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Microstructure and dynamics of a polymer glass subjected to instantaneous shear strain

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Abstract

The application of instantaneous shear deformations to a polymer glass modifies the energy landscape of the glass in non-trivial ways. Using molecular dynamics simulations on a freely jointed chain model, we investigate the effect of the strain on the dynamical heterogeneities in the glassy system. The resulting behaviour can be separated into two regimes: elastic for small shear deformations, and plastic for large deformations. Dynamic heterogeneity in the system tends to diminish with deformation. This increased homogenization can be seen, for instance, through changes in the distribution of particle mobilities, both in space and in time, as the glass relaxes following an affine deformation. We are able to directly correlate changes in the overall diffusion in the system with local configurations of mobile and immobile particles. The effect of the deformation on the ageing process is briefly addressed, as we present some new insight into the local dynamics of the polymer chains.

1. Introduction

Recent work has yielded a better understanding of the glass transition (see papers in this special issue), but its true nature remains elusive, mainly because it is a transition associated with a critical slowing down of the system. The dynamical and structural properties of glassy and more generally, 'jammed' materials, are not well-understood. It is only recently that the importance of dynamical heterogeneities near the glass transition has become apparent [1–5]. In this brief paper, we propose a new approach, based on instantaneous shear deformations of a glass, geared towards understanding both the local structure of the glass and its overall dynamical behaviour as it undergoes shear. Our simulations enable us to use these deformations, which are different from more common rheometry-based work and can be either plastic (irreversible) or elastic, to investigate subtle changes in microstructure which underlie the macroscopic stability or rigidity of the glass. Observing these effects would generally require excessively long computational times when using unsheared systems (relying on thermal fluctuations, for example, to observe the relaxation dynamics). Our preliminary results suggest that deformations reveal the importance of local rearrangements in

the rigidity of a glassy polymer melt and can alter its ageing process in a non-trivial manner. Most importantly, the strain leads to a reduction in the dynamical heterogeneity naturally present in a system just below the glass transition.

2. Method

In previous work, we have used a bead-spring model of 105 polymers containing 10 'beads' each, with periodic boundary conditions (PBC), in order to reproduce a dense polymer melt in the canonical (NVT) ensemble [6–8]. The competing length scales induced by the FENE (finitely extensible non-linear elastic) potential between neighbours along a given chain, combined with a Lennard-Jones (LJ) potential between all monomers, impede any nucleation in the system, thus allowing a readily observable glass transition (GT) to occur. We integrate the speeds and positions of the particles using a standard Verlet-velocity algorithm, with a time-step of 0.005 (in LJ time units). In order to obtain a glassy system which is in a relatively low configurational-energy state, i.e. does not age rapidly, we have used an algorithm based primarily on compression to cross the GT, allowing the system to reconfigure at each step of the process. Naturally (and by

definition), even after fairly long runs, some ageing remains apparent. The end result was the identification of an underlying rigidity transition (RT) below the glass transition, whereby the system displays true, long-time rigidity and resistance to imposed shear strain. When extrapolating to long times, there appears to be a connection between this RT and estimates of critical temperatures using the Vogel–Fulcher–Tammann (VFT) approach or the universal scaling approach developed by Colby [9]. The rigidity transition, based on the increased dominance of ‘cage effects’ is consistent with what has been found for other ‘jammed’ systems [6]. It can also be noted that this rigidity transition corresponds to the onset of zero-frequency modes as evidenced by the cusp before the sudden rise in the heat capacity and therefore is a well-defined experimental temperature [6].

In the present work, we begin with 20 independent samples of such glassy systems, just below the RT temperature ($T = 0.41$ in LJ units), such that, at medium to long timescales, there is not enough cooperative movement to easily attain any type of long-range relaxation. These systems are then made to undergo instantaneous, one-time and affine shear deformations in the xy plane by moving each particle according to $x' = x + \epsilon_{xy}y$. The PBC are also adjusted accordingly. Given the highly anisotropic nature of the system below the GT, the process is repeated in five other directions for each independent sample. It must be noted that in the limit of zero shear, the additional deformations do not yield more independent samples. On the other hand, as will be discussed below, large (plastic) deformations essentially produce entirely ‘new’ systems. It is found that deformations of $\epsilon > 0.1$ are generally plastic, which can also be interpreted as the system being forced into a new ‘well’ on its energy landscape, from which it does not have the thermal activation required to return to its original state. From a structural perspective, the chains are stretched beyond their ‘equilibrium’ positions, followed by a fairly rapid initial reconfiguration. Our primary interest, however, is in the behaviour of the deformed system (with respect to its undeformed counterpart) at fairly long times after the deformation.

3. Stress and macroscopic relaxation

Naturally, when applying these shear deformations, we are initially interested in how the system responds to the imparted stress. Indeed, despite the lack of permanent bonds, the fragile glass can support moderate (elastic) deformations. The concept of ‘force chains’, as a new paradigm to explain fragility in jammed matter, may provide some insight into how a yield strain arises during instantaneous deformations [10]. However, it is not trivial to understand how the relaxation modes present below T_G respond to these perturbations. We are more concerned with the long-range α -relaxation process that dominates the ageing process of our polymer melt. We therefore monitor when large ‘jumps’ occur, as defined by an *irreversible* collective movement, i.e. the particles together move more than a specified distance (0.7σ , where sigma is the diameter of the monomers) without returning close to their initial positions, following the deformation (figure 1). We

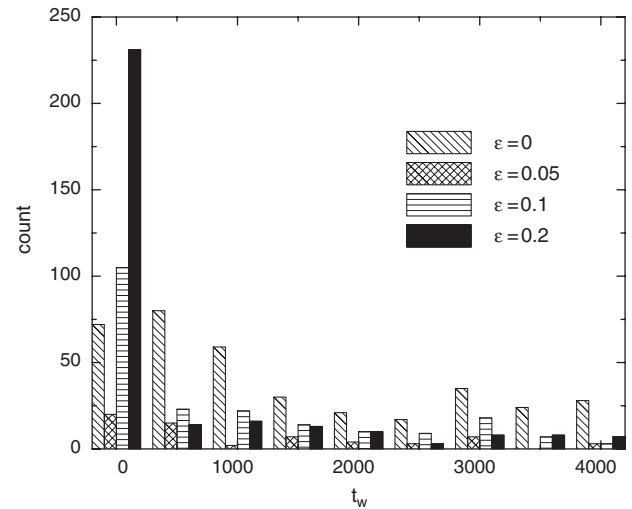


Figure 1. A count of the number of large, irreversible, ‘collective’ jumps in the system following a deformation at $t_w = 0$. The initially high frequency of such movement in the system following large deformations shows the system reconfiguring after the ‘perturbation’, in contrast with a relative infrequency of the jumps at later times. The $\epsilon = 0$ values have been renormalized to be on the same scale as the $\epsilon \neq 0$ values.

can say that, after undergoing a large shear deformation and a ‘forcing’ from its initial meta-stable equilibrium, relaxation in the system occurs earlier. This leads us to believe that instantaneous shear can somehow lead to a more ‘stable’ glass by substantially altering the overall picture of how stress evolves in the system (for a more complete discussion of the stress response to applied shear, see [6]). The energy landscape approach seems especially promising in this regard: we can interpret the change as not only a new *position* of the system on its landscape, but also as a new *trajectory* being undertaken along this hypersurface [11, 12].

4. Mobility and dynamic heterogeneity

Probability distributions of the individual particles’ displacement reveal the presence of large pockets of ‘fast’ particles, which is confirmed by the non-Gaussian parameter (NGP) $\alpha_2(t) = \frac{3\langle \Delta r^4(t) \rangle}{5\langle \Delta r^2(t) \rangle^2} - 1$ at different timescales. A large value of the NGP does not, strictly speaking, imply a maximum in the number of ‘fast’ particles, but rather a maximum in the spatially correlated, cooperative movement, and seems to coincide with the onset of sub-diffusive (cage-dominated) movement. Figure 2 shows the marked impact of plastic deformations on the system’s dynamics, which is confirmed by investigations into the diffusion of individual particles.

Our next task is to identify both the fastest and slowest particles in the system [1]. This can be done by either arbitrarily assigning a minimum (or maximum) displacement of a particle in order to consider it fast (or slow). The non-Gaussian tails found on the probability density function of the displacement show that this method is particularly suitable for fast particles, and has given meaningful results in the present case. The primary disadvantage is that, depending on

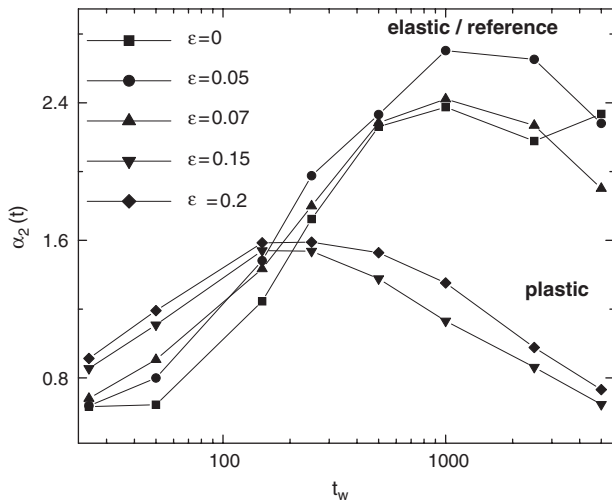


Figure 2. The effect of shear deformations on the non-Gaussian parameter (NGP). The peak has been found to correspond to the onset of long-time sub-diffusive, cage-dominated dynamics.

the timescale investigated, these ‘mobile’ particles are more or less difficult to identify. The second method consists simply in arbitrarily selecting the 5% of the particles which are fastest and slowest (see figures 3 and 4). These criteria, while arbitrary and also more or less meaningful depending on the timescales investigated, have the advantage of ensuring a certain consistency in the data and the results presented here will be limited to this case (although they have been confirmed by other techniques).

As expected, immediately after a large shear strain is applied, the regions of fast and slow particles are greatly disrupted. Just as in the case of continuous shear, we can say that the one-time shear *instantaneously* ‘liquifies’ the system, but no *real* work is being done, so a glassy state, albeit a different one, is immediately recovered. We then wait a

sufficiently long time ($\sim 10^3$ LJ time units) for the system to stabilize in order to see how regions of fast and slow particles change when subjected to shear strain. Figure 3 shows how the distribution of distances between fast and slow particles is affected. The slow particles maintain a similar spatial distribution, while the fast particles are dispersed and exhibit a distribution that is increasingly normal. If, specifically, we look at how many of these fast particles are nearest neighbours or along the same polymer chain (figure 4), we can gain some insight on how cooperative movement is inhibited. While ‘chains’ of cooperative movement are also present in binary systems [13], *physical* chains in the present polymeric system enhance this effect [14]. Inversely, polymers also contribute to the stability of the ‘cages’ which provide the geometrical frustration (eventually tending towards ‘rigidity’) of the glass transition [6]. The fraction of monomers along the same chain which are ‘fast’ (figure 4) illustrates the striking impact of a plastic shear deformation on the system and thus a substantial reconfiguration on a local level. The one-time perturbation essentially causes the chains themselves to move less cooperatively. We can tentatively think of this ‘yield’ strain from a dynamic perspective, in that the local *propensity* is disturbed in an irreversible manner (cf [15]).

What we would like to emphasize is that the dynamical heterogeneity can be locally reduced by the application of shear deformations, as evidenced in figures 2 and 3 by a lower NGP, an earlier onset of sub-diffusion and a reduction in the size of regions of fast particles. Since there is more local organization in terms of the ‘fast’ regions than the ‘slow’ ones (figures 3 and 4) [16], the former are more susceptible to an irreversible disruption caused by the shearing. While the NGP can only *hint* at how mobility is distributed *overall*, a closer examination reveals how the collective rearrangements in the system can become more or less difficult (figure 4). One should note that the magnitude of the shear deformation itself, i.e. the forced displacement of the particles, cannot be solely

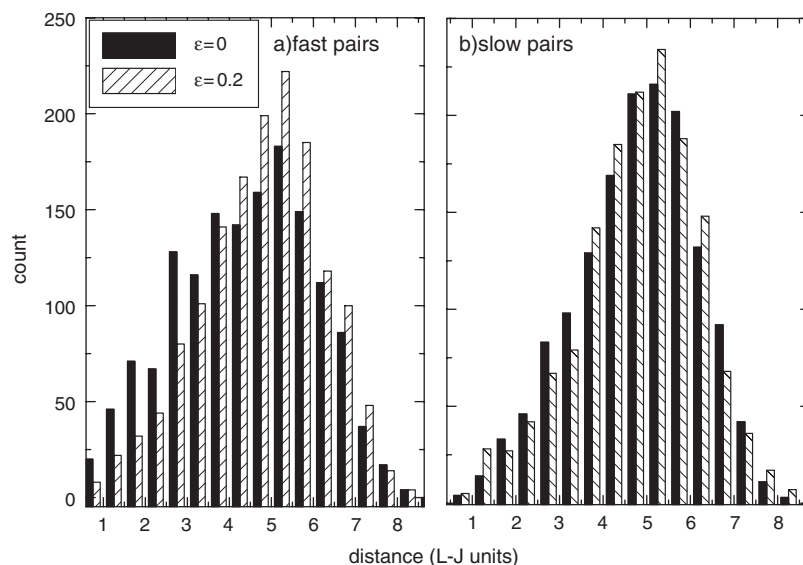


Figure 3. Distribution of distances between pairs of the 5% fastest and slowest particles. $\epsilon = 0$ is the reference equilibrated and aged system. The distribution for the plastically deformed system ($\epsilon = 0.2$) was recorded after about 10^3 LJ time units. In the case of the fast particles, initial deviations from a normal distribution become much less pronounced at long times after the plastic deformation.

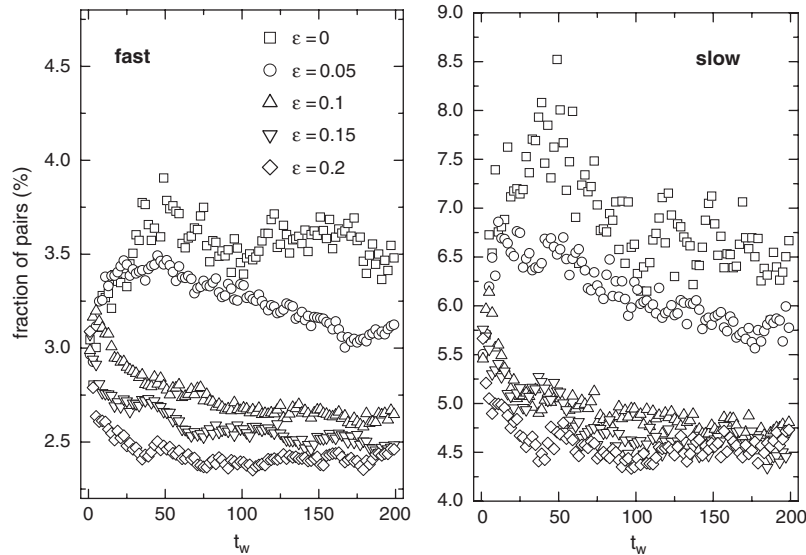


Figure 4. Left: the fraction of nearest neighbour pairs among ‘pairs’ of fast particles, following a deformation applied at $t_w = 0$. Right: the fraction of ‘pairs’ of fast particles located on the same chain. In both cases, note how the (5%) most mobile particles become increasingly spatially uncorrelated following plastic shear deformations. As discussed in section 2, the statistics on unsheared systems are worse, since there is no deformation to be repeated in many directions.

responsible for the dispersal of fast particles; the essence of the problem lies in understanding the local structure of the system. Most importantly, the effects are felt at long times after the deformation which, underlines the *irreversibility* of the change (after plastic shear), and in a sense, confirms what recent energy-landscape-based studies have told us (see previous section). While they ‘look’ similar, the two (undeformed and plastically deformed) glasses are, in fact, markedly different.

5. Microstructure

Our previous work [7, 8] has tentatively shown how instantaneously applied shear strain can have subtle implications for the structure of a glass. In other words, we are using these deformations to look for *direct* evidence of structural changes which are reflected in the more pronounced dynamical effects which we observe. Recent work on the subject suggests that other structural parameters may be more useful, depending on the system studied [17]. The polymer system, however, provides a natural way of observing structural (orientational) change on a local level, as shown in figure 5. The lower free-energy states accessible to the system tend towards individual polymer configurations with a low radius of gyration (R_G). At all times, our values of R_G^2 lie slightly above the values found for a ‘liquid’ polymer melt [18]. When shear strain is applied, the chains initially tend to stretch, but paradoxically, the system also gains easier access to what appear to be lower-energy configurational states. We believe this to be connected to the reduction in the dynamic heterogeneity of the system: the spatial correlation of the fast particles, for instance, diminishes as the polymers ‘fold in’ on themselves and the microstructure becomes increasingly fine-grained. We also believe that further research into the small-scale structure of the system should

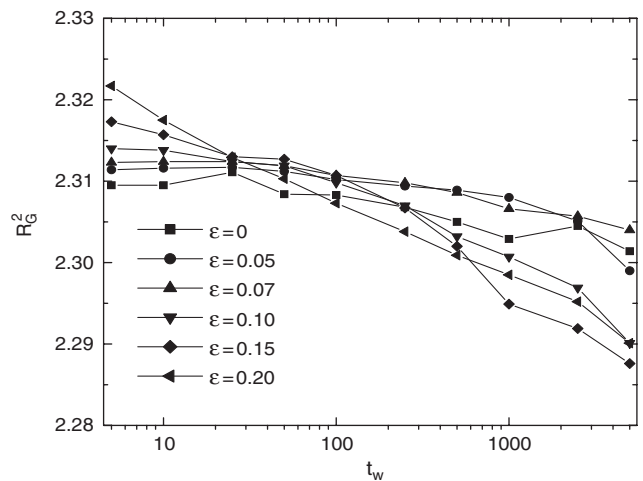


Figure 5. Evolution of the mean-squared radius of gyration (R_G^2) of the polymer chains, following different values of the shear deformation applied at $t_w = 0$.

reveal a more general connection with the structure and self-organization pertaining to local ‘jamming’ in glassy systems.

6. Conclusion

This paper is not meant to be an exhaustive discussion of the dynamical or microstructural properties of fragile glass-formers below T_G , but simply to elucidate some of these aspects (especially in the case of polymeric glasses), as they become apparent under shear deformations. We have also shown the relevance of new and useful simulation-based techniques for investigating the subtleties of ageing (and, more generally, relaxation) processes. We can, on some level,

equate the mobile regions' resistance to dispersion (via subtle self-organization) with the elastic response of the system as a whole. Unlike the case of continuous or cyclic shear, instantaneous deformations allow to access *similar* (though largely unconnected) glassy states. Further research will be focused on establishing a more precise connection between these two types of experiments. In addition, we believe that this type of work can eventually lead to a better understanding of the dynamics of jammed systems in general, where tapping experiments on granular systems, for instance, show behaviour analogous to that of liquids below T_G [19].

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