Mechanical testing of glassy and rubbery polymers in numerical simulations: Role of boundary conditions in tensile stress experiments

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(Received 19 December 2008; accepted 12 May 2009; published online 2 July 2009)

We use coarse-grained molecular dynamics simulations to perform tensile test deformation on glassy and rubbery polymer samples using two types of driving for the deformation. We compare the outcome from a standard homogeneous deformation procedure with that of a boundary driven procedure in which the sample is driven by the nanometric equivalent of grips. No significant difference is observed in both uniaxial and triaxial tensile experiments. Implications for testing the behavior of nonhomogeneous polymer materials are briefly discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3148381]

I. INTRODUCTION

Molecular dynamics (MD) simulations have become a standard tool to investigate the mechanical response of model polymer systems under various conditions of deformation.1–4 Despite their well known shortcomings (small system sizes and large deformation rates), they are able to give a precise description of the molecular mechanisms at work during the deformation process5 and of the changes in entanglement networks6 or to describe elastic heterogeneities.6,7

Despite their success, MD simulations are sometimes questioned in terms of their relevance to actual experiments. We already mentioned the issue of length and time scales. A third question arises from the method that is used to strain the samples, in particular when periodic boundary conditions are used. The typical MD calculation proceeds by straining the whole system at each time step in a completely homogeneous manner with an imposed deformation rate or deformation velocity. Such a procedure is clearly different from the one used in experiments in which the strain is transmitted to the sample through the imposed motion of the boundary. Indeed, homogeneous deformation procedure leads to nonphysical local stretching (small fluctuations), which could possibly be amplified for stochastic phenomena, e.g., the onset of plasticity. This is especially true in the case of glassy polymers, where the plastic deformation proceeds by individual plastic events that correspond to local instabilities of the system. Such instabilities will, generally speaking, be dependent on the precise deformation trajectory.

Another reason for interrogating the different deformation procedures is the current interest in nonhomogeneous polymeric systems, e.g., semicrystalline polymers, segregated block copolymers, or polymer nanocomposites. In such systems, the stress is transmitted from hard zones to softer zones of the material with zones that are often of nanometric dimensions. The strain in the soft part will obviously be much larger that in the hard zones, which may even be considered as nondeformable. The situation is then similar to a mechanical testing experiment at the nanometer scale, where the role of the “grips” is played by the harder zones in the composite material. In studying the deformation of the material as a whole, it is therefore interesting to understand the scale and size effects on the deformation of the softer part. To what extent can the deformation of a soft nanometric zone be described using the stress-strain relation of a homogeneously deformed bulk material of the same nature?

In order to investigate these two aspects, we have studied the deformation of glassy and rubbery polymer systems using standard periodic boundary conditions and homogeneous strain and compared the resulting stress-strain curves to those obtained using a boundary driven method. The boundary driven method introduces the molecular equivalent of grips adapted to both uniaxial and triaxial tests. The grips are identical to the deformed material in terms of interaction potentials but impose a constrained motion to the system boundary.

The next section describes sample preparation and the different deformation methods. Our results are presented in Sec. IV.

II. SIMULATION TECHNIQUES AND SAMPLE GENERATION

Our simulations are carried out for a well established coarse-grained model8,9 in which the polymer is treated as a chain of $N$ beads, which we refer to as monomers, of mass $m = 1$ connected by a spring to form a linear chain. The beads interact with a classical Lennard–Jones interaction...
Cooling and relaxation are achieved in a method,11 which is an extension of Gao’s work.12 The whole system is relaxed during 300 MD steps between each growth step is studied. A larger value of kBT˙ leads to better equilibrated systems, which MSID fits nicely with FPO and the target function of Auhl et al. (Ref. 13).

\[ U_{\text{FENE}}(r) = \begin{cases} -0.5kR_0^2 \ln(1-(r/R_0)^2), & r \leq R_0 \\ \infty, & r > R_0, \end{cases} \]

where the cutoff distance \( r_c = 2.5\sigma_{ab} \). In addition to Eq. (1), adjacent monomers along the chains are coupled through the well known anharmonic finite extensible nonlinear elastic (FENE) potential

where the virial stress is used to measure the true stress of our systems. The thermal contribution is small and can be neglected at these densities and temperatures.

Newton’s equations of motion are integrated with velocity-Verlet method and a time step of \( \Delta t = 0.006 \). Periodic simulation cells of cubic size \( L \) containing \( M \) chains of size \( N \) were used under a Nosé–Hoover barostat, i.e., in the N-V-T ensemble. The pressure is fixed to \( P = 0.5\sigma^3 \).

Our specimens are prepared using radical-like polymerization method,11 which is an extension of Gao’s work.12 Chains grow in monomer bath at \( k_B T = 2\epsilon \) and \( P = 0.5\epsilon/\sigma^3 \). The whole system is relaxed during 300 MD steps between each growth step, and polymerization is stopped when chains reach the chosen length of \( N = 200 \) beads. Remaining single beads (solvent) are then removed, and the resulting melt is equilibrated during \( 10^5 \) MD steps in N-P-T ensemble at low compressive pressure of \( P = 0.5\epsilon/\sigma^3 \) (see Ref. 11 for more details). Figure 1 shows a good agreement between the normalized mean square internal distance (MSID) compared to the target function published by Auhl et al.13

Rubbery and glassy states are obtained by cooling to \( k_B T = 0.5\epsilon \) and \( k_B T = 0.2\epsilon \), respectively. With a cooling rate of \( k_B T = -1.6 \times 10^{-3} \epsilon/\tau_{LJ} \), the glass transition temperature is equal to \( k_B T_g = 0.43\epsilon \). Finally, an isothermal relaxation is applied to reach zero pressure at a rate of \( P = 8 \times 10^{-5} \epsilon/\sigma^3 \tau_{LJ} \). Cooling and relaxation are achieved in N-P-T ensemble. The resulting glass and rubber have densities of \( \rho_{\text{glass}} = 1.07\sigma^3 \) and \( \rho_{\text{rubber}} = 1.02\sigma^3 \), respectively.

III. METHODOLOGY: TRIAXIAL AND UNIAXIAL TENSILE TESTS

A. Homogeneous deformation technique

The most common method used to strain a polymer specimen in numerical simulation is the homogeneous affine deformation.2–4,14 This technique is a finite sequence of two steps: Deformation and relaxation. The deformation is imposed by modifying the simulation cell size in one or more direction and remapping all beads to the new box by a simple rescaling of all coordinates. The simulation box can be deformed at a constant elongation rate (constant velocity)5 or nonlinear logarithmic strain rate.2 Depending on the nature of load, homogenous tensile test allows one to modify the loading condition by controlling the amount of deformation in the three directions independently.

Axisymmetric triaxial tests—called hereafter triaxial tests—are performed by deforming the simulation box in only one direction (the tensile direction, say, \( y \)), the two other dimensions remaining constant. The relaxation MD steps are integrated in the N-V-T ensemble (Nosé–Hoover thermostat—rate of 0.1\( \tau_{LJ} \)). The magnitude of the pressure tensor components in triaxial tests obeys the relation \( |P_{yz}| > |P_{xy}| > |P_{zz}| > 0 \).

Uniaxial tests are performed by deforming the simulation box in one direction (the tensile direction, say, \( y \)), the two other dimensions varying so that the pressure remains equal to zero in these directions. The relaxation MD steps are integrated in NL\( y \), \( P_x P_z \) ensemble with anisotropic barostat, which controls pressure only in \( x \) and \( z \) directions independently [Nosé–Hoover thermostat and barostat rates of 0.1\( \tau_{LJ} \) (Refs. 15 and 16)]. The magnitude of the pressure tensor components in uniaxial tests obeys the relation \( |P_{xy}| > |P_{xx}| \).

The virial stress is used to measure the true stress of our systems. The thermal contribution is small and can be neglected at these densities and temperatures.

Albeit natural, the homogenous affine method has some restrictions. The deformation is applied without respecting the bond strengths. In some case, particularly near the yield stress, this might activate violent motions or even break some high energetic stretched FENE bond.

B. Boundary driven deformation technique

1. Triaxial tensile test

In order to simulate a tensile test in a way that is analogous to a macroscopic experiment, we propose a method in which the deformation is applied first at boundaries and is then transmitted to the core of the sample by the material itself. To achieve this boundary driven deformation, we first remove the periodic boundary condition on the tensile axis (say, \( y \)-axis), keeping the two other directions periodic. The grips are set to be the top and bottom parts of the sample (of size \( L_y \) in the \( y \)-direction), each of them having a thickness of 2.6\( \sigma \) (see Fig. 2),

\[ y < 2.6\sigma \rightarrow \text{lower grip}, \]

\[ 2.6\sigma < y < L_y - 2.6\sigma \rightarrow \text{gage length}, \]
y > L_y = 2.6\sigma \rightarrow \text{upper grip.} \quad (5)

Forces acting on the beads belonging to the grips are set to zero. The initial velocity of lower and upper grip beads are set to zero and \( v_0 \), respectively. The lower grip is then an immobile rigid body, and the upper grip is submitted to a constant velocity as a rigid body. This velocity is adjusted to get the desired strain rate at initial time \( v_0 = \epsilon_0 L_y \). During the tensile test, the motion of the beads inside the loaded part of the sample is integrated in a \( N-V-T \) ensemble (Nosé-Hoover thermostat); \( N-V-E \) ensemble is employed to drive the motion of the grip. The volume of the loaded part \( L_x(L_y - 5.2\alpha)L_z \) is used to compute the stress within the sample.

As chain breaking is not possible due to FENE bonds, it has been checked in each simulation that no chains are held by two opposite grips simultaneously. Note that with the boundary driven deformation method, as applied here on a triaxial tensile test, the deformation is limited to a single direction.

2. Uniaxial tensile test

In uniaxial deformations, the dimensions of the simulation box have to be relaxed in the directions perpendicular to the tensile direction \( 14,18,19 \) in order to fulfill the condition \( P_{xx} = P_{zz} = 0 \). Such a relaxation is not possible when using the grips of the triaxial case that behave as rigid bodies.

A naive solution would be to zero the component of the force parallel to the traction axis (\( F_y = 0 \)) for all atoms belonging to the grips and to apply the same velocity conditions as for the triaxial test (\( v_y = 0 \) for the lower grip and \( v_y = v_0 \) for the upper grip). However, this would lead to a very high rigidity of the grips, as their atoms would be constrained to stay in a plane perpendicular to the traction axis.

A linearly increasing force could also be applied to all beads of both grips. \( N-P-T \) integration with zero lateral pressure would then lead to a uniaxial tensile test. However, it would be a force-controlled tensile test, which is not well adapted to polymers exhibiting softening after the yield. This softening would lead to instabilities in such force-controlled tensile test.

The technique used in this paper is inspired from the work of Izrailev et al., who suggested a way of extracting a ligand from the binding pocket of a protein by the use of steered molecular dynamics (SMD). The basic idea of SMD is to restrain the ligand to a point in space (restraint point) by an external, e.g., harmonic, potential.

In our case, instead of setting the force on grips beads to zero, we add a force to all beads of the grips such that the mean velocity of all these beads is the desired one: 0 for the lower grip and \( v_0 \) for the upper grip (\( e_y \) is the unit vector in \( y \) direction). The external force applied to all beads of upper and lower grips is given by

\[
F^u = -K[r^u_{\text{com}}(t) - r^u_{\text{com}}(0) - v_0 e_y],
\]

(6)

\[
F^l = -K[r^l_{\text{com}}(t) - r^l_{\text{com}}(0)],
\]

(7)

where \( r^u_{\text{com}}(t) \) and \( r^l_{\text{com}}(t) \) are the positions of the upper and lower grip centers of mass at time \( t \). Equation (6) forms a feedback loop on the force applied to the upper grip. The specimen is therefore submitted to \( N-V-T \) conditions. Figure 2 shows the deformation methods used in both uniaxial and triaxial tensile tests. To ensure a zero lateral pressure, Verlet integration is performed in \( N-P-T \) ensemble for all beads in \( x \) and \( z \) directions. As a consequence, at each MD step, the motion of the restrained points induces a force on all beads of both grips, leading to a boundary driven deformation-controlled uniaxial tensile test.

The stiffness \( K \) of the springs has to be optimized. A too small value would lead to a loose spring absorbing all the deformation in place of the sample, and a too large value would lead to numerical instabilities (due to high forces applied on grip beads; see Fig. 4). A spring ten times as stiff as the initial sample leads to a numerically stable deformation scheme; this value will be kept in the following.

There are two ways of calculating the stress experienced by the gauge length (or working zone) of the sample:

(i) divide the force of the spring (\( F^u \) or \( F^l \)) by the instantaneous surface of the sample (\( L_x L_z \)) perpendicular to the traction axis and

\[
\sigma_x = \frac{F^u}{L_x L_z}.
\]

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(ii) compute the virial stress of the gauge length beads and divide it by the instant volume of the working zone.

The first method is simpler, but as it is averaged on few beads, it leads to a noisier measure of the stress. The second method requires the gauge length $L_g$, which has been assumed to be proportional to the distance between upper and lower grips center of mass at time $t$ $d(t)$ over the same distance at time $t=0$, leading to the volume of the working zone,

$$V_{WZ} = L_g L_x L_z = \left[\frac{d(t)}{d(0)}\right] L_y (5.2\sigma)L_x L_z.$$

In order to check the accuracy of the former equation, $V_{WZ}$ has been also calculated by a layer analysis at different deformation stages; the sample is divided in bins along the $y$ axis, and an analysis is made from the local concentration (in each layer) of grip beads and gauge length beads. This analysis leads to concentration profiles from which it is possible to measure the gauge length: Distance between the two inflexion points (as shown in Fig. 3). This analysis, performed for several states of strain allowed us to validate the expression of the working zone volume [Eq. (8)].

Figure 4 compares the stress obtained from the forces on springs or from the virial. For the values of the spring stiffness used in this work, these two measures are exactly equivalent. In what follows, the virial stress will be used preferentially as it is less noisy.

Figure 5 shows the time averaged velocity (averaged from initial to actual time) of upper grip center of mass during a tensile test performed in $10^7$ MD steps. It gives exactly the target value of 0.00223$\sigma/\tau$. In order to compute the appropriate temperature of any isothermal ensemble under deformation, the drawing velocity contribution is eliminated before computing the temperature.

### C. Effect of deformation rate

In order to model as realistic tensile tests as possible, we have to ensure that the deformation velocity is small compared to the sound velocity. The typical sound velocity here is of the order of $\sqrt{E'/\rho} \approx 10\sigma/\tau$, where $E'$ is the principal modulus. If the velocity of the upper grip is small compared to this sound velocity, the imposed deformation will redistribute throughout the sample nearly “instantaneously,” as the homogenous method does.

This condition might not be valid anymore for higher deformation rates. To illustrate this particular point, we plotted in Fig. 6 the response of the sample submitted to (i) boundary driven deformation and (ii) homogenous deformation performed at a drawing velocity of $5\sigma/\tau$. It can be observed in this figure that the mechanical behavior of the

![Figure 3](image-url)  
**FIG. 3.** Concentration profile of the sample deduced from layer analysis: The $L_g$ (gauge length) is defined as the distance between the two inflexion points of the working zone beads concentration profile.

![Figure 4](image-url)  
**FIG. 4.** Stress-strain curves (boundary driven deformation uniaxial tensile tests) at $k_B T = 0.2\epsilon$ using various spring stiffness; $r$ is the ratio of the spring stiffness over the sample stiffness. The line is the viral stress divided by the working zone volume [Eq. (8)]. Points (c) correspond to stress computed by the spring length. Both techniques lead to similar results.

![Figure 5](image-url)  
**FIG. 5.** Boundary driven deformation: Distance between upper and lower grips center of mass (COM) vs time. Secondary axes: Time averaged velocity of upper grip COM with respect to lower grip COM and target velocity (0.00223$\sigma/\tau$). The mean velocity is very close to the target velocity, thus validating the uniaxial tensile technique.
sample is completely different, depending on the solicitation method. All the deformation is indeed localized near the upper grip for the boundary driven deformation method, whereas it is homogeneously distributed with the homogeneous method, which is obviously unphysical. In the following, all results will be presented for the low deformation rate (0.00223σ/τ), which is negligible compared to the speed of sound.

IV. RESULTS: TENSILE TESTS

The aim of this section is to compare the homogeneous and boundary driven deformation techniques presented in the previous section. Tensile tests are performed on 12 different cubic samples at two temperatures: $k_B T=0.2\epsilon$ (glassy state) and $k_B T=0.5\epsilon$ (rubbery state) (see Sec. II). Stress-strain curves, as well as yield stress and associated strain, are investigated.

A. Uniaxial deformation

1. Glassy state

The uniaxial tensile test performed on a glassy polymer specimen typically proceeds in three stages: The stress rises to a maximum, which for our system is located at a strain $\epsilon_{yy}=0.05$. In accordance with other previous studies it was found that the total deformation is completely recovered for $\epsilon_{yy}=0.02$ after removing the deformation or load constraint. This value can be taken as the limit of the elastic region (at least at a mesoscopic scale, as local irreversibility is known to take place below this value). The deformation leaves some hysteresis when the sample is deformed beyond this value and relaxed.

From the elastic regime we extract a Young’s modulus of $E=38.9 \pm 0.1\epsilon/\sigma^3$ and a Poisson ratio of $\nu=0.36 \pm 0.02$, which are in good agreement with other works using the same flexible model. The maximum is identified with a yield stress $\sigma_{y_{yy}}=1.28 \pm 0.02\epsilon/\sigma^3$, which marks the onset of plastic flow. The yield is followed by a smooth decrease in the stress (strain softening) until the stress becomes essentially constant, $\sigma_{\text{flow}}=1.08 \pm 0.02\epsilon/\sigma^3$.

The third part of the stress-strain curve is the so-called “strain hardening” regime associated with the debonding of the entanglement network. This part of the curve can be modeled by the Gaussian strain hardening expression as

$$\sigma_{yy} = \sigma_{\text{flow}} + G_R g(\lambda).$$

$G_R$ is the hardening modulus, $g(\lambda)=\lambda^2-1/\lambda$, and $\lambda=y_0/y_0$ is the elongation in y direction [true strain $\epsilon_{yy}=\ln(\lambda)$]. The stress-strain curves were plotted with $\epsilon_{yy}$, and $g(\lambda)$ in Fig. 7 show a nice fitting of the strain hardening regime to Eq. (9). However, as was extensively discussed in a recent work by Hoy and Robbins, the value of the hardening modulus $G_R$ is much larger than the value that would be expected from an elastic model of the entanglement network at this temperature.

Figure 8 compares stress-strain curves resulting from homogeneous and boundary driven deformations techniques. In the glassy state ($k_B T=0.2\epsilon$), the two curves are completely superimposed. Despite removing the periodic boundaries in

![FIG. 6. High speed (drawing velocity of 5σ/τ) tensile test: triaxial tensile test applied to a glassy specimen by using different methods; the mechanical responses are very different. Snapshots at a strain of $\epsilon_{yy}=1.4$ show that homogeneous deformation (right) results in an unphysical ductile behavior compared to the localized deformation when grips are used (left), which is more realistic.](image1)

![FIG. 7. Stress-strain curves of uniaxial tensile test plotted vs true strain (upper axis) and $g(\lambda)$ (lower axis). The strain hardening regime is fitted linearly by the Gaussian expression [Eq. (9)] of strain hardening, $\sigma_{yy}=1.08+0.1346 g(\lambda)$, see Sec. II.](image2)

![FIG. 8. Behavior curves of uniaxial tensile test glassy ($k_B T=0.2\epsilon$) and rubbery ($k_B T=0.5\epsilon$) specimen. A zoom of the yield region is shown in the inset. No significant differences can be observed. The two snapshots correspond to a true strain of 1.5 at $k_B T=0.2\epsilon$.](image3)
TABLE I. Some mechanical properties measured all stress-strain curves. Uncertainties represent the variations observed for six different samples. Bound. dri.: boundary driven tests. Homog. def.: homogenously deformed tests.

<table>
<thead>
<tr>
<th></th>
<th>$k_B T=0.5\varepsilon$</th>
<th></th>
<th>$k_B T=0.2\varepsilon$</th>
<th></th>
<th>$k_B T=0.01\varepsilon$</th>
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<tbody>
<tr>
<td>Yield stress ($\sigma/\sigma^0$)</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
<td>1.33 $\pm$ 0.02</td>
<td>1.3 $\pm$ 0.03</td>
<td>1.8 $\pm$ 0.04</td>
</tr>
<tr>
<td>Yield strain</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
<td>0.06 $\pm$ 0.02</td>
<td>0.05 $\pm$ 0.01</td>
<td>0.06 $\pm$ 0.01</td>
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<tr>
<td>Poisson ratio $\nu$</td>
<td>0.49 $\pm$ 0.01</td>
<td>0.48 $\pm$ 0.03</td>
<td>0.41 $\pm$ 0.01</td>
<td>0.4 $\pm$ 0.02</td>
<td>0.41 $\pm$ 0.01</td>
</tr>
<tr>
<td>Young’s modulus $E$ ($\sigma/\sigma^0$)</td>
<td>0.19 $\pm$ 0.01</td>
<td>0.21 $\pm$ 0.01</td>
<td>39.1 $\pm$ 1.7</td>
<td>37.9 $\pm$ 1.7</td>
<td>49.1 $\pm$ 1.8</td>
</tr>
</tbody>
</table>

### 2. Rubbery state

The same procedures were applied to perform uniaxial tensile tests in the rubbery region of our polymer model at $k_BT=0.5\varepsilon$. Compared to the glassy state, the rubbery state has a much weaker elastic response regime. This response can be fitted with a rubber modulus that is about from two to three orders of magnitude below the glassy modulus and a Poisson ratio very close to 1/2, as expected from a rubber. Strain recovery after a strain of 0.8 is about 0.18.

As shown in Fig. 8 homogeneous and boundary driven deformation techniques lead to the same behavior. The test has then repeated on all specimens and again no significant differences were found.

It may seem surprising that the boundary driven deformation technique and the homogeneous deformation technique give such similar results. In fact periodic boundary conditions were originally introduced in order to minimize boundary effects for thermodynamic properties. Here, our results show on the one hand that the possible shortcomings of homogeneous deformation (i.e., an exaggerated deformation of the intramolecular bonds) can be ignored, and on the other hand the boundary effects have negligible influences on the mechanical properties. This result is obtained with grips that have somewhat artificial properties in the sense that they are allowed to deform freely in the same manner as the working zone in the direction transverse to the traction. In the following, we consider the more realistic case of a triaxial deformation with grips that do not follow the deformation of the sample.

### B. Triaxial deformation

#### 1. Glassy state

Triaxial tensile tests were also performed using boundary driven and homogeneous deformation techniques. The stress-strain curves obtained with each method are plotted in Fig. 9 showing different regimes. As in uniaxial tensile tests, the stress first rises to $\sigma_{yield}=4.2 \pm 0.08\varepsilon/\sigma^0$; the elastic modulus of $E'=80.35 \pm 1.3\varepsilon/\sigma^0$ is consistent with other pre-

![Stress-strain curves](image-url)
rious works and with the one predicted from the Young’s modulus and Poisson ratio obtained in uniaxial tests, \( E_p = \frac{1}{1 - \nu^2} \). At the yield point the polymer failure starts, voids nucleate, and the stress becomes localized and carried by polymer “fibris”. After these fibris or crazes are formed, the stress becomes essentially a constant drawing stress of \( \sigma_{\text{drawing}} = 0.95 \pm 0.05/\sigma^2 \). The plastic flow proceeds at this constant stress value with a progressive transformation of the bulk polymer into a fibril network connected by entanglements. When the entire bulk is completely transformed into crazes, the stress would eventually rise again, as the chains align in the direction of traction.

Stress-strain curves resulting from each deformation method are nicely superposed as displayed in Fig. 9. Again the agreement is essentially perfect, and the craze development, as shown in the corresponding snapshots, proceeds in a very similar manner. The small differences at the yield point are of purely statistical origin, as they are smaller than the difference between two different samples tested with the same method, with different widening directions.

2. Rubbery state

The rubbery specimen behaves in a very similar manner as the glassy specimen. However, the high temperature favors yield at a lower stress of \( \sigma_{\text{yield}} = 2.15 \pm 0.03/\sigma^2 \), and the drawing stress falls to \( \sigma_{\text{drawing}} = 0.15 \pm 0.05/\sigma^2 \). Despite the high temperature, the specimen exhibits the same behavior as the low temperature one. This is due to applied triaxial stress that prevents any relaxation of stress. Thus, failure starts by crazing instead of shearing. The two methods are compared in Fig. 9 (right). Once again, a nice agreement is observed.

V. CONCLUSIONS

Table I summarizes the elastic and yield properties obtained in this work at various temperatures and solicitations using the homogeneous deformation and the boundary driven methods. In the homogeneous deformation technique, a periodic sample is stretched by deforming the fully periodic simulation box size. In the boundary deformation technique, periodicity is partially cleared and molecular grips are introduced to deform the sample by moving its ends apart.

Our main conclusion is that the two techniques yield perfectly consistent results and that the uniaxial and triaxial tests result in a consistent determination of linear elastic properties. This similarity between homogeneous and boundary driven methods was not a priori expected. In general, boundary effects are important for thermodynamic and dynamic properties of small systems. Bulk properties can be obtained from simulations of such systems through the use of periodic boundary conditions. Our results show that the mechanical testing of glassy or rubbery polymer is not affected by the presence of rigid (in triaxial tests) or “soft” (uniaxial case) grips. Both the elastic and plastic responses are equivalent. The similarity of the plastic response also indicates that the artificial aspect of the homogeneous deformation methods in which intramolecular bonds are deformed affinely at each step does not introduce any statistical artifact in the activated events that constitute the plastic flow.

Finite element modeling of complex materials is based on the notion of elementary representative volumes with local mechanical properties that can be described by stress-strain curves determined at the macroscopic level. Our results show that this notion of elementary representative volume can in fact be applied to extremely small systems. Here the glassy polymer constrained between the molecular grips behaves exactly in the same way as the “bulk” polymer represented by a sample with periodic boundary conditions and could therefore be modeled using the same constitutive equation.

Finally, we conclude that the use of nonperiodic boundary conditions could be advantageous for the simulation of complex heterogeneous samples. For example, simulating an ABC triblock copolymer in its lamellar phase requires four lamellae (ABC stacking) if periodic boundary conditions are used, while an ABC stack is sufficient in the boundary driven case.

ACKNOWLEDGMENTS

Computational support by the Federation Lyonnaise de Calcul Haute Performance is acknowledged. Part of the simulations was carried out using the LAMMPS MD software (http://lammps.sandia.gov). Financial support from ANR Nanomeca is also acknowledged.

17. The grips’ thickness must be larger than the cutoff radius to guarantee that all beads (especially those nearest to interface with the grip) have a similar environment.
21. Recovery is performed by zeroing the spring forces \( F^x \) and \( F^y \) and relaxing the sample in the anisotropic \( N-P-T \) ensemble for the grip method.
For homogenous method only relaxation in anisotropic $N$-$P$-$T$ ensemble is required.


