Monte Carlo Simulation of Uniaxial Deformation of Polyethylene-Like Polymer Glass: Role of Constraints and Deformation Protocol

Tim Mulder,* Jing Li, Alexey V. Lyulin, Matthias A. J. Michels

The deformation of a glassy amorphous polymer has been simulated by Monte Carlo. A molecular model with constrained chemical bonds (rigid-bond model) and one with chemical bonds represented by Gaussian springs (flexible-bond model) have been compared. Furthermore, two different deformation protocols have been tested. Comparisons on the basis of stress–strain behavior, contributions of various interactions to stress and energy, evolution of density and distribution of dihedral angles, and of pair correlation functions show that both the introduction of constrained bonds and the deformation protocol influence the results dramatically. The results obtained using the flexible-bond model, employing a deformation protocol in which all the monomers are displaced affinely with the box size, show the best agreement with experimental facts.

Introduction

The mechanical behavior of glassy amorphous polymers during deformation is a long-standing problem in polymer science. Many experimental and theoretical studies have been performed to investigate phenomena such as strain softening and strain hardening.[1–11] In a later stage, computer simulations started to be employed as well to investigate the deformation of glassy polymers at a molecular level.[12–16] One of the first publications on molecular simulations of glassy polymers under mechanical deformation concerns the work of Brown and Clarke,[12] who performed detailed molecular dynamics (MD) computer simulations of an amorphous polyethylene (PE)-like melt under uniaxial tension. With a tension rate of the order of $10^9 \text{ s}^{-1}$ and time scales up to 1 ns, they found similar elastic deformation, yield and plastic-flow behavior at low temperatures as observed in the laboratory on time scales that are many orders of magnitude longer. In spite of problems such as small system sizes and huge cooling and deformation rates, MD has proved to be a useful tool in studying deformation behavior of amorphous polymers.[12,15,16] Although Monte Carlo (MC) simulation does not contain any dynamics, this tool is also starting to be used for the study of polymer deformation.[17–22] Various lattice-model MC simulations have
been used to study the deformation behavior of polymeric models.\textsuperscript{[19–22]} 3-D off-lattice MC simulations of PE-like crosslinked networks have been performed by Chui and Boyce.\textsuperscript{[17]} The authors of the present paper recently simulated the uniaxial extension of multichain PE-like systems employing a mix of very local atomic and more collective MC moves.\textsuperscript{[18]}

In many simulations of deformation, the strain is prescribed by changing monomer positions affinely with the box size.\textsuperscript{[15,17,18,23]} Such a simulation protocol is not very efficient for polymers since it affects the hard degrees of freedom of the polymer molecules, i.e., bond length and valence angles. Changes in these hard degrees of freedom occur in very short time scales and simulating them requires a lot of computational resources.\textsuperscript{[24]} By using constraints such as rigid (infinitely stiff) chemical bonds and bond angles, the simulation of the deformation process can be speeded up. For simulation of deformation this means that one has to use a deformation protocol that keeps bond lengths and bond angles constant. The easiest way to do this is by changing the relative positions of the polymer chains, without changing the relative positions of monomers within the same chain. The consequences of introducing constraints and of changing the deformation protocol, which are not very well documented in literature yet, form the subject of the present study.

To gain some insight into the consequences of the introduction of constraints or of the deformation protocol, we have performed MC simulations of PE-like systems of 25 polymer chains with an average degree of polymerization of 200, in the NpT ensemble. MC simulations, using connectivity-altering moves,\textsuperscript{[25]} have been performed to produce well-equilibrated initial samples: both samples with flexible bonds (bonds represented by Gaussian springs) and samples with rigid bonds (bond represented by a rod with a fixed length). The behavior of samples with rigid bonds (the rigid-bond model) and that of samples with flexible bonds (the flexible-bond model) have been compared during deformation, employing a deformation protocol in which the relative positions of chains are altered. Furthermore, deformation of a flexible-bond system by changing monomer positions affinely with the box size has been compared to the deformation of the same system by changing the relative positions of chains. For the different models and deformation protocols, the comparisons have been made on the basis of stress–strain curves and density–strain curves as well as on stress partitioning and energy partitioning, i.e., the contributions of different interactions to the stress and to the internal energy of the system.

The paper is organized as follows: in the next section, the model, the MC algorithms, the stress calculation and other relevant details of the simulation method are explained. All the results concerning the preparation and equilibration of initial samples as well as the uniaxial deformation via various constraint conditions and deformation protocols are extensively discussed in the Results and Discussion section. Finally, conclusions are drawn in the Conclusion section.

### Model, MC Algorithms and Stress Calculation

In the present study a united-atom model of PE is used, in which each CH$_2$-group is considered as a bead with its mass centered at the carbon atom of the backbone. Total 5 000 beads (monomers) are contained in an orthorhombic box of about 50 Å with periodic boundary conditions\textsuperscript{[24,26]} containing 25 chains with a number-averaged degree of polymerization $X = 200$. The chain-length distribution is uniform in the interval from 0.5 to 1.5$X$. In case of the flexible-bond model, the monomers interact via a force field that employs a harmonic bond-stretching potential, a harmonic angle-bending potential for the valence angles, the Ryckaert-Bellemans potential for dihedral angles and a Lennard-Jones-type potential for nonbonded interactions. The monomers in the rigid-bond model interact via the same force field without the harmonic bond-stretching potential. Further details on the various contributions to the force fields are given in Table 1.

### Table 1: Force field.

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>Functional form</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond stretching</td>
<td>$U_l = \frac{1}{2} k_l (l - l_0)^2$</td>
<td>$k_l = 1.674 \text{kJ} \cdot \text{Å}^{-2} \cdot \text{mol}^{-1}$, $l_0 = 1.54 \text{Å}$</td>
</tr>
<tr>
<td>Angle bending</td>
<td>$U_\theta = \frac{1}{2} k_\theta (\theta - \theta_0)^2$</td>
<td>$k_\theta = 481.8 \text{kJ} \cdot \text{rad}^{-2} \cdot \text{mol}^{-1}$, $\theta_0 = 1.955 \text{rad}$</td>
</tr>
<tr>
<td>Torsion</td>
<td>$U_\phi = \sum_{k=0}^5 c_k \cos^k(\phi)$</td>
<td>$c_0 = 9.279 \text{kJ} \cdot \text{mol}^{-1}$, $c_1 = 12.16 \text{kJ} \cdot \text{mol}^{-1}$, $c_2 = -13.12 \text{kJ} \cdot \text{mol}^{-1}$, $c_3 = -3.060 \text{kJ} \cdot \text{mol}^{-1}$, $c_4 = 26.24 \text{kJ} \cdot \text{mol}^{-1}$, $c_5 = -31.49 \text{kJ} \cdot \text{mol}^{-1}$</td>
</tr>
<tr>
<td>Nonbonded</td>
<td>$U_{UL} = 4\varepsilon \left(\frac{r}{\sigma}\right)^{12} - \left(\frac{r}{\sigma}\right)^{6}$</td>
<td>$\varepsilon = 0.410 \text{kJ} \cdot \text{mol}^{-1}$, $\sigma = 3.94 \text{Å}$</td>
</tr>
</tbody>
</table>
The evolution of the system is realized by a mix of six types of MC moves (see Figure 1) including flip, end rotation, concerted rotation (CONROT), reptation (REP), end bridging (EB) and volume fluctuation, which have all been explained in ref.\textsuperscript{[18]} Flip, end rotation and CONROT are local-scale moves where only 4–9 monomers are involved, while REP, EB and volume fluctuation are large-scale moves which concern the displacement of whole chains or displacement of all the monomers in the system. All the moves are in principle the same for both the flexible-bond model and the rigid-bond model, except the volume-fluctuation move. During a volume-fluctuation move, the size of the box is changed in one of the directions $x, y$ or $z$. In case the flexible-bond model is used, either the coordinates of all the monomers in the box are changed affinely with the box size or the centre-of-mass (COM)-coordinates of the chains are changed; in the latter case the bond lengths and bond angles are not changed during a volume-fluctuation move. In case the rigid-bond model is used, only COM coordinates of chains are changed affinely with the box size, so that the bond lengths and bond angles are always maintained constant during a volume fluctuation.

The initial sample is prepared by constructing polymer chains, one after the other, inside the box with periodic boundary conditions. The individual chains are created by placing the first monomer at a random position inside the box and then successively attach the other monomers to the chain. A new monomer is added in such a way that the bond length, whereas the newly introduced bond angle and dihedral angle are selected from the Boltzmann distribution determined by their respective potentials. During the process of sample preparation hard-sphere overlap (the situation in which the distance between monomers is so small that their potential energy is much larger than $k_BT$) is prevented.

It is proved by Theodorou and co-workers\textsuperscript{[27]} that fast equilibration of PE in the melt can be well achieved with the combination of the moves mentioned above. In the present study we use a mix of moves similar to the one Theodorou used\textsuperscript{[27]} both for the equilibration of our PE samples at melt temperature and for subsequent cooling to temperatures below the glass transition. After cooling, the samples are deformed by stepwise deformation of the box size in one direction and changing either the monomer positions affinely with this box size or the positions of the COMs of chains affinely with this box size. The REP and EB moves are switched off during deformation, to avoid a direct intervening in the slowest processes (that take place on time scales that also exceed experimental timescales of the order of seconds or larger), other moves are performed in the same proportions as during equilibration. Further details on the equilibration, cooling and deformation are given below in the Results and Discussion section.

The stresses in the flexible-bond model are calculated from the standard atomic stress expression\textsuperscript{[26,28]}

$$
\tau_{\alpha\beta}^\alpha = \left\langle \sigma_{\alpha\beta} \right\rangle = -\frac{N_s k_B T \delta_{\alpha\beta}}{V} - \frac{1}{V} \sum_i \sum_j \left( F_{ij}^\alpha - F_{\text{min}}^\alpha \right) F_{ij}^\beta_{\text{min}}
$$

(1)

where $\tau_{\alpha\beta}^\alpha$ is the component of stress, $\sigma$ denotes the instantaneous mechanical quantity whose average gives the thermodynamic stress $\tau$ and the subscript $\alpha$ indicates that the stress is calculated on the basis of interactions between atoms. $N_s$ is the number of atoms (or monomers), $k_B$ the Boltzmann constant, $T$ the system temperature, $\delta_{\alpha\beta}$ the Kronecker delta, $V$ the system volume. $r_i$ is the position vector of atom $i$, $F_{ij}^\alpha$ is the force on atom $j$ with respect to atom $i$ and $F_{\text{min}}^\alpha$ is the force on $i$ due to the interaction with $j$, $F_{\text{min}}^\alpha$. Bonded and nonbonded forces $F_{ij}$ can readily be calculated from the system’s potential energy $U$ at any moment during the MC simulations by using $F_{ij} = -\nabla_{r_i} U$. Thus, the atomic stress can be explicitly calculated in the flexible-bond model.

Such a calculation of the atomic stress is not possible anymore when the rigid-bond constraint is introduced. To calculate the constraint forces one needs the atomic accelerations, which are not available in MC. Thus, the
atomic stress expression, Equation (1), is unsuitable for the rigid-bond model. A molecular analogue of the double summation form, Equation (1), has been invoked in equilibrium and nonequilibrium MD calculations,[29,30] with indices $i$ and $j$ labeling molecular COM. This approach is correct as long as no periodic boundary conditions are used or for simulations of systems of monatomic molecules. In simulations of polymer systems with periodic boundary conditions, the approach of ref.[29,30] is inadequate, since in general the periodic box contains (parts of) more than one image of the same chain; all interactions between images of either different or the same molecules inside the periodic box have to be taken into account explicitly.[28] To calculate the thermodynamic stress $\tau$ in model systems with periodic boundary conditions, Theodoreu et al.[28] suggested a molecular stress expression (it does not require knowledge of bonded forces) in which all these interactions are taken into account

$$
\tau_{\text{NB}} = \left( \frac{N_m k_B T \delta_{ij}}{V} \sum \sum_{i} \left( r_{\text{cm},c(i)} - r_{\text{cm},c(j_{\text{min}}(i))} \right) \right) F_{\text{NB};\text{min}}
$$

(2)

where $N_m$ is the number of polymer chains of the system, $i$ refers to atom $i$ and $j_{\text{min}}(i)$ to the minimum image of atom $j$ with respect to atom $i$, $c(i)$ indicates the chain image to which atom image $i$ belongs and $r_{\text{cm},c(i)}$ denotes the COM position of chain image $c(i)$. The subscript $m$ means that the stress calculation is based on interactions between molecules and the superscript NB denotes nonbonded interactions. Further details can be found in ref.[28] In the remaining sections of the paper, the calculation of stress is based on Equation (1) and (2).

**Results and Discussion**

**Equilibration at 450 K**

The initial PE sample is first equilibrated in the $NpT$ ensemble at an external pressure of 0.1 MPa and at a temperature of 450 K, which is above the experimental melting temperature for this polymer. A mix of MC moves with different attempt probabilities is used, similar to that used by Mavrantzas et al.[27] 6% REP, 6% end rotation, 6% flip, 32% intrachain rebridging, 49% end bridging and 1% volume fluctuation.

It is shown in Figure 2 that density and total energy are equilibrated after $2 \times 10^3$ MCS, where 1 MCS (Monte Carlo step) is the number of attempt moves divided by the total number of monomers in the system. The pressure reaches its equilibrium value after $\approx 10^2$ MCS. The final values of the density and the total energy are different for the two models. It can be seen from Figure 2(c) that the pressures in both models show the same fluctuation of about 50 MPa. In the flexible-bond model these pressure fluctuations are caused by fluctuations of bond lengths during volume fluctuations (monomer positions are changed affinely with
the box size), whereas in the rigid-bond model they are caused by fluctuations in the strength of intermolecular nonbonded interactions (relative positions of chains are changed).

The occurrence of these differences in the physical quantities according to the different models, shown in Figure 2, is almost inevitable. Since the purpose of this study was to determine the influence of the introduction of constrained bonds into the model, only the part of the force field that controls the bond lengths had to be changed. However, physical quantities are determined by all the interactions in the system. If one type of interaction, e.g., the one controlling the lengths of chemical bonds, is changed, without any compensatory changes of other interaction type(s), the result will almost certainly be a change of the physical properties of the system.

Cooling to 200 K

After the equilibration at 450 K, the cooling process is conducted by gradually cooling down the PE sample at the rate of 0.05 K·MCS⁻¹ (≈10¹¹ K·s⁻¹, see ref.[18]) to the target temperature of 200 K, followed by equilibration at that temperature.

As the temperature decreases the density increases, whereas the total energy decreases, as shown in Figure 3. The fast responses last until the cooling stops after 5×10⁵ MCS, after which the sample keeps on equilibrating at 200 K. It can be observed from Figure 3 that the density (total energy) keeps increasing (decreasing) after the cooling stops, and that the density (total energy) in the rigid-bond model shows a faster increase (decrease). Based on previous studies,[18] we assume that the final structure after cooling to 200 K is glassy.

Uniaxial Deformation

The equilibrated samples are uniaxially deformed at a constant velocity in the x-direction at 200 K and 0.1 MPa. Deformation is performed by stepwise increasing the box size \( L_x \) in the x-direction, once every 20 MCS, by an amount \( \Delta L_x = 1 \times 10^{-4} L_{x,0} \), where \( L_{x,0} \) denotes the box length prior to deformation. This corresponds to a deformation rate of 5×10⁻⁶ MCS⁻¹ (≈5×10⁷ s⁻¹, see ref.[18]). In between strain steps the following mix of moves is used: 13.3% end rotation, 13.3% flip, 71.1% intrachain rebridging and, finally, 2.3% lateral-size fluctuation. The REP and EB moves are switched off during deformation, to avoid direct intervention in the slowest processes (that take place on time scales that also exceed experimental timescales of the order of seconds or larger), other moves are performed in the same proportions as during equilibration. The “lateral-size-fluctuation” move (similar to a “volume-fluctuation” move) modifies simultaneously the box sizes in the y- and z-directions.

Three cases are studied. In the first place, a simulation in which the flexible-bond model (F) is employed and coordinates of all the atoms (AA) are changed affinely with the box size both in the direction of deformation and in the lateral directions by the lateral-size-fluctuation move (FAA). Second, a simulation employing the flexible-bond model, in which COM coordinates of all the chains are changed affinely with the box size (FCOM). Finally a simulation, employing the rigid-bond model (R), in which COM coordinates are changed (RCOM) affinely with the box size, was performed.

Stress-Strain Behavior

The stress–strain curves are plotted for all the three cases (FAA, FCOM and RCOM) in Figure 4. RCOM results in a very high stress value for all the strain values. For FCOM this is also true at lower strain values, but to a lesser extent.
Finally FAA gives reasonable results; the curve has the shape that is typical for glassy amorphous polymers and also the values for Young-modulus and yield stress, see Table 2, have the right order of magnitude, i.e., of the order as experimentally found by, for example, Arruda and Boyce.\([31]\)

To facilitate a quantitative comparison, the values of Young-moduli \(E\), yield stresses \(\sigma_y\) and strains \(\varepsilon_y\), and strain-hardening moduli \(G_k\) have been determined for all the three cases, see Table 2. The Young-moduli result from a linear fit to the stress–strain data for strains smaller than 0.02, for the yield point the intersection of the stress–strain curve with its tangent at zero strain, but shifted over 0.02 along the strain axis,\([32]\) is taken, and the strain-hardening moduli \(G_k\) are determined as a linear fit to the final parts of the stress–strain curves (the final 0.1 strain increment). Although the definition of the strain-hardening modulus is somewhat arbitrary, it provides at least some lower bound to the value of the strain-hardening moduli in our systems.

FAA results in Young-moduli similar to those from other computational studies (e.g., by Brown and Clarke\([12]\)) and of the same order of magnitude as experimentally measured \((\text{of the order GPa at temperatures below } T_g)\). The values found for FCOM and those for RCOM are, respectively, one and two orders of magnitude too high. For the case of FCOM no strain hardening is found at all; from a strain of approximately 0.4 the stress–strain curve remains fluctuating around the same value.

The yield stress for FAA is comparable to experimental values as well.\([31]\) The value is lower than that found in some other computational results; for example, Capaldi et al.\([15,23]\) found 200–300 MPa for deformation rates of \(5 \times 10^7\)–\(5 \times 10^{10}\) s\(^{-1}\) at 200 K. This also supports our estimate\([18]\) that our deformation rate is lower than in ref.\([15,23]\). So the FAA model and protocol results in feasible values for \(\sigma_y\). The same is true for FCOM. RCOM gives values that are high both with respect to experiment and to existing computational results.

Values of strain-hardening moduli of glassy amorphous polymers are typically of the order of a few tens of MPa.\([31]\)

In the current study, strain-hardening moduli are found by FAA and RCOM that are, respectively, one and two orders of magnitude too high. For the case of FCOM no strain hardening is found at all; from a strain of approximately 0.4 the stress–strain curve remains fluctuating around the same value.

### Table 2. Young moduli, yield stresses, yield strains and strain-hardening moduli of PE in both the flexible-bond model and the rigid-bond model deformed at the temperature of 200 K and strain rate of \(5 \times 10^{-6}\) \(\text{MCS}^{-1}\).

<table>
<thead>
<tr>
<th>Model</th>
<th>Deformation protocol</th>
<th>(E) MPa</th>
<th>(\sigma_y) MPa</th>
<th>(\varepsilon_y)</th>
<th>(G_k) MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexible bond</td>
<td>AA</td>
<td>((1.2 \pm 0.2) \times 10^3)</td>
<td>((7 \pm 1) \times 10)</td>
<td>0.08</td>
<td>((5.7 \pm 0.2) \times 10^2)</td>
</tr>
<tr>
<td>Flexible bond</td>
<td>COM</td>
<td>((4.1 \pm 0.1) \times 10^3)</td>
<td>((1.2 \pm 0.2) \times 10^2)</td>
<td>0.05</td>
<td>((-3 \pm 2) \times 10)</td>
</tr>
<tr>
<td>Rigid bond</td>
<td>COM</td>
<td>((1.6 \pm 0.0) \times 10^4)</td>
<td>((4.5 \pm 0.3) \times 10^2)</td>
<td>0.05</td>
<td>((3.5 \pm 0.0) \times 10^3)</td>
</tr>
</tbody>
</table>

Stress Partitioning and Energy Partitioning

To obtain insight into the details of deformation, the contributions from various interactions to the total stress and to the total energy have been followed in their evolution with strain. In the case of FAA \(\text{[see Figure 5(a)]}\), the stress contribution of the nonbonded interactions rises first, then at approximately strain 0.1 this contribution levels off. This picture of the initial increase followed by leveling off of \(\text{(the contribution of nonbonded interactions to the total stress is often seen, for both polymer[17] and monatomic glasses[33])}\). The contribution of the bonds shows an initial increase as well although at a slower rate than the nonbonded contribution. At a strain of 0.2 the contribution of the bonds levels off, and eventually, at a strain of 0.45, rises again. The contributions of valence angles and dihedral angles are negligible. The large fluctuation in stress can be attributed mainly to a large fluctuation in the bond-length’s contribution.

The contribution of the various interactions to the total energy has for the FAA case been shown in Figure 5(b). Initially the work performed on the sample is converted (apart from heat) into nonbonded (both intermolecular
and intramolecular) energy and to a lesser extent into torsional energy. As the deformation proceeds, the non-bonded energy of the system rises further at a slower rate and the torsional energy decreases. The amount of energy stored into bonds and bond angles is relatively small (whereas certainly the bonds contribute substantially to the total stress).

A possible explanation of these results is as follows: Initial deformation is accommodated by a decrease in the density (an increase in the average distance between monomers) and by an increase in bond lengths and bond angles. At intermediate strain values, a further increase in bond lengths and angles is prevented by conformational changes via dihedral angles; apparently the penalty for climbing the energy barriers of the torsion potential is smaller than the penalty for further increase in the bond lengths. In the final stage, the number of conformational changes via the dihedrals is very limited; probably further conformational changes via dihedrals are accompanied by high nonbonded-energy penalties. As a consequence the bond lengths increase further, resulting in an increase in the contributions from bond lengths to stress and energy.

For the FCOM case [Figure 5(c) and 5(d)], the picture is qualitatively similar to the FAA case for strains smaller than 0.4, although there are also essential differences for larger strain values. Whereas at strain values higher than 0.4–0.5 strain hardening, caused by a rise in the contribution of bond lengths and to a lesser extent by nonbonded interactions to the total stress, is observed for the FAA case, no strain hardening is observed for the case of FCOM. Furthermore, an increase in the intramolecular nonbonded energy is observed in the FAA case. In the
FCOM case, this increase is absent. Quantitatively there are large differences. The amount of work turned into energy is more than twice higher than in the FAA case, which has to be attributed to the stronger increase in nonbonded energy in the FCOM-case. Furthermore, the fluctuations of the total stress, primarily caused by the fluctuations of the bond lengths, are lesser than those in the FAA case.

The differences between FAA and FCOM are not entirely clear. The fact that in both cases, in spite of the clear differences in the two deformation protocols, the contribution to stress from the nonbonded interactions and from the bond lengths first increase and then level off can be understood. In the FAA protocol the bond lengths are actively changed during deformation steps, and therewith the contribution of the bond lengths to the stress. In between deformation steps the bonds are relaxed to some extent, thereby transferring a part of the stress to the nonbonded interactions. As a result, both contributions from bond lengths and nonbonded interaction rise simultaneously. For FCOM the bond lengths and angles do not change during the deformation steps; however, the deformation protocol can result in close approach of monomers in different chains. This results in very large contributions of intermolecular nonbonded interactions to the total stress. In between deformation steps, a part of the stress is transferred to the bonds. Therefore, also for FCOM both contributions increase at the same time. Figure 6 shows two short parts of different chains. Immediately after a deformation step (FCOM) monomers \(i\) and \(j\) are very close. Shortly after, adjacent bonds deform to increase the distance monomers \(i\) and \(j\). For intermediate strain values the contributions of nonbonded interactions and bond lengths level off, for both FAA and FCOM; further increase is prevented by conformational changes via dihedrals. The reason for the different strain-hardening behavior is not clear. For FAA, it can be explained that there is strain hardening, see above. However, the absence of strain hardening for FCOM is not obvious. It might have to do with the fact that in case of FCOM the initial density drop is larger, so that at larger strain values the chance on close approach of the two monomers is smaller. The larger fluctuations in the FAA case (as compared to FCOM) of the total stress, caused by the fluctuation of bond lengths, is caused by the fact that in both the volume-fluctuation and the lateral-size-fluctuation moves all the bond lengths are changed in the FAA case (for FCOM, this does not hold).

For the case of RCOM the information on the evolution of the various contributions to the stress, see Figure 5(e), is limited because the stress was calculated according to Equation (2), based on interactions between chains. Since the kinetic contribution to the total stress is negligible, there is only one relevant contribution to the total stress, namely the intermolecular interactions, i.e., the non-bonded interactions between entire chain images, see the Model, MC Algorithms and Stress Calculation section. The evolution of the various contributions to the total energy is for RCOM given in Figure 5(f). An even larger increase in the nonbonded energy is observed than in case of FCOM. The torsional energy initially increases and then decreases again. At strain 0.5, all the contributions go up sharply.

The very high values of both stress and energy in case of RCOM with respect to FAA and FCOM can be understood from the fact that high nonbonded stress and energies caused by close approaches of monomers cannot be transferred to bond lengths, because the bonds are rigid. Only at intermediate strain values, between yield and strain hardening, this is less important, since in this strain region stress and energy increase are slowed down by conformational rearrangements via dihedrals.

In summary, one may conclude that only the FAA case reproduces the typical stress–strain behavior of glassy amorphous polymers and produces reasonable values for quantities like Young-modulus and yield stress. Furthermore, it was shown that the nonbonded-interaction contributions to the total stress and to the total energy increase sharply in the initial stage of deformation in all
the three cases. Subsequently, at intermediate strain values, a decrease in torsional energy takes place in all the three cases, indicating conformational changes involving the dihedrals. Finally stress and energy increase further, also via contributions involving the bond lengths and the bond angles (for FAA and RCOM only).

**Structural Properties**

To verify our picture, we also monitored the structural evolution of our sample during deformation. As shown in Figure 7, the densities evolve differently for all the three cases. The density for FAA initially decreases in the elastic

![Figure 8. Probability densities of dihedral angle and nonbonded distance before and after the deformation: in the flexible-bond model using AA (a and b), in the flexible-bond model using COM rescaling (c and d) and in the rigid-bond model using COM rescaling (e and f). The temperature is 200 K and the deformation velocity is $5 \times 10^6$ MCS$^{-1}$.](image-url)
regime until the yielding sets in. After yielding, constant-volume deformation of the sample is observed. In case COM rescaling is used, the same qualitative picture is obtained; however, with an exaggerated initial decrease in volume. The density in the rigid-bond model keeps decreasing as deformation progresses, which is very unrealistic.

To show more detail, the probability densities of structural parameters before and at the end of deformation have been plotted, see Figure 8. The results for FAA [Figure 8(a) and 8(b)] are quite similar with what was observed in our previous study of the deformation of an amorphous PE-like polymer glass. In Figure 8(a), it is shown that the fraction of dihedrals in the trans state grows under deformation. Furthermore, the intramolecular pair-correlation function, see Figure 8(b), reveals that during deformation the heights of the peaks beyond the first peak (at $r = 2^{1/6}, \sigma = 4.4 \text{ Å}$) increase, indicating the unfolding of chains.

For FCOM the same picture is obtained, although the intramolecular pair-correlation function shows a less pronounced increase in the peaks beyond the first peak (before comparing them, pair correlation functions have been normalized by the height of the first peak, at approximately 4.4 Å).

For RCOM, we observe once more an increase in the number of trans dihedrals and an increased height for peaks beyond the first peak of the intramolecular pair correlation function. In addition, all the peaks of both the intramolecular and the intermolecular pair-correlation function rise during deformation, indicating larger spatial density fluctuations in the material after deformation than before. These strong spatial density fluctuations are also seen in Figure 9, where lateral snapshots are shown at the end of deformation both for FAA and for RCOM. Clearly the density fluctuations are stronger for the RCOM case.

One point of concern when comparing FCOM and RCOM is the fact that in the two cases the starting materials are different (see Figure 8), e.g., the fraction of dihedrals in the trans state is quite different for the two models. It is not clear how this difference in materials, prior to deformation, contributes to the observed differences during deformation.

![Figure 9. The lateral snapshots of the PE structures at the end of uniaxial deformation in (a) the flexible-bond model using AA and (b) the rigid-bond model using COM. The temperature is 200 K and the deformation velocity is $5 \times 10^{-4}$ MCS$^{-1}$.](image)

**Conclusion**

The deformation of glassy amorphous polymers has been studied by MC. The influence of both the internal molecular constraints and the deformation protocol on the details of the deformation process has been investigated.

First, well-equilibrated initial samples have been prepared in the melt. Subsequently, these samples have been cooled into the glassy state. Finally, the resulting samples have been deformed. Three cases have been investigated: (1) deformation of the model polymer without constrained bond lengths, employing a deformation protocol where the positions of all the atoms (monomers) are scaled affinely with the box size (FAA), (2) idem, employing a deformation protocol where the COM coordinates of all the chains are changed affinely with the box size (FCOM) and (3) deformation of the model polymer with constrained bond lengths, employing a deformation protocol where the COM coordinates of all the chains are changed affinely with the box size (RCOM).

The different models and deformation protocols have been compared on the basis of stress–strain curves, density–strain curves and contributions of different interactions to the stress and to the internal energy of the system. A comparison of the three cases on the basis of the stress–strain curve shows that only the FAA case gives the typical behavior of glassy, amorphous polymers, with realistic values for Young-modulus and yield stress. For FCOM and RCOM, the values of these quantities are, respectively, half an order and one order of magnitude too high. A drawback of all the three approaches (FAA, FCOM and RCOM) is that they fail to reproduce the typical experimental values of strain-hardening moduli in glassy polymers. From the comparison of the evolution of the contributions of various interactions to the total stress and total energy, the following picture has been obtained. The nonbonded-interaction contributions to the total stress and to the total energy increase sharply in the initial stage of deformation in all the three cases; in case of FAA and FCOM this is accompanied by an increase in the contribution of bond lengths. Subsequently, at intermediate strain values, stress and energy increase slow down; a decrease in the torsional energy indicates that conformational changes involving the dihedrals take place in all the three cases. Finally stress and energy increase further, also via contributions involving the bond lengths and the bond angles (for FAA and RCOM only).

Also only for the FAA case, a realistic density evolution was observed. Both for FAA and for FCOM an initial decrease in the visco-elastic regime is
obtained, followed by constant-volume deformation after yield. However, in FCOM the initial decrease is exaggerated. For the RCOM case, the density keeps decreasing during the whole deformation. Closer inspection of evolutions of dihedral angle distribution shows an increase in the fraction of dihedrals in the trans state; from the intramolecular pair-correlation functions one can learn that chains become more extended during deformation in all the three cases. Furthermore, in case of RCOM, from the evolution of both intermolecular and intramolecular pair-correlation functions, it is observed that the spatial density fluctuations increase strongly during deformation.

All in all, both the introduction of constrained bonds and the deformation protocol have a huge influence on results obtained from molecular simulation of glassy polymer deformation. After studying three different combinations of constraint conditions and deformation protocol (FAA, FCOM and RCOM), the results obtained with the flexible bond model in combination with a deformation protocol where the positions of all the monomers are scaled affinely with the box size (FAA) show the best agreement with experimental observations. However, the high value of the strain-hardening modulus remains a problem.

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