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Molecular plasticity of polymeric glasses in the elastic regime

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We examine the plastic deformation of a model polymeric glass under tension. Local plastic events are found at extremely small strains, well below the yielding point, in a regime where the material is traditionally described as perfectly elastic. A distinct relationship is identified between these irreversible displacements (plastic events), the amplitude of segmental motion, local structure, and local elastic moduli. By examining the motion during the deformation of individual sites, we arrive at a mechanistic explanation for how these events arise. It is shown that, upon deformation, polymer sites that exhibit relatively small but positive elastic moduli are prone to failure. Such sites are also found to exhibit a large vibration amplitude, as indicated by their respective Debye-Waller factors. Sites that fail first tend to have a higher degree of nonsphericity than the rest of the material. We also find the collective occurrence of local plastic events where percolation or concerted action leads to global failure of the material above a certain strain.

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I. INTRODUCTION

During the last decade, a series of experiments have found evidence of dynamical heterogeneities [1–3] in amorphous glassy systems. This body of experimental work, whose main outcome has been to establish the existence of *dynamic* heterogeneity, has been accompanied by several simulation studies that provide support for the existence of *mechanical* heterogeneities in model glasses [4–8]. Polymeric glasses have been found to exhibit domains of several nanometers whose elastic moduli can vary appreciably; in some cases, they even exhibit negative local values [4,9]. Taken together, these findings have established that one of the defining characteristics of glassy materials is heterogeneity, both dynamic and mechanical. More importantly, they challenge traditional mechanical treatments of amorphous materials that assume a mechanical continuum with uniform elastic moduli [10].

In an attempt to quantify the heterogeneous nature of glassy systems, Léonforte *et al.* [5] have introduced a characteristic length scale below which classical elasticity no longer applies. Little is known, however, about the mechanical response of amorphous glasses below that length scale. One proposed mechanism for the deformation and failure processes at nanometer length scales is thought to consist of a series of reversible, elastic deformations interrupted by sudden inelastic, plastic events [11–16]. Recent numerical studies of Lennard-Jones glasses indicate that plastic events occur at strains as small as 10^{-4} [5,17,18], and experiments in a variety of materials suggest that residual displacements (also referred to as "internal friction") can occur at extremely small strains ($\epsilon \approx 10^{-6}$) [19]. Few studies, however, have identified which sites will fail, why they fail, and what the actual failure mechanism is, even though these local failures have been observed for over a decade [11].

An issue that remains unanswered is whether domains of large or small elastic moduli exhibit smaller or larger molecular vibrations, and whether regions undergoing irreversible displacements are in any way related to particular values of the local moduli or structure. It is not known whether plastic events consist of isolated or cooperative rearrangements, and it is this series of questions that we address in this paper. Recent work on two-dimensional (2D) models suggests that local plastic events exhibit a quadrupolar character [18]. In this work we use uniaxial deformations to investigate how plastic events occur in a three-dimensional amorphous polymeric system. We show that, consistent with experiments, in a polymeric glass irreversible displacements appear from the beginning of the deformation process. Early irreversible events are not manifest in the global stress-strain response of the material and can only be identified by quantifying the local, atomic-level relationship between stress and strain. We show how the occurrence of irreversible events is connected to the local values of the elastic moduli and we find a clear correlation between the local characteristics of elasticity, structure, and vibrations.

II. METHODOLOGY

A. Simulations

Given that experimental data for glasses under deformation are more widely available for polymeric materials than for small-molecule glass formers, and given that local elastic moduli have only been reported for polymers, our calculations are performed on a polymer model whose behavior at rest has been fully characterized in previous studies [4,20].

In our simulations, the segments of the polymer molecules interact via a pairwise, 12-6 Lennard-Jones truncated potential energy function, shifted at the cutoff $r_c = 2.5\sigma$,

$$U_{nb}(r) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right] - U_{LJ}(r_c), & r \le r_c, \\ 0, & r > r_c, \end{cases} \qquad (1)$$

where ε and σ are the Lennard-Jones parameters for energy and length, respectively, and r is the distance between two interaction sites. The bonding energy between two consecutive monomers in the same chain is given by

$$U_b(r) = \frac{1}{2}k(l - l_0)^2. \tag{2}$$

The polymer molecules consist of a linear chain of 32 spherical sites bonded by harmonic springs whose equilibrium length is $l_0=\sigma$. The springs can be stretched indefinitely, but the spring constant for the harmonic potential is sufficiently large $(1000k_bT)$ to prevent significant deviations from the equilibrium length $l_0=1\sigma$. All quantities are reported in reduced units normalized by the LJ parameters of the polymer monomers (i.e., the temperature $T=RT^*/\epsilon$, pressure $P=P^*\sigma^3/\epsilon$, and length $L=L^*/\sigma$, where the $*$ implies real units).

A Monte Carlo (MC) method is used to simulate the systems of interest to this work. Random monomer trial displacements are utilized, as well as configurational-bias reptation moves to increase performance [21]. While reptation can be effective in dilute systems of short chains, for intermediate- to long-chain molecules it is essential to resort to trial moves capable of rearranging inner segments of the polymer. To further enhance sampling, we also implement double-bridging trial moves [22,23]; these moves consist of a simultaneous exchange of distinct parts of two neighboring chains and are highly effective for configurational sampling of long-chain molecules. Double bridging allows for effective equilibration of the systems considered in this work [22]. It is particularly important in these systems, where sampling the correct structure and arrangement of long-chain molecules can be particularly demanding.

B. Equilibration and deformation procedure

The MC algorithm was used to equilibrate the systems of interest at high temperatures. Configurations for subsequent energy minimization were prepared by gradual cooling, at a pressure of 0.3, down to a temperature of $T=0.2$. The average density of our samples at $T=0.2$ was $\rho=1.042$. We then performed a quench to zero temperature by minimizing the energy using a conjugate gradient method. A quasistatic deformation path was subsequently implemented by applying an elementary uniaxial affine extension in strain along the x dimension, while keeping the y and z dimensions fixed, and the energy was minimized again under constant strain. The "nonaffine displacement" field was determined from the difference between the coordinates of all particles in the affinely deformed system and the subsequent, energy-minimized system [7]. From this point on, we either continued to strain and minimize the energy of the system to reach higher total strains or reversed the strain and went back to the unstrained state to obtain the so-called "residual" or "irreversible-displacement" field. Further details of the equilibration and the deformation procedure have been presented in the literature [6,7].

Local stresses were determined through the site-based methodology of Zhou [24]. Such stresses are defined at distinct interaction sites and vanish between sites. If the stress experienced by each site in the system is known, it is possible to determine a local elastic modulus by introducing an appropriate measure of the local strain. To that end, we use the approach of Falk and Langer [12]. The local strain tensor corresponding to a specific site is calculated by considering the neighboring sites that lie within a domain of radius 2.5σ. The strain at the central site is obtained by minimizing the mean-square difference between the actual displacements of the neighboring sites (relative to the central one) during a deformation step and the relative displacements that they would have experienced in a region of uniform strain; i.e., the local strain is defined as the strain tensor that minimizes the nonaffine character of the local displacements. We therefore define the effective local modulus at particle i as

$$C_{11}^i = \frac{\Delta\sigma_{xx}^i}{\epsilon_{xx}^i}, \tag{3}$$

where $\Delta\sigma_{xx}^i$ is the change in stress on particle i after an infinitesimal global deformation $(\epsilon_{xx}=10^{-5})$ and ϵ_{xx}^i is the local strain on particle i. We note that this definition of the local modulus differs from our earlier definitions [4,25], which required calculating the modulus in local, cubic domains. If we compare average the moduli as obtained from Eq. (3) over local cubes and compare to the method employed in Ref. [4], they agree very well.

III. RESULTS AND DISCUSSIONS

The quasistatic deformation behavior of the polymeric glass considered in this study has not been reported in the literature. For completeness, we begin by presenting a few characteristics of this model. Figure 1(a) shows the global stress-strain curve of our model glass determined from a series of deformations with $\varepsilon_{xx}=5\times10^{-4}$ and subsequent minimizations. The inset of Fig. 1(a) shows the stress as a function of strain for the early stages of deformation. Deviations from linearity in Fig. 1(a) become apparent at strains of 5×10^{-3}. At strains slightly above 10^{-2} one starts to detect small sudden drops in the global stress, in agreement with results for small-molecule glass formers [13,26]. The material exhibits a global yield at a strain of approximately 9×10^{-2}. The inset of Fig. 1(a) shows that, in the early stages of the deformation, the global stress is perfectly linear and does not exhibit any of the sudden drops that are seen at larger strains.

A closer inspection in terms of local stresses, however, reveals that local plastic events are occurring at strains as small as 10^{-4}. Figure 1(b) shows how the local stresses change after a series of strain steps (in steps of $\Delta\varepsilon=10^{-5}$), as a function of the effective local modulus (denoted by C_{11}) of the undeformed material evaluated at rest. After only a few strain steps, the stresses on several sites drop abruptly [Fig. 1(b)]. A further increase of the strain causes additional sites to exhibit discontinuous stress drops. These drops correspond to local plastic events; when the changes in stress on each site upon deformation are compared to the residual displacements, we find that the sites that exhibit large, sudden stress drops are those with the highest residual displacements. It is

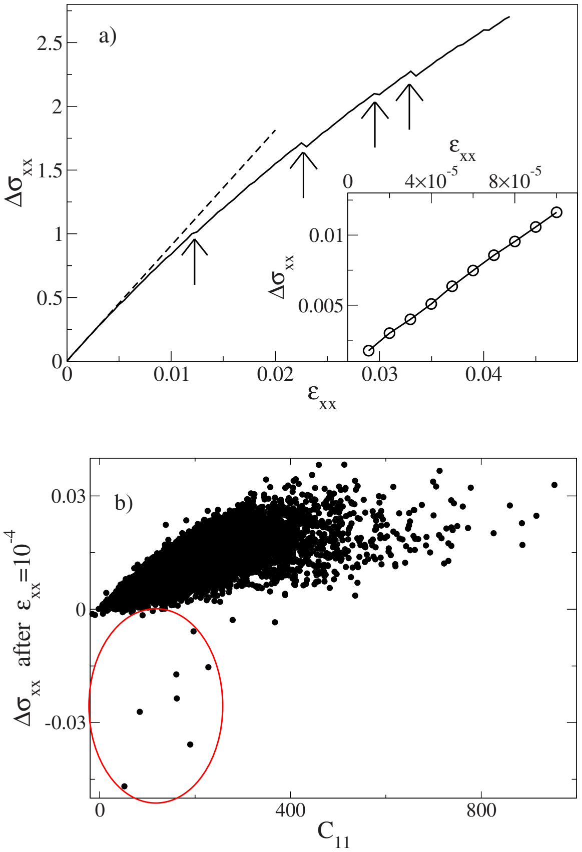

FIG. 1. (Color online) (a) Stress-strain curve for a single configuration. Arrows identify plastic events. The dashed line is tangent to the stress strain curve and denotes the initial slope. Inset: stress-strain curve for small strains up to a value of $\varepsilon=10^{-4}$. (b) Change in stress on each site plotted against their local modulus for a chosen strain $\varepsilon=10^{-4}$.

clear that even at a strain as small as 10^{-4}, where the material is usually considered to be elastic and the global stress-strain curve is linear [Fig. 1(a), inset], some sites exhibit large decreases in stress. We also point out that there appears to be no correlation with C_{11} for these failures at such small strains. If we focus instead on the total stress, these events average out to give the appearance of a perfectly elastic response, even though some sites have failed at strains smaller than the first discontinuous jump in the stress-strain curve [Fig. 1(a)]. Additionally, we can see from Fig. 1(b) that several sites exist with a negative local modulus, consistent with previous findings in a pure polymer [4] and a polymer nanocomposite [6,7]. In the previous studies, it was demonstrated that the negative modulus domains are stabilized by surrounding extraordinarily stiff domains, giving rise to an overall mechanically stable material [4].

Past studies of small-molecule glasses in two dimensions have also found evidence of local plastic events at small strains [13]. In such studies, however, plastic events were detected by studying the displacement of individual atoms and the local stresses were not evaluated. By considering a three-dimensional model of a polymer and calculating the actual stresses, it becomes possible to make a direct connection to laboratory experiments [27] and establish whether the phenomena seen in simulations of our model polymer glass are physically relevant. For simplicity, we assume that each interaction site (of diameter σ) corresponds to a typical persistence length: i.e., $\sigma=1$ nm. We set the energy scale according to $\varepsilon=1k_BT$ and assume a temperature of $T=300$ K. The Lennard-Jones units for the elastic moduli are ε/σ^3 which, for our model, would correspond to $\sim 4\times 10^6$ Pa. The values of the bulk elastic constants for our polymeric glass are therefore 1.0 GPa, in good agreement with experimental values for common polymeric glasses. The local plastic events alluded to earlier, which start to arise at small strains, therefore correspond to extremely small stresses, on the order of 1 MPa. Recent experiments have examined the deformation of polymers at ultrasmall strains [27], employing stresses of precisely that order of magnitude (from 0.14 to 1.7 MPa); with a strain sensitivity of 2×10^{-7}, such experiments [27] observed an overall linear response for strains below 10^{-3}, but with a distinct nonlinear component of the strain that is consistent with our observations.

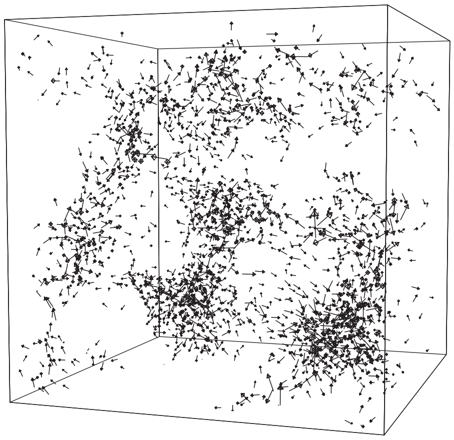

FIG. 2. Indication of quadrupolar plastic events as seen from the three-dimensional plot of the residual site displacements.

Having outlined the main features of the mechanical response of our model polymer glass to uniaxial deformation, we can turn our attention to the central findings of our paper: namely, the relation between local elastic moduli, plastic events, structure, and molecular vibrations. For concreteness and to facilitate comparison to past studies of glasses, we focus on a value of the strain ($\epsilon=0.0225$) for which, as shown in Fig. 1(a), the material exhibits a *global* stress drop. Plastic events can be identified in terms of the residual displacement field. It is found that, consistent with results for 2D atomic glass formers [18], the residual site displacements for our polymeric system under uniaxial deformation are quadrupolar in nature (Fig. 2).

As mentioned above, past work has shown that the local moduli of polymeric glasses are heterogeneous [4]; our next goal is to demonstrate whether the local moduli, which are defined at infinitesimal strains, can be used to predict which particles will take place in the plastic events that occur at larger values of strain. Figure 3(a) shows the residual site displacements as a function of their respective longitudinal moduli. It reveals that those sites whose elastic moduli are slightly lower than the average value ($C_{11}=180$) exhibit

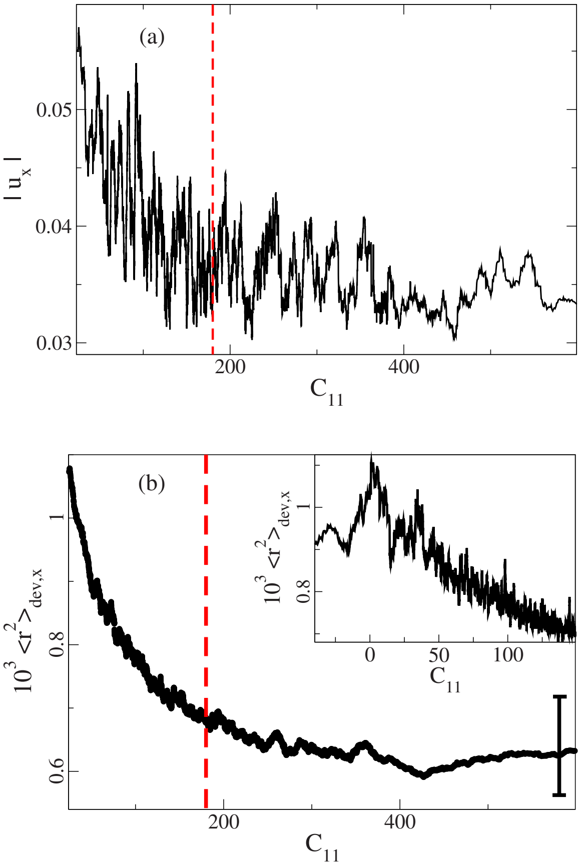

FIG. 3. (Color online) (a) Residual displacements of polymer sites as a function of the local elastic moduli. The dashed line indicates the bulk value of C_{11} for a specific configuration. (b) Average local displacements (mobilities) as a function of local elastic moduli of the polymer sites. The inset shows the local displacements on an expanded scale.

larger residual displacements (and are therefore more prone to failure). Figure 3(a) also shows that domains with a large initial positive modulus exhibit smaller residual displacements. We again emphasize that the moduli in Fig. 3(a) are those at the start of the deformation process, after only an infinitesimal deformation. In other words, the information that determines which sites eventually fail under elongation is encoded in the elastic moduli of the material at rest. Although this finding is intuitively appealing on the basis of purely mechanical arguments, we are unaware of any previous studies demonstrating which particles will fail at large strains from the local properties of the material at rest.

In order to provide further evidence that domains having a small positive modulus are relatively soft, we calculate a dynamic quantity that is closely related to the Debye-Waller factor. The Debye-Waller factors are an attractive quantity to characterize because they are easily obtainable both from molecular simulations and from neutron scattering experiments. They are often related to local mechanical properties through a harmonic approximation [28]; however, a direct connection between a more traditional elastic constant and the inverse of the Debye-Waller factor has never been explicitly demonstrated. Not only do Debye-Waller factors have potential as measures of the local elastic constants, but recent work has demonstrated that a universal scaling law exists between the local elastic constants and the relaxation times above the glass transition temperature [29]. To calculate the Debye-Waller factors, we begin with the minimized and unstrained configurations; the velocities of all sites were first initialized at a low temperature. The systems were equilibrated with molecular dynamics for 50 000 steps. The equilibration period was followed by a production run of 200 000 steps, with time step $\Delta t = 0.001$. For our Debye-Waller factors, denoted by $\langle r^2 \rangle_{dev}$, we calculate a local mean-square displacement of each atom around its average position. Figure 3(b) shows the average x component of the local displacements as a function of the local elastic moduli for each site. We find that sites of high modulus exhibit smaller vibrational amplitude, while those with elastic moduli close to zero exhibit the highest. Interestingly, negative-modulus sites exhibit smaller amplitudes than zero-modulus ones [inset of Fig. 3(b)]. Intuitively, one might expect that the domains of negative moduli would be unstable and more likely to fail. However, the results presented here show that this is not the case. Our results, which are consistent with previous studies observing negative elastic constants in polymer glasses, reveal that the negative domains are stabilized by surrounding stiff domains of large positive modulus [4].

We next attempt to identify a correlation between the local structure of the undeformed material and plastic events by analyzing its local structure in terms of Voronoi polyhedra. The Voronoi polyhedra are a geometric tesselation of the space around a collection of points; in our case, the points are the positions of the polymer monomers. The Voronoi polyhedron for a given particle is the collection of space that is closer to that particle than any other. The distortion of the local volume can be measured through the nonsphericity or anisotropic factor parameter $\alpha = \frac{RS}{3V}$, where V, S, and R are the volume, surface, and average curvature radius of the convex body, respectively [30]. The Voronoi volumes for each site are plotted as a function of the local moduli in Fig. 4(a); we find that low-modulus sites exhibit a higher Voronoi volume. Furthermore, Fig. 4(b) also shows that the sites with the highest residual displacements have the highest Voronoi volumes as well. If we plot the nonsphericity of each site with respect to its local modulus, we fail to observe a correlation between them. However, plotting the nonsphericity of each site with respect to its residual displacement, we find that the sites that fail have the highest values of nonsphericity. As stated earlier, the sites with positive values of moduli lower than the bulk value of the material are more likely to fail. Going one step further, we find that among these low modulus sites, the ones that fail are those that exhibit a high nonsphericity, while those of lower nonsphericity do not.

We conclude our discussion by mentioning that while the findings presented so far reveal that weak domains and early plastic events are ultimately responsible for the global failure of the polymer glass, the question that remains is, how many sites are involved cooperatively and do such clusters originate from low-modulus regions? To address this question, we calculate the participation ratio (P), defined as

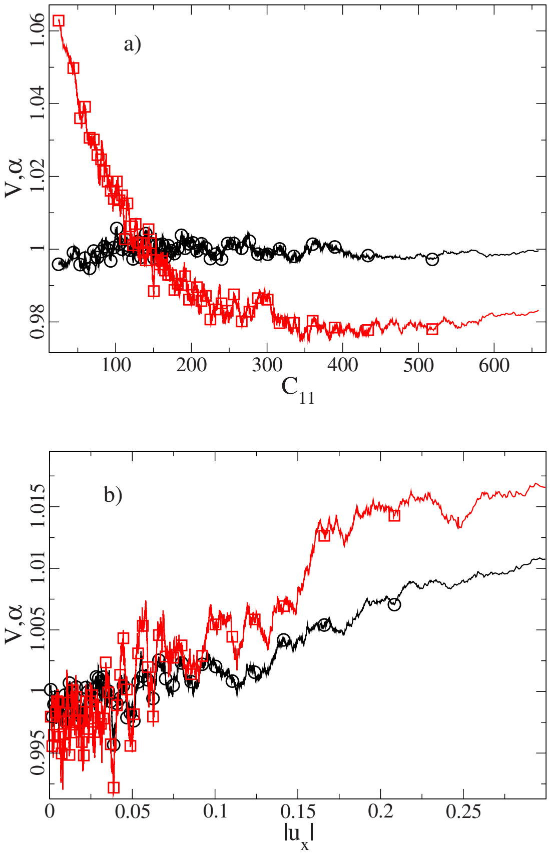

FIG. 4. (Color online) Average Voronoi volume V (□) and asphericity α (○) plotted against the local moduli (a) V and α as a function of the residual displacements $|u_x|$ (b).

$$P = \frac{1}{N}\frac{\left(\sum_i u_i^2\right)^2}{\sum_i (u_i^2)^2}, \tag{4}$$

where u_i is the residual displacement of site i and P provides a measure of the fraction of sites involved in residual displacements (or plastic events). By plotting P as a function of strain, we find that below a critical strain of $\epsilon_{xx} \approx 0.02$, P is quite small [Fig. 5(a)]. Above that critical strain, there is a sudden increase in P and it continues to rise until it reaches a plateau value at high strains. This change in the behavior of the participation ratio is compared to the residual stresses in the system as a function of strain. As shown in Fig. 5(b), we find that below the same critical strain for P, the residual stresses are negligible, implying that the material is globally elastic. Last, we examine how the sites involved in a plastic event are related. For a system of N atoms with participation ratio P, we single out the $P \times N$ sites with the largest residual displacements. By tracking the sites that have failed it becomes possible to actually observe the spatial propagation of the plastic events for a series of strains (Fig. 6). Increasing the imposed strain also increases the number of sites that have failed. At small strains we observe the aforementioned clusters, whose size increases with strain, and additional plastic events arise in the neighborhood of existing ones. Above a critical strain, which is related to a drop in the global stress, a large number of sites fail; at this point, the clusters percolate through the system. We associate this critical strain with a transition from a pseudoelastic (locally plastic) to the globally plastic regime.

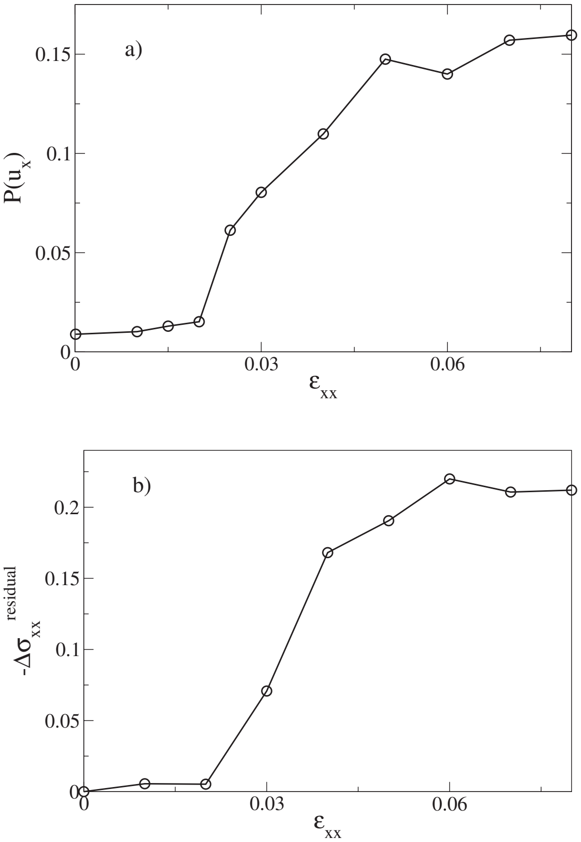

FIG. 5. (a) Participation ratio of the residual displacements over a large range of strains. (b) xx component of the residual stress as a function of strain for a series of strains encompassing a plastic event).

IV. CONCLUSIONS

The results reported in this work indicate that the regions of a polymeric glass that fail under deformation can be an-

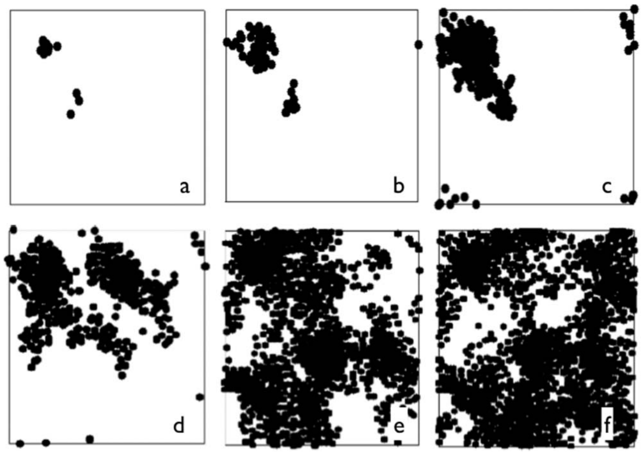

FIG. 6. Sites that failed for a series of strains 10^{-4} (a), 10^{-3} (b), 10^{-2} (c), 2.25×10^{-2} (d), 2.30×10^{-2} (e), and 3×10^{-2} (f).

ticipated from knowledge of the local elastic moduli of the material at rest, in the undeformed state, and the local structure. We note that the local moduli are not a single-particle quantity, but rather, a many-particle quantity that measures the stiffness that arises as a result of specific particle arrangements. Our findings point to a distinct connection between the molecular structure of the material and its deformation and failure under stress. Regions of low modulus are more mobile and more prone to failure than regions of large positive modulus; upon deformation, the domains of low positive modulus exhibit local plastic events at extremely small strains. As the strain is increased, more of the low-modulus regions fail and these failures percolate throughout the system. While similar phenomena have been observed in previous studies [11–16], here we have identified properties of the material at rest that can provide an indication of where the plastic events will occur. Additionally, similar structural properties related to the Voronoi volume and asphericity have been shown to correlate well with faster dynamics in glassy polymers above T_g [31–33]. The connection between structural properties and dynamic heterogeneity above T_g, taken in combination with the connection between structural properties and mechanical heterogeneity below T_g, provides evidence to the view that mechanical heterogeneity corresponds to dynamic heterogeneity that becomes frozen below T_g. This topic, including examining how we can manipulate both dynamic and mechanical heterogeneity with antiplasticizer and nanoparticle additives, is currently under investigation.

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