε_{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 $(x + \epsilon_{xy}y, y, z)$. The boundaries of the simulation box consequently are shifted for $x_{\min}$ from 0 to $\epsilon_{xy}y$ and for $x_{\max}$ from L to $\epsilon_{xy}y + L$. 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,

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

where the wave vector $\mathbf{q}$ is close to the first peak in the structure factor $S(\mathbf{q})$, and 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 time scales in relaxation [2]. We use $\tau_{1/2}$, the time it takes for $C_{\mathbf{q}}$ to decrease to 0.5, in order to gauge the local decorrelation in the system. The effect of the deformations is seen in Fig. 1. As was found in Ref. [10], for large deformations ($\epsilon \gtrsim 0.1$), immediately after the deformation, the transient effects show 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. These are the curves of interest to us. As seen in the inset in Fig. 1, a 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 $\langle e_{\mathrm{IS}}\rangle$ immediately after and a rela-

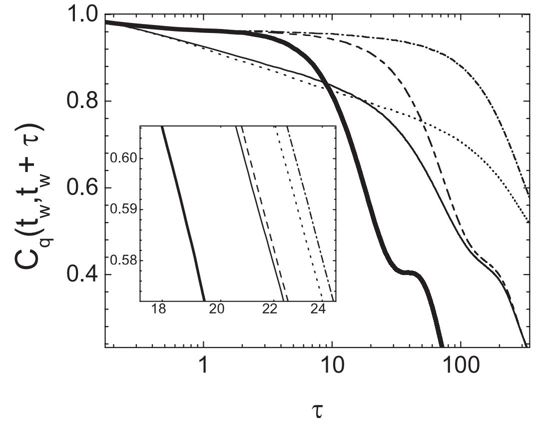

FIG. 1. Correlation function of Eq. (1) showing the effects of repeated shear on the slow relaxation modes of the system, compared with the reference (unsheared) case (bold line). For each deformation, there are two sets of correlation functions, one taken immediately after the deformation ($t_w = 0$) and the other ($t_w = 10^3$) time units later. The following legends apply to both the inset (a small shear: $\epsilon = 0.05$) and main frame (a large shear: $\epsilon = 0.2$). First deformation: solid ($t_w = 0$) and dashed ($t_w = 10^3$) lines. Second deformation: dotted ($t_w = 0$) and dashed-dotted ($t_w = 10^3$) lines. For large shear, note the initial combination of rejuvenation and overaging, settling into pure overaging. For small shear, only a small overaging is observed.

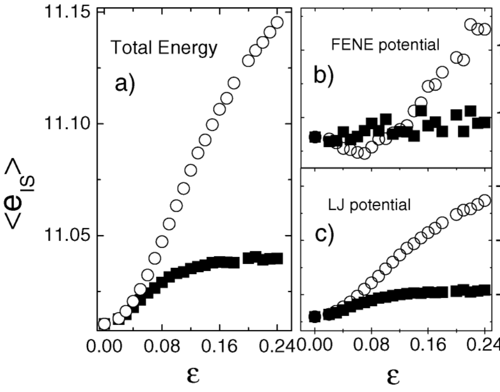

FIG. 2. Average energy of the inherent structures (IS) of the system, calculated for various ϵ immediately after (open circles) and $t_w = 10^3$ (squares) after the deformation. (a) Total energy; (b) FENE (bond) energy; (c) LJ energy. Changes in $\langle e_{\rm IS}\rangle$ are dominated by the LJ part. Note that, for large (plastic) deformations, the inherent structure of the system is able to evolve after the shear deformations.

tively 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. [10]. After a reasonable waiting time ($t_w = 10^3$), there is a net increase in $\tau_{1/2}$, as shown in Fig. 3. The increase in relaxation time $\Delta\tau_{1/2}(\epsilon)$ shows a clear exponential behavior, in the plastic regime.

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 $Q_{6,\rm local}$:

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

where Y_{6m} are spherical harmonics, n_b^j the number of nearest neighbors of particle j, and θ_i and ϕ_i, the polar and azimuthal angles, respectively, of nearest neighbor bond i as seen by particle j. This parameter is maximum for an fcc packing [6,7,22]. Since we are essentially dealing with a LJ system where the chains (FENE potential) inhibit the formation of an fcc structure, $Q_{6,\rm local}$ is a measure of local evolution towards fcc packing.

Indeed, $Q_{6,\rm local}$ increases slightly as we increase ϵ in the elastic regime ($\epsilon \lesssim 0.1$), 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 intrachain bonds, whose lengths vary little at $t_w = 10^3$ after the deformation (Fig. 2). The rearrangement affects primarily the long-range LJ potential. The increased order is at the expense of the potential energy and leads to a pressure increase similar to the internal energy increase after relaxation in Fig. 2, reaching a plateau for plastic deformations. This behavior has also been observed in LJ binary mixtures [14]. The plateau is characteristic of a yield strain. The increased $\tau_{1/2}$ is an indication that there are larger energy barriers between configurations. For elastic strains, the system "jams"; in the case of plastic shear, the potential

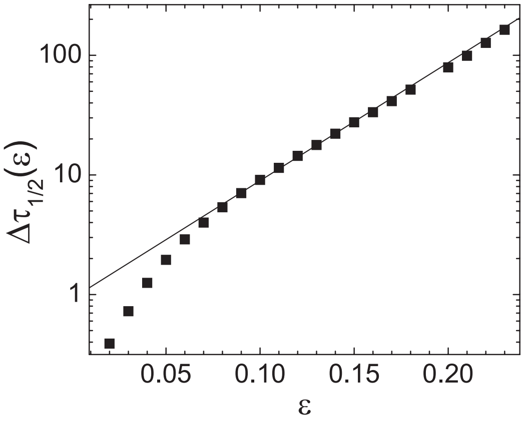

FIG. 3. Incremental relaxation times after $t_w = 10^3$ for various ϵ. The line is a guide to the eye and shows an exponential dependence on ϵ for plastic deformations.

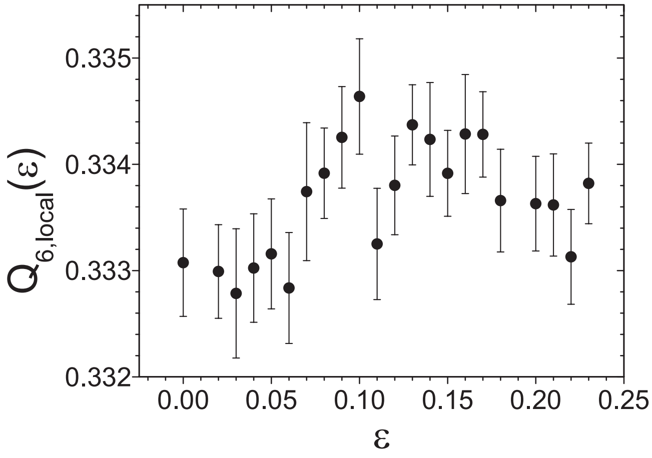

FIG. 4. Evolution of the local bond-orientational order parameter $Q_{6,\rm local}$ at $t_w = 10^3$ after the deformation. While the statistics are poor, there is a clear increase in $Q_{6,\rm local}$, at least for $\epsilon \lesssim 0.1$. Data based on 40 samples deformed twice and treating each deformation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

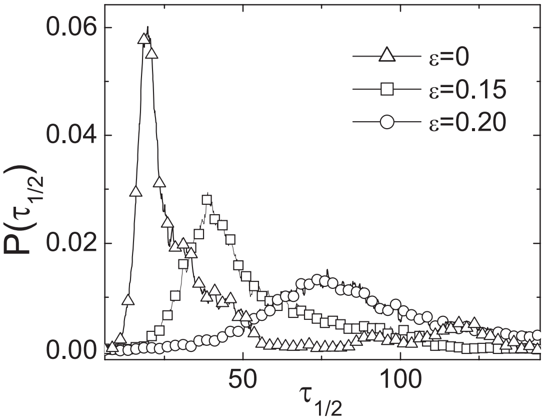

FIG. 5. Changes in the distribution of the relaxation times within the system, found by computing $\tau_{1/2}(\epsilon)$ for each particle in each sample at $t_w = 10^3$ after the deformation.

wells are reorganized. The dynamics are also affected. Small strains have little or no effect, while large strains reduce the "heterogeneity" in the system, as seen in the distribution of characteristic relaxation times which shifts to longer times and resembles a broad Gaussian (Fig. 5). Other effects observed are a decrease in the shear modulus [18] and an increase in the mobility of the particles [23]. The latter is an indication of displacements on longer time scales and likely reflects intermittent collective motion in the sample [24].

An interesting aspect of this study is the similarity with "tapping" experiments on granular matter [25] and glassy systems [26], which can produce jammed structures. Common features in the structure and force distributions of granular and "glassy" jamming have also recently become apparent [27]. 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); $\langle e_{\rm IS} \rangle$ does not decrease and neither does the mobility. The very similar behavior observed in colloids [9,10], the present polymer glass [18], and binary Lennard-Jones mixtures [14] suggests a universal behavior and unique origin of the overaging, observed so far in two of these systems. Shear can also produce 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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