

## Free Volume and Finite-Size Effects in a Polymer Glass under Stress

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Molecular dynamics simulations of the nonlinear creep response of a polymer glass under tension and compression have been performed at the glass transition temperature. The dynamics were measured as the deformation proceeds using the bond autocorrelation function, and the relaxation times measured as the system is compressed or elongated exhibit a universal response. In tension, the volume increases with strain rate and the relaxation times decrease. In compression, however, the volume decreases by approximately the same amount for all of the applied stresses. Thus, decreases in free volume take place alongside a decrease of the relaxation times by over a factor of 100. We find direct evidence that a characteristic length scale exists below which the deformation of the system exhibits distinct anomalies.

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Polymeric glasses are arguably one of the least understood states of condensed matter. Recent experimental and theoretical work has established some defining features of these materials, including dynamic [1] and mechanical heterogeneities [2,3], and the discovery that molecular mobility is enhanced during uniaxial extension [4]. The pioneering NMR experiments of Loo *et al.* [4] showed that the mobility of Nylon-6 at  $T_g$  increases during uniaxial tension. Recently, Lee and Ediger have employed fluorescence recovery on poly(methyl methacrylate) to demonstrate that, for samples undergoing creep below  $T_g$ , the relaxation times are up to 2 orders of magnitude smaller than those of the material at rest [5]. Given that these two sets of experiments were performed in extension, one question that arises is whether the increased mobility is due to an increase in free volume, or whether the underlying potential energy landscape (PEL) is altered by the deformation process.

Several simulation studies have examined the effects of strain on the properties of small-molecule glassy materials. Lacks and co-workers have shown that shear strain can lead to the destruction of the barriers between adjacent minima of the PEL of a Lennard-Jones (LJ) binary glass and of quenched *n*-butane [6], which should lead to enhanced dynamics in these glassy materials. Several studies of the LJ glass reported evidence of enhanced dynamics under strain [7,8], although we are not aware of any works studying the effects of volume on the enhanced dynamics.

While molecular simulations of the effects of strain on polymeric glasses have been scarce, studies indicate that their behavior is different from that of the binary LJ system [2,9]. Experiments reveal a modest, but distinct enhancement of relaxation below yield [4]; however, Lyulin and co-workers [10] reported that in atomistic simulations of poly(carbonate) and poly(styrene) under uniaxial strain the dynamics are *not* enhanced below the yield strain. In contrast, simulations of glassy poly(ethylene) under a compressional strain indicate that the torsional transition rates of the molecules become significantly faster prior to

yield [11]. In a different set of studies, Rottler and Robbins have explored the effects of temperature and strain rate on the yield behavior of amorphous polymeric materials [12].

Our study aims to complement and help explain emerging experimental evidence of enhanced dynamics under active deformation, and to clarify the apparent contradictions that exist in the simulation literature regarding the deformation of polymeric glasses. In a departure from previous work, but in direct analogy to creep experiments [13], a *stress* is directly applied to a glassy sample; any resulting strains and dynamic features are then determined as a function of deformation. The deformation process is studied both under tensile and compressive stress, enabling an assessment of the role of free volume on the response of the material. The system sizes examined in this work are significantly larger than those considered in most past studies, thereby allowing us to determine whether molecular mobility and deformation are correlated below a certain length scale. This last issue is particularly relevant because glassy systems have recently been reported to exhibit mechanical heterogeneities over relatively large length scales [2,3,9]; a well-defined characteristic length for such heterogeneity (denoted by  $\xi$ ) can be calculated by examining correlations in the nonaffine displacements after an infinitesimal strain [3]. We surmise that if such heterogeneities exist, the overall mechanical response of an amorphous system under active deformation should be significantly different for system sizes near  $\xi$ . Consistent with that view, we report here that the response changes dramatically when that length scale is artificially truncated, i.e., as simulation box lengths are changed from above  $2\xi$  to near  $\xi$ , even when the results are averaged over multiple realizations of the system. We also find that, consistent with experimental observations [5], molecular mobility can be enhanced by several orders of magnitude when our model glasses are subject to active deformation. Remarkably, we find that the relaxation time as measured by the bond autocorrelation function appears to be a uni-

versal function of strain rate, regardless of whether the system is deformed by compression or by extension.

The equilibrium properties and glass transition of the model considered here have been characterized extensively in previous works [14–16]. Each polymer molecule consists of 32 LJ sites connected by stiff harmonic springs; additional details are provided in the literature. All units in this work are reduced by the parameters of the polymer monomer. The average density and lengths of the principal directions of the simulation box before applying the stress were  $\rho = 1.02$  and  $L = 8.8, 11.7, 17.7,$  and  $33.9$  for the four system sizes studied here, respectively; at least five independent initial configurations were simulated in each case. These configurations were generated at high temperatures by means of double-bridging Monte Carlo and molecular dynamics techniques. The systems were then slowly cooled in an  $NPT$  ensemble at  $P = 0$  from a high temperature ( $T = 1.0$ ) to  $T_g$ , which has been previously found to be  $0.37$  [14]. After cooling to  $T_g$ , the ensemble was changed from  $NPT$  to  $N\sigma T$  using the Parrinello-Rahman equations of motion [17], which allow the simulation box to take any parallelepiped shape and relax stresses in any direction, including shear stresses. Here,  $\sigma$  represents the full stress tensor. Our configurations were aged with all components of  $\sigma$  set to zero for  $2 \times 10^6$  time steps before a constant stress was applied in the  $z$  direction,  $\sigma_{zz}$ . All other components of the stress tensor remained set to zero. All deformation simulations were performed using the Gromacs simulation package [18]. The correlation length [3] associated with the mechanical heterogeneity for this model has been reported to be  $\xi = 8.0$  [9].

We begin by measuring the creep response at a tensile strain of  $\sigma_{zz} = 0.54$ ; Fig. 1(a) shows the average response to this applied stress for each system size. The smallest system,  $L = 8.8$ , deforms rapidly and at a constant strain rate, it soon reaches strains greater than  $\epsilon_{zz} = 0.3$ . The next-smallest system,  $L = 11.7$ , does not reach strains as large as those observed in the smallest system. The response begins at a slow strain rate, then goes through a period of higher strain rates, before finally settling on a lower strain rate again. The two largest systems exhibit a nearly constant strain rate with time. Their respective average responses are similar, suggesting that these configurations are approaching the continuum response. Figure 1(b) shows the response of individual configurations for each system size. Significant differences are observed in the behavior of the two smaller systems, which exhibit fast transitions between regions of low strain rate and high strain rate. These transitions become less abrupt as the system size increases; the average response is similar for the two system sizes for which  $L > 2\xi$ . The inset of Fig. 1(b) shows that the response to extension is drastically different for the small system sizes, even for short times and small values of strain. The fact that we find evidence of substantial finite-size effects in our polymeric glasses, even after averaging over multiple configurations, raises the

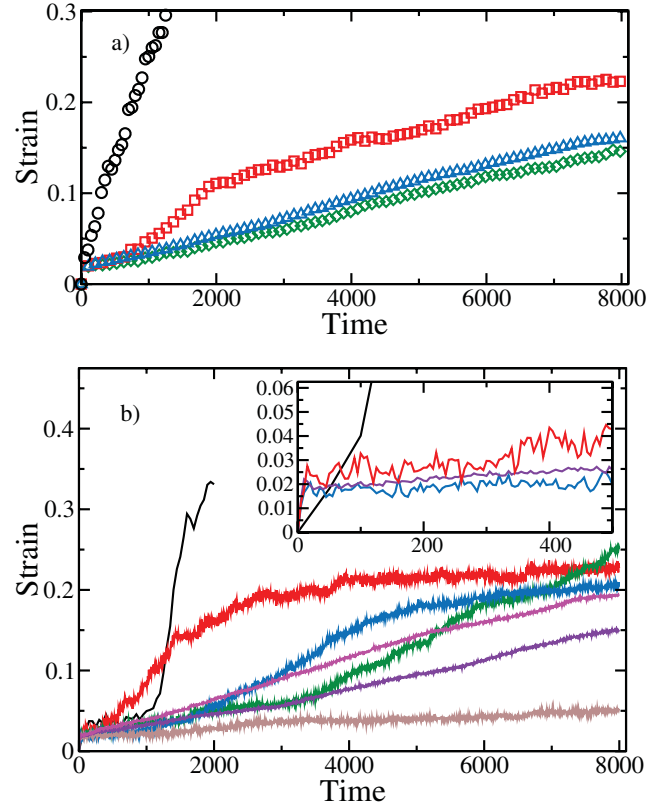


FIG. 1 (color). (a) The strain response of configurations of different sizes exposed to a stress of  $\sigma_{zz} = 0.54$ . Black, red, green, and blue curves represent results averaged over all configurations for four different system sizes, namely  $L = 8.8, 11.7, 17.7,$  and  $33.9$ , respectively. (b) Sample strain response curves for individual configurations for each system size. The black and red curves are from  $L = 8.8$  and  $11.7$  respectively; the brown, green, and blue curves are from  $L = 17.7$ , and the pink and purple curves are from  $L = 33.9$ . Inset of (b): Same as (b) for the early part of the strain response curves, for one configuration of each size.

possibility that previous works in this area might have been inadvertently probing phenomena below the characteristic length scale for mechanical deformation, as opposed to the continuum behavior of the materials under consideration. Similar finite-size effects are observed under compression (not shown).

The creep compliance,  $J$ , for both compressive and tensile stresses is given by  $J = \epsilon(t)/\sigma_{zz}$ , where  $\epsilon(t)$  is the instantaneous strain. We define the strain of the system as  $\epsilon(t) = L_z(t)/L_z(0) - 1$ , where  $L_z(t)$  is the instantaneous length of the simulation box in the  $z$  direction. Results for  $J$  (not shown) confirm that we are well into the nonlinear creep regime [13] for all but the smallest applied stresses, which approach the linear regime.

As shown in Fig. 1, the mechanical responses of different configurations can be considerably different. Furthermore, an individual configuration can exhibit a markedly varied response, with regions of slow strain rate followed by regions of more rapid strain rate and

vice versa. It is therefore instructive to measure the dynamics of each system during distinct “time windows” of the response. For brevity, we only report results for the bond autocorrelation function, denoted by  $C_b(t)$ ; in past studies  $C_b(t)$  has proven to be a useful measure of the dynamics of polymeric glasses [14,19], and is defined here as  $C_b(t) = \langle P_2[\hat{b}(t) \cdot \hat{b}(0)] \rangle$ , where  $P_2$  is the second Legendre polynomial, and  $\hat{b}(t)$  is a unit vector along the bonds of the polymer chain. In order to remove any trivial contributions to the observed dynamics, the affine displacements of all of the particles (those resulting from deformation of the simulation box) are removed before  $C_b(t)$  is calculated. Figure 2 shows  $C_b(t)$  during various time windows of tensile simulations with  $\sigma_{zz} = 0.54$ . At the beginning of the creep simulations, for times  $t < 1000$ , there already is evidence of enhanced dynamics in each configuration, as indicated by a faster decay of  $C_b(t)$ . The second time window,  $4000 < t < 5000$ , exhibits a more diverse behavior. The configuration represented by the brown curve experiences only a small enhancement of the dynamics when compared to the other samples. In contrast, the configurations represented by the blue and green curves experience large strain rates during this time window, accompanied by a significant decay of  $C_b(t)$ . For times greater than  $t > 7000$ , it is found that the dynamics of the configuration shown in green is still significantly faster than those observed for the other configurations. Meanwhile, the blue configuration has returned to a relatively slow strain rate and exhibits a reduced molecular mobility compared to that observed in the previous time window.

The results shown in Fig. 2 imply that the dynamics experienced during a given time window are related to the strain rate experienced by the material during that window. To explore this idea in some detail, a quantitative measure of the dynamics during these time windows is needed. Since our simulations of deformation are performed at  $T \approx T_g$ , it is unrealistic to expect to observe the complete

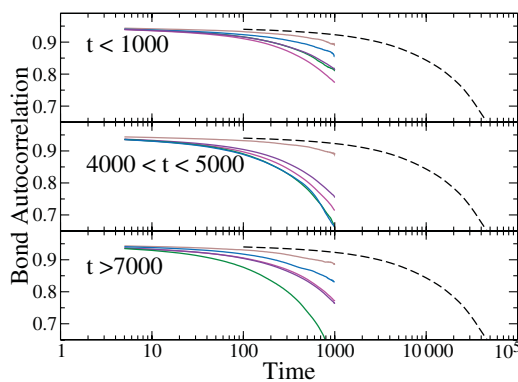


FIG. 2 (color).  $C_b(t)$  for the  $L = 17.7$  and  $L = 33.9$  configurations shown in Fig. 1 calculated during the time windows indicated on the figure, and correspond to the time axis in Fig. 1. The dashed black curve is  $C_b(t)$  for the undeformed sample.

relaxation of the bond autocorrelation function or the incoherent structure factor on computationally accessible time scales. We circumvent this difficulty by first performing long molecular dynamics simulations with no applied stress in order to obtain as much of  $C_b(t)$  as possible; the results are shown in Fig. 2. Next, we fit  $C_b(t)$  to a stretched exponential,  $C_b(t) = \exp[-(t/\tau)^\beta]$ , and we obtain relaxation times  $\tau$  corresponding to the time windows during deformation by keeping  $\beta$  fixed at the undeformed value and fitting  $C_b(t)$  for different time windows. Note that we do not consider these estimates of  $\tau$  to be quantitative measures of the relaxation time, but merely a measure of the relative changes in the dynamics in each system during deformation.

Figure 3(a) depicts  $\tau$  for all values of stress considered in this work as a function of the absolute value of  $\dot{\epsilon}$ , where  $\dot{\epsilon}$  is the average strain rate during the time window associated with  $\tau$ . It is found that the relaxation times decrease considerably with strain rate. Remarkably, when plotted in this manner the relaxation times exhibit the same behavior during both tensile and compressive deformation.

It is of interest to consider whether or not volume changes can explain the observed changes in molecular mobility. Free volume theories are often invoked to explain changes in dynamics [13] and, during extension, it is intuitively attractive to attribute enhanced mobility to greater accessible volume. Figure 3(b) shows the relaxation times as a function of the change in volume relative to the value before the load was applied. Two distinct behaviors are observed on this plot. For systems under tension, the dynamics are correlated with the volume; the smaller relaxation times correspond to larger volume increases. Note, however, that larger volume increases likely correspond to greater deformations of the underlying PEL and it is therefore unclear which of these two effects (volume change or landscape deformation) is responsible for the observed enhanced mobility. Our results for compression, during which volume decreases are small (less than 0.5%) and approximately the same for all applied stresses, argue in favor of a landscape change. The fact that enhanced mobility is also observed at reduced volumes suggests that free volume is not responsible for faster dynamics. This finding is consistent with Ref. [11], which reported the lack of correlation between free volume and enhanced torsional rotation dynamics during compression of polyethylene.

One can obtain an approximate measure of the real units associated with the strain rates observed in this work by examining the frequency of the boson peak,  $\omega_{bp}$ ; previous studies have reported  $\omega_{bp} = 2.3$  for this model [15]. In experiments,  $\omega_{bp}$  typically lies in the range of 1–5 THz [20]. The strain rates observed here are 4 to 6 orders of magnitude *below* the boson peak frequency, and therefore correspond to the range of 1–100 MHz in laboratory units. In contrast, past simulations of polymeric glasses [10,11] have been performed at strain rates in the vicinity of the frequency of the boson peak. Given that the boson peak has

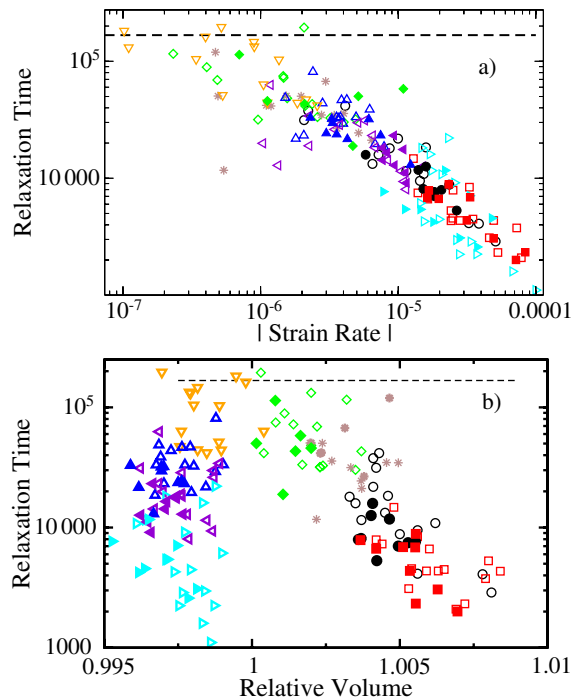


FIG. 3 (color online). (a) Relaxation time plotted against the absolute value of the strain rate during various time windows. (b) Relaxation time against the relative volume during various time windows. For both figures, the symbols represent systems under tension with  $\sigma_{zz} = 0.62$  ( $\square$ ),  $0.52$  ( $\circ$ ),  $0.425$  ( $*$ ),  $0.27$  ( $\diamond$ ) and under compression with  $\sigma_{zz} = 0.75$  ( $\triangleright$ ),  $0.62$  ( $\triangleleft$ ),  $0.54$  ( $\triangle$ ) and  $0.27$  ( $\nabla$ ). The dashed horizontal line indicates the value of the relaxation time from the undeformed sample. Open symbols are from configurations with  $L = 17.7$ , closed symbols with  $L = 33.9$ .

been associated with the mechanical properties [21] and mechanical heterogeneity [3,9] of amorphous materials, we suspect that the mechanical response observed for frequencies near the boson peak are different from those observed when deformations are applied at strain rates well below the boson peak frequency.

The results presented in this Letter suggest that the mechanical response of polymeric glasses subject to active deformation can probe the existence of a characteristic length scale below which molecular displacements are highly correlated [2,3,9]. It is proposed that, in a periodic system below that correlation length, all particles in the parent cell are coerced to move in unison, at a rate determined by the fastest moving regions. For systems well above the characteristic length scale for mechanical inhomogeneity, the mechanical response of the sample is relatively uniform, and dominated by the average mechanical characteristics of the material. All large systems undergoing deformation are found to exhibit enhanced dynamics. Consistent with experiments [5], the relaxation times associated with segmental dynamics are increased by several orders of magnitude. The faster relaxation times follow a relatively uniform behavior with strain rate, regardless of whether the material undergoes tension or

compression. In the absence of available experimental data, it is tempting to view this overall behavior as universal. The experiments under tension [4,5] both likely involved a volume increase, and it is therefore unclear whether active deformation was the sole cause for the observed increased mobility. The fact that we find the same enhanced mobility with strain rate for both elongation and compression, and that volume decreases in our samples under compression, argues that changes of free volume are not responsible for the experimentally observed enhanced mobility.

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- [1] M.T. Cicerone and M.D. Ediger, *J. Chem. Phys.* **104**, 7210 (1996).
  - [2] K. Yoshimoto *et al.*, *Phys. Rev. Lett.* **93**, 175501 (2004).
  - [3] F. Léonforte *et al.*, *Phys. Rev. Lett.* **97**, 055501 (2006); *Phys. Rev. B* **72**, 224206 (2005).
  - [4] L. Loo, R. Cohen, and K. Gleason, *Science* **288**, 116 (2000).
  - [5] H.-N. Lee and M.D. Ediger, presented at the American Physical Society 2007 Meeting: <http://meetings.aps.org/link/BAPS.2007.MAR.V4.1>.
  - [6] D.J. Lacks and M.J. Osborne, *Phys. Rev. Lett.* **93**, 255501 (2004); M.M. Frey and D.J. Lacks, *J. Chem. Phys.* **112**, 2909 (2000).
  - [7] M. Nandagopal and M. Utz, *J. Chem. Phys.* **118**, 8373 (2003); M. Utz, Q. Peng, and M. Nandagopal, *J. Polym. Sci., Part B: Polym. Phys.* **42**, 2057 (2004).
  - [8] L. Berthier and J.-L. Barrat, *J. Chem. Phys.* **116**, 6228 (2002).
  - [9] G.J. Papakonstantopoulos *et al.*, *Phys. Rev. E* **75**, 031803 (2007).
  - [10] A.V. Lyulin *et al.*, *Macromolecules* **37**, 8785 (2004); *Europhys. Lett.* **71**, 618 (2005).
  - [11] F.M. Capaldi, M.C. Boyce, and G.C. Rutledge, *Phys. Rev. Lett.* **89**, 175505 (2002); *Polymer* **45**, 1391 (2004).
  - [12] J. Rottler and M.O. Robbins, *Phys. Rev. Lett.* **95**, 225504 (2005); *Phys. Rev. E* **68**, 011507 (2003).
  - [13] L.C.E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, New York, 1978).
  - [14] R.A. Riggleman *et al.*, *Phys. Rev. Lett.* **97**, 045502 (2006).
  - [15] T.S. Jain and J.J. de Pablo, *Phys. Rev. Lett.* **92**, 155505 (2004); *J. Chem. Phys.* **120**, 9371 (2004).
  - [16] K. Yoshimoto *et al.*, *J. Chem. Phys.* **122**, 144712 (2005).
  - [17] M. Parrinello and A. Rahman, *J. Chem. Phys.* **76**, 2662 (1982).
  - [18] H.J.C. Berendsen, D. van der Spoel, and R. van Drunen, *Comput. Phys. Commun.* **91**, 43 (1995).
  - [19] C. Bennemann *et al.*, *J. Phys. Condens. Matter* **11**, 2179 (1999).
  - [20] A.I. Chumakov *et al.* *Phys. Rev. Lett.* **92**, 245508 (2004).
  - [21] V.N. Novikov, Y. Ding, and A.P. Sokolov, *Phys. Rev. E* **71**, 061501 (2005).