Analysis of structural changes during plastic deformations of amorphous polyethylene

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Molecular dynamics (MD) simulations have been used to analyze yielding and stress-softening processes during stepped simple tensile loading of bulk amorphous polyethylene (PE) at temperatures (T def) well below the glass transition temperature (T g). Specimens formed by 20 linear chains of 1000 beads each (2 × 104 coarse grained -CH2- units), with energetics described by a united atom potential, were deformed at T def = 100K. Configurations at axial strains (εxx) ranging from 0% to 30% were allowed to reach steady state equilibration. Subsequently, configurations in a time period of 5 ps were saved for analysis of their local structure. Local structural characteristics were analyzed using three methods: (i) a geometric description by computing the evolution of self and inter-chain entanglements, the number of bead contacts and the free volume, (ii) the method of Empirical Orthogonal Functions (EOF) to obtain a reduced description of the displacement field at each strain level and the vibration of each bead around its equilibrium position, and (iii) Hardy’s method to compute the time averaged local stress tensor to obtain a detailed description of the distribution of internal forces. It was found that at early stages of deformation (εxx < 13%) the inter-chain entanglement continuously decreases while the self-entanglement showed no significant variation and no distinct patterning. Also the energy content in each eigenmode of the normalized displacement correlation matrix used in the EOF analysis is almost the same for a large portion of the frequency range regardless of the imposed axial strain level. Furthermore, distribution of the local pressure presented a positive expected value at the initial (εxx = 0%) configuration; the expected value continuously decreases toward the point where the axial stress peaks (εxx = 13%).

1. Introduction

Glassy polymers are integral components in many modern industrial applications [6] because of their outstanding mechanical properties [7–9]. When subjected to large deformations, instead of failing abruptly, materials such as polycarbonate (PC) and polymethyl methacrylate (PMMA) show strain hardening for large strains [8], a valuable mechanical response required in many structural applications.

Even though glassy polymers, and in general polymeric materials, pervade many aspects of our everyday life, a deep understanding rooted in the micro-structure-property relationship of their behavior is still needed [10–13]. As the dimensions of structural components reach the nanometer scale in-homogeneities in the microstructural characteristics of the constituent materials start to dominate and deviations from the observed macroscopic
Changes are not significant to promote mass transfer, low temperature plasticity should not be expected in an increasing number of dihedral angles in the trans-conformation. It was also reported that as the strain rates increase (~10^10/s) and for small and intermediate strain levels, the number of dihedral angles in the trans-conformation stays almost constant and equals that in the undeformed state. By using MD simulations of compression tests on the same polymeric material, Capaldi et al. [19] computed the variation of the percentage of angles in trans state with strain at different strain rates (5 x 10^10, 1 x 10^9, 5 x 10^10/s) and concluded that these changes are not significant prior to the strain hardening regime. The authors also stated that conformational changes in the dihedral angles do not play a major role in the mechanics of deformation during yielding. It is well known that conformational variations are required in order to allow changes in dimensions and shapes of coils and hence changes of the geometry of polymeric structures as a whole. Although the chain straightening mechanism is essential in describing the deformation process of glassy polymers it is still unresolved whether or not the same mechanism is responsible for plastic deformations at small and moderate strains [12,13].

Plastic deformation is a mass transfer process that changes shapes of a solid due to the applied external forces and the process involves irreversible relative atomic (molecular) motions [26]. During the solidification process and upon cooling to temperatures well below the melting point (T_m) or T_g, polymeric materials suffer a complete deactivation of the diffusional modes of mobility, i.e., non-existence of translational motion of polymer chains as a whole [8]. In this sense, low temperature plasticity in glasses at T_def << T_g has to proceed via specific solid-like (solid state) rather than liquid-like structural rearrangements. At low temperatures only short scale motions without significant translational displacements of the conforming chains are allowed. Since thermal energy is insufficient to promote mass transfer, low temperature plasticity should be developed primarily through mechanical activation. Under this scenario, the two main characteristics regarding the plastic deformation in glassy polymers at T_def << T_g are [13]: (i) molecular motions responsible for mass transfer (plastic events) have to be small scale processes, and (ii) the source of mobility (plasticity carriers) is related to the nucleation and growth of new stress-induced structural defects that do not exist in the initial undeformed configuration. The second mechanism is similar to dislocation assisted plastic deformations in crystalline materials.

Plastic deformations in glassy materials have been explained as the nucleation and evolution of quasi-defects precipitated by the existence of a loose local environment (free volume) [1,12,14]. Similar characteristics in plastic processes occurring in both polymeric and non-polymeric glasses reveal that the plasticity of macromolecular objects is not necessarily controlled by chain straightening or major conformational changes [30]. Mechanisms behind the relaxation process after the structure has been perturbed seem to be the same for different glasses regardless of their chemical nature (polymeric or metallic). Internal structure, packing and packing imperfections seem to control the evolution of structural defects in amorphous solids [31,32]. Intuitively it can be expected that the newly formed plastic events will be nucleated in the vicinity of loosely packed atomic configurations where the local density is smaller than that at other locations in the material. Different theories state that plastic deformations in amorphous materials might be due to the nucleation of local defects such as local shear displacements [1,4], linear defects such as dislocations [33] or free volume holes [27]. Due to similarities in local deformation patterns between amorphous materials with and without an internal structure, it is reasonable to expect that local structural rearrangements cause plastic events at the early stages of deformation rather than major changes in dimensions and shapes of the constituent polymer coils. Experiments have shown that uncoiling in polymer glasses is not important at early stages of deformation for T_def << T_g and plays a role only after the system has reached the maximum axial stress [13,34,35].

In the present work, by using MD simulations of isothermal (T_def = 100 K) uniaxial stepped simple tensile tests on bulk glassy PE, geometry, energy and stress based arguments are used to show that non-polymeric structural rearrangements are responsible for the general plastic deformation patterns at low and intermediate strains in linear amorphous polymers. As stated by Argon et al. [1,2] in the analysis of plastic deformations of amorphous materials, these stress-induced short-scale defects, termed shear transformation zones (STZ), are carriers of plastic deformation in amorphous materials regardless of their chemical structure [13].

For macro-molecular bodies chain straightening processes come into play later during the strain hardening regime. The rest of this paper is organized as follows. The simulation model, the method for generating specimens and the loading processes are first described. Subsequently, characteristics of the uniaxial stress—strain curve and components of the total potential energy are highlighted for small and intermediate strain levels. The geometry of deformation is analyzed by computing distributions of the local core volume (V_c) and the local atomic volume (V_v). The number of bead-contacts and the self and intra-chain entanglements are quantified to describe the interaction between constituent chains. In section 4 a data reduction technique, the Empirical Orthogonal Functions (EOF) method [36], is used to describe the vibrational motion of polymer chains around their equilibrium positions at prescribed strains and to determine the energy contents in each eigenmode of the normalized displacement correlation matrix. Following ideas of [37] for the definition of the atomic level stress tensor, and of works in biochemistry regarding the analysis of conformational changes in proteins termed as protein quakes [38], an approximation of the local stress tensor is obtained for each bead (united atom) at every prescribed strain by using Hardy's method [39]. The time averaged values of two
Expressions for various terms in the united atom potential, and values of material parameters.

Even though the present simulations have not been performed under constant strain rates, the uniaxial stress-strain curves and the variation with time of the bonded and non-bonded components of the total potential energy agree well with those of previous works that used the same class of force fields and the coarse graining model [23,41]. Based on the analyses of results of our MD simulations we conclude the following regarding early stages of plastic deformations in a glassy polymer: (i) non-polymeric structural rearrangements describe the general deformation patterns of macro-molecular bodies; this is evidenced by the expected increase in values of the free volume and decreasing values of inter-chain entanglement with an increase in the strain; (ii) the chain straightening related phenomena do not play a significant role during yielding and stress-softening regimes; this follows from the almost identical intra-molecular energy distributions of eigen-modes of the displacement correlation matrix at different strains; (iii) plastic deformations in glassy polymers initiate with the nucleation of short-scale (local) stress-induced defects; this is supported by an increase in the number of atomic positions with negative pressures (increasing free volume) with an increase in the axial strain; (iv) even though the overall yielding is described by a pressure modified von Mises criterion [42] no substantial changes in the magnitude of the local von Mises stress were observed and its distribution seems unaffected by the magnitude of the imposed strain level.

2. Simulation model and method

Bulk amorphous PE specimens were subjected to uniaxial stepped tensile loading at 100 K with energetics described by a united atom force field with the same functional forms as those used in [43] for studying structural changes during quenching processes of the same material. The united atom was considered as an adequate level of coarse graining since our main goal is to study changes in degrees of freedom (d.o.f’s) in the backbone of each chain and inter-molecular interactions. The interactions in an H–C–H group are strong enough to treat it as a rigid cluster and lumped into a single bead. This force field has four functional components: a harmonic bond energy, a harmonic bending energy, a four term cosenoidal torsional energy with two minima, one at 1.152 rad and the other at π rad corresponding to gauche-trans configurations, respectively, and a 6–12 Lennard Jones (LJ) potential which simulates van der Waals interactions (see Table 1). Values of parameters in the potentials are the same as those used in simulations of uniaxial tensile deformations of amorphous PE in [23]. Initial configurations of PE specimens have been obtained by performing Free Self-Avoiding Random Walks (FSARW). In this procedure a backtracking algorithm is used to place one united atom (−CH2− bead) at a time in a prescribed simulation box with dimensions Lx = Ly = Lz = L for L ~ 40 Å. Initial dimensions of the simulation box were determined according to material’s density at 500 K and 1 atm pressure (~0.7567 g/cm³ [44]). Specimens for uni-axial tensile tests having 1000 monomers per chain are constructed sequentially. A total of 20 chains with 125 beads each were built using constant values for the bond distance and the bond angle of 1.54 Å and 1.92 rad, respectively. Torsion angles were in the range of (0 - π) rad and selected randomly in an iterative process rejecting those values that produced overlap between atomic positions (enforcing excluded volume condition). MD simulations of the equilibration and deformation processes were performed using the freely available software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [45]. After all chains were placed in the rectangular simulation box, velocities were assigned to each bead to give an initial temperature of 500 K to the system. The velocity-Verlet scheme was used for time integration of the resulting equations of motion. Periodic boundary conditions (PBCs) were used during all simulations in this work. An NVE-MD simulation of 500,000 time steps (Δt = 1 fs) was performed allowing chains to reorganize and alleviate all possible unbalanced internal forces derived from the random conformation procedure. Subsequently, the systems were allowed to equilibrate by an NPT-MD simulation for 500,000 time steps using a Nose-Hoover thermostat [46,47] to keep the temperature constant at 500 K (coupling the system with a thermal bath with infinite thermal capacitance) and a Nose-Hoover barostat to keep components $P_{xx}$, $P_{yy}$, $P_{zz}$ of the global pressure tensor at 0 bars. During this step, the system volume is allowed to expand/contract in each direction so that the configurational part (force part) of the pressure tensor cancels the kinetic part coming from atom’s momenta. At the end of the equilibration process at 500 K

### Table 1

<table>
<thead>
<tr>
<th>Energy term</th>
<th>Functional form</th>
<th>Parameters</th>
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<tbody>
<tr>
<td>Stretching</td>
<td>$E_{Bond} = k_b(\delta_{a}-\delta_{0})^2$</td>
<td>$k_b = 350\text{kcal/(mol)}/\AA^2$, $\delta_0 = 1.54\AA$</td>
</tr>
<tr>
<td>Bending</td>
<td>$E_{Bending} = k_\theta(\theta_{a}-\theta_{0})^2$</td>
<td>$k_\theta = 60\text{kcal/(mol)}/\text{rad}^2$, $\theta_0 = 1.911\text{rad}$</td>
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<tr>
<td>Torsion</td>
<td>$E_{Torsion} = \sum_{\phi} C_\phi \cos(\phi/\phi_{0})$</td>
<td>$C_\phi = 1.736 \text{kcal/mol}$, $\phi_0 = 1.121 \text{rad}$</td>
</tr>
<tr>
<td>van der waals</td>
<td>$E_{vdw} = 2\epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) r_{ij}^{(0)} &lt; r_{c}$</td>
<td>$\epsilon = 0.112 \text{kcal/mol}$, $\sigma = 4.01\text{Å}$, $r_{ij} = 10\AA$, $E_{vdw} = 0$ for $r^{(0)} &gt; r_{c}$</td>
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a constant value of the mass density of ~0.750 g/cm³ was obtained.

The initial temperature of all specimens equaled 500 K. At this temperature and with zero external pressure the systems were allowed to relax. During the relaxation process the autocorrelation function (ACF) corresponding to the mean value of the unit end-to-end vector \( \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle \) was monitored. It is important to note that the relaxation periods of the magnitude of the end-to-end vector \( (R_{ee}) \) and the radius of gyration \( (R_g) \) are some of the longest among the geometrical parameters describing the time variation of the structure for a linear polymeric chain. The unit end-to-end vector \( \langle \mathbf{u}(t) \rangle \) of each chain was computed and its average value at each time step recorded. The relaxation period was extended until the ACF started to oscillate around zero with decreasing amplitude.

For samples with 125 monomers per chain values for the average \( R_{ee} \) and the average \( R_g \) at the end of the relaxation process oscillate around 2250 Å² and 340 Å², respectively. The corresponding relaxation period was 40 \( \times 10^6 \) fs. Foteinopoulou et al. [44] used the end-bridging and intra-molecular-end-bridging Monte Carlo methods to simulate relaxation processes for linear PE chains with different degrees of polymerization at 1 atm pressure and temperatures ranging from 300 K to 600 K. Energetics were also described by the united atom representation but the functional forms of the energy terms for PE were different. Systems considered were not mono-disperse but average values of the degree of polymerization reported were between 24 and 1000. For an average degree of polymerization of 125 at 500 K Foteinopoulou et al. [44] reported values of the average \( R_{ee} \) and the average \( R_g \) of 2375 Å² and 396 Å², respectively.

Following the procedure proposed by Subramanian [48], atomic coordinates of the three relaxed configurations of samples with degree of polymerization 125 were scaled by a factor of 2\(^{1/2}\). By fixing the bond angle at the equilibrium value new beads were added between two existing ones in order to generate chains with twice the degree of polymerization of the originals. Details of the procedure are given in Appendix A. The new specimens passed through the first two stages of the sample preparation process to reach the prescribed pressure and temperature. For these new specimens with 250 monomers per chain the relaxation period was 100 \( \times 10^6 \) fs. Values for \( R_{ee} \) and the average \( R_g \) near the end of the relaxation process oscillate about 4400 Å² and 700 Å², respectively. For a mean degree of polymerization of 250, Subramanian [48] reported values of the average \( R_{ee} \) and the average \( R_g \) of 4750 Å² and 792 Å², respectively. The process was repeated for samples with 500 and 1000 monomers per chain with relaxation periods of 300 \( \times 10^6 \) and 700 \( \times 10^6 \) fs, respectively. At the end of the relaxation period and for specimens with 500 (1000) monomers per chain the average \( R_{ee} \) and the average \( R_g \) oscillate around 10000 Å² (20200) and 1600 Å² (3270), respectively.

Additional statistics characterizing relaxed bulk amorphous PE specimens at 500 K and no external pressure were obtained. Upon relaxation of specimens with different degree of polymerization, bond lengths and bond angles showed a nearly Gaussian distribution centered about equilibrium values. The dihedral (torsion) angle is a structural parameter of the material with more disperse distribution. This dispersion is due to higher flexibility of torsional d.o.f. as compared to those of bending and the bond length; the last one being the stiffest out of the three. For PE the two most probable torsion angles are the two minima at ±66° (gauche) and 180° (trans).

After the relaxation process at 500 K specimens with different degree of polymerization were quenched from 500 K to 100 K for 400,000 time steps of \( \Delta t = 1 \times 10^9 \) fs under zero pressure. The process was repeated for quenching rates of 0.1 k/ps and 0.01 k/ps. Even though the quenching rates cover three different orders of magnitude differences in the variation with temperature of the total potential energy density and the volume fraction are not significant. More details about this comparison are given in Appendix B.

Once the final temperature of 100 K was reached the specimens were equilibrated by keeping the temperature constant in an NPT ensemble for \( 10^8 \) time steps of \( \Delta t = 1 \times 10^9 \) fs and zero pressure. The selected temperature is well below the glass transition temperature for bulk amorphous PE with degree of polymerization 1000. \( T_g \) was determined by the temperature variation of \( \Omega_T/\Omega_{T_{200K}} \). The computed value of \( T_g = ~2800 \) K agreed with those obtained in [19,23] using the same kind of force field. The present work focused on the solid-like behavior of the glassy polymers rather than on the fluid-like behavior of the material close to and above \( T_g \). At the end of the equilibration process at 100 K a constant value of the mass density of ~0.941 g/cm³ was obtained.

For specimens with 1000 monomers per chain twelve configurations of the system corresponding to \( \varepsilon_{xx} = 0, 1, 3, 5, 8, 10, 12, 15, 18, 20, 25, \) and 30% were selected. Between two successive configurations the simulation box was deformed at a constant strain rate of \( 10^4/\text{s} \); for the specimen dimensions this value is equivalent to ~0.5% of the speed of sound \((c)\) in the material at \( T_{def} = 100 \) K \((c \approx 1629 \text{ m/s})\). Uniaxial loading was applied by using a \( N_{xy}/N_{zz} = T \) ensemble [49], i.e., the number of atoms, the temperature and the global transverse normal virial stresses \((\sigma_{yy} - \sigma_{zz} = 0 \text{ MPa})\) kept constant. In this ensemble positions of atoms are scaled according to dimensions of the simulation box following the Parrinello-Rahman formalism [50]. At each selected axial strain the length of the simulation box was kept constant and the system was allowed to equilibrate for 500,000 time steps of \( \Delta t = 1 \times 10^9 \) fs.

It is important to point out limitations imposed by time scales when describing processes with relaxation times much longer than the smallest natural period of vibration of a given molecular structure. We note that the energetics of the system being studied are described by terms that impose high frequency vibrations on intra-molecular degrees of freedom. In order to accurately resolve the displacement of each bead and to ensure stability of the integration algorithm the time step used must be less than the smallest time period of vibration.

In previous works [51,52] different levels of coarse graining have been implemented. The simplifications and assumptions made in those models are adequate in the sense that the system represented is a good glass former. The energetics are divided into bonded and non-bonded interactions described by a FENE anharmonic spring potential and a 12-6 LJ potential, respectively. At higher time scales (ns-ps) such models impose less restrictions on the integration time step size, therefore simulations can be performed for longer periods. An objective of the present work is to provide a more detailed description of the dynamics of the deformation process in amorphous polymers. Thus intra-molecular degrees of freedom are required. Even though coarse grained models such as the ones used in [51,52] do not account for all intra-molecular degrees of freedom they capture the overshoot, the stress softening and the strain hardening regimes observed in amorphous polymers. These models are valuable for understanding complexities in materials without the computational cost required for more detailed approaches. Regardless of the model (degree of coarse graining) used, relaxation times especially the time related to geometrical parameters such as the end-to-end and the gyration ratio, might reach the order of hundreds of nanoseconds and more depending upon the mobility restrictions imposed by the entanglements (longer chains) and system’s temperature/pressure.

3. Results for stepped uniaxial tensile tests

The selected strain levels cover three deformation regimes: (i) linear elastic, (ii) nonlinear, and (iii) softening. The first two regimes
are frequently recognized as elastic until the point where the axial stress peaks, i.e., the overshoot in the axial stress—strain curve (see Fig. 1(a)). Computed values of Young’s modulus (E) and the softening modulus (Es) were ~2.5 GPa and 0.07 GPa, respectively. These values of E and Es were obtained by using a linear approximation of the axial stress—strain curve within the intervals (εxx = 0%, εxx = 1%) and (εxx = 13%, εxx = 25%), respectively. The computed value of E is of the same order of magnitude as that found experimentally for glassy polymers at Tdef = 300 K [8]. The value for Es is much less than that derived from the experimental data (~2 GPa) for glassy polymers at Tdef = 300 K [8]. Other works using MD simulations have reported higher values of Es, showing that stress-softening is more pronounced for monotonic tensile tests performed at strain rates close to those simulated here, and Tdef ≪ Tg [23,41]. The maximum axial stress reached ~150 MPa at εxx = 13%. This value of the axial strain was reported in [41] for the overshoot in the axial stress—strain curve for a system with conforming chains with a degree of polymerization of 100 and Tdef = 50 K.

An estimate of Poisson’s ratio (ν) was obtained from the variation of changes in the diagonal of the cross section Δd (d = (Lx2 + Ly2)1/2) with changes ΔLx in the simulation box length. A curve fit of this variation using the equation Δd/d = (1 − (1 + ΔLx/Lx)−2) gave ν = −0.41. Experimental values of Poisson’s ratio for HDPE obtained by following the ASTM E 132, Standard Test Method for Poisson’s Ratio at Room Temperature, are between 0.4 and 0.45 [53].

During the deformation process the strain energy density (energy per unit volume) continuously increased and seemed to saturate at 23 MJ/m³ toward the end of the stress-softening regime. This change is ~20% of the total potential energy stored in the initial undeformed configuration. The strain energy vs. the axial strain curve has an inflexion point at εxx = ~13%, i.e., the same strain level where the axial stress peaks (see dashed vertical lines in Fig. 1(a,b)). This inflexion point marks the initiation of the softening regime. Fig. 2(a–d) show changes in components of the strain energy density: non-bonded (van der Waals - vdw), torsion (dihedral), stretching (bond) and, bending (angle), respectively. Changes in the bond stretching and bending energies are not significant during the loading process. The contribution of the torsion energy to the total potential energy is more significant than that from bond stretching and bending energies but only represents ~13% of its maximum value. The overall behavior of the strain energy density is given mainly by the contribution from the non-bonded interaction (~87% of the maximum value). This energy component also monotonically increases and saturates at εxx = 30%. In early stages of deformation (εxx < 3%) the bending and torsion energies decrease, both reaching a local minimum at εxx = 3%. Contrary to the bending and torsion energies, the bond stretching component of the energy density increases reaching a local maximum at εxx = 3%. The bending and torsion components of the energy increase after reaching the local minimum but the bond energy shows a slightly decreasing trend over the observed axial strain levels.

We note that statistics at 100 K of some of the structural parameters such Rg, Rg and components of the inertia tensor of each chain might not reach steady state values within the equilibration period of 0.5 ns. We emphasize that at each strain level the total energy (kinetic plus potential) and pressure oscillate around constant values both prior to loading and after each load step. Even though chains in each system change and evolve toward geometrical conformations with fixed statistics at prescribed temperature/pressure conditions, those conformations give to each specimen very similar global characteristics (total volume, potential energy, kinetic energy and global stress tensor).

Fig. 3 depicts the time variation of changes in the total potential energy and its bonded and non-bonded components for a specimen with 1000 monomers per chain. It can be observed that the time period of 0.5 ns is long enough for the time average of these quantities to equilibrate. It is clear that the energies, temperature and pressure of the specimen are not constant but oscillate around a constant value at the end of each equilibration period. The overshoot in the total potential energy and the time needed to reach this constant value increase with an increase in the axial deformation. Conformations of polymer’s chains at this low temperature evolve over a very long period, undoubtedly much longer than the time window used for the present analysis, but with no substantial changes in the potential energy density as long as the axial strain is kept constant. At each strain level one can also verify that after the equilibration period each bead oscillates around a given spatial position. Thermally activated diffusion is very limited at temperatures well below Tg. It permits analyzing effects of external loads on the internal structure of each specimen and the mechanical activation of the plasticity carriers. After the equilibration period, configurations in time window of 5 ps were saved for subsequent analysis.

In order to compare qualitatively present results with those of Refs. [18,23], bulk amorphous PE specimens were subjected to simple tensile loading at constant strain rates of 10⁹/s - 10¹⁰/s, keeping the temperature constant at Tdef = 100 K (or 250 K) in a NτγγΩΩT ensemble [49] following the Parrinello-Rahman formalism [50]. The loading process was performed for 10⁸ time steps of Δt = 1 fs. The final configurations of all specimens correspond to εxx = 100%.

Values of the maximum stress εyy, Young’s modulus, E, softening modulus, Es and hardening modulus, Eh, are summarized in Table 2. Values of Eh were obtained by using a linear approximation of the
axial stress - axial strain curve in the interval \( \varepsilon_{xx} = 40\% \), \( \varepsilon_{xx} = 100\% \). These results reveal that Young’s modulus increases with an increase in the degree of polymerization, with a decrease in the value of \( T_{def} \), and an increase in the axial strain rate. For the same degree of polymerization and the axial strain rate of 10\(^8\)/s specimens tested at \( T_{def} = 250 \) K had 43\% lower value of Young’s modulus than those tested at \( T_{def} = 100 \) K. The temperature seemed to influence most the value of \( E \). Values of \( E \) increased with an increase in the strain rate and decreased with an increase in the degree of polymerization. No stress softening behavior was observed for specimens at \( T_{def} = 250 \) K. The computed data were not conclusive regarding the behavior of \( E_h \) at the prescribed axial strains. Tensile strength increased with an increase in the strain rate and with an increase in the degree of polymerization. No overshoot in the axial stress–strain curves at \( T_{def} = 250 \) K was observed.

Computed results cannot be directly compared with experimental data since reported values of mechanical properties for PE are for semi-crystalline specimens and different loading conditions between experimental setups and MD simulations. Experimental data for Young’s modulus of high density PE (HDPE, 0.940–0.965 g/cm\(^3\)) at room temperature and quasi-static loading conditions are in the range of 0.6–1.4 GPa. Experimental values for the maximum stress are between 20 and 32 MPa [53]. Experimental values of variables at room temperature for other glassy polymers are: PC (1.2–1.22 g/cm\(^3\)) \( \sigma_y = 55–75 \) MPa, \( E = 2–2.4 \) GPa; PMMA (1.17–1.20 g/cm\(^3\)) \( \sigma_y = 48–76 \) MPa, \( E = 1.8–3.1 \) GPa [8]. Considering differences in temperature between simulations and experiments that are generally conducted at room temperature and atmospheric pressure, the values of \( E \) and \( \sigma_y \) found from MD simulations and experiments differ; values of the maximum stress from MD simulations are an order of magnitude higher than those found from the test data. This is primarily due to high strain rates used in MD simulations which are necessary to reach desired strain levels in a reasonable number of time steps. It is important to state that the macroscopic values of stresses are an ensemble average or a space-time average of values obtained from global and local stress measures at nanoscale. Besides the inherent time scale differences, it is probably unreasonable to expect good agreement between a macroscopic measure of the stress and the instantaneous values of the space-average virial stress tensor.

Values of material parameters obtained in the present work agree well with those obtained in [23]. Even though the loading
conditions are not the same the magnitude of the maximum stress for the stepped uniaxial tensile tests with the same temperature and the same degree of polymerization ($\sigma_y \approx 150$ MPa) is close to that obtained from simulations at a constant strain rate ($\sigma_y \approx 147$ MPa).

4. Kinematical description of the deformation process

4.1. Distribution of free volume

At temperatures higher than $T_g$, polymers are considered ideal Gaussian chains with very little intra-molecular chain contributions to the total potential energy [54]. At such temperatures, the transport phenomenon responsible for plastic (irreversible) deformations is associated mainly with thermal activation. The kinetic energy of particles is enough to overcome any energy barrier that might prevent the translational motion of atoms. For linear polymer chains, the structure of the backbone is preserved while atoms explore larger volumes as compared to those at temperatures well below $T_g$. Due to the thermally activated motion, the polymer chains vibrate and explore a region in space known as the pervaded end distance. Upon equilibration at each strain level and in order to obtain a local description of the volume explored for each bead ($\mathbf{V}_c$ - core volume), we have used the amplitude of vibrations along the three Cartesian coordinates ($A_x$, $A_y$, and $A_z$) at each atomic equilibrium position. The position vector for particle $i$ is given by $\mathbf{r}^{(i)}(t) = (x^{(i)}(t), y^{(i)}(t), z^{(i)}(t))^T$. Within the time window of the equilibration period each bead has vibration amplitudes along the $x$, $y$, and $z$ directions given as $A_x = \max(x^{(i)}(t)) - \min(x^{(i)}(t))$, $A_y = \max(y^{(i)}(t)) - \min(y^{(i)}(t))$, and $A_z = \max(z^{(i)}(t)) - \min(z^{(i)}(t))$, respectively. The core volume is approximately given by $\mathbf{V}_c = A_xA_yA_z$ (see Fig. 4(c,d)). It can be observed that $A_x$ continuously increases and peaks at around $\varepsilon_{xx} \approx 13\%$, the strain level where the maximum axial stress occurs. Thereafter, $A_y$ decreases while $A_x$ and $A_z$ continue to increase. The three amplitudes decrease toward the end of the stress-softening regime.

Fig. 4(b) shows the probability density functions (p.d.f.’s) of $\mathbf{V}_c$ at prescribed strain levels. The variation of the expected values of $\mathbf{V}_c$ obtained from the corresponding p.d.f.’s as a function of $\varepsilon_{xx}$ is shown in Fig. 4(a). The expected value of $\mathbf{V}_c$ increases with an increase in $\varepsilon_{xx}$ at the strain level where the plateau of the stress-softening regime begins ($\varepsilon \approx 20\%$).

Eyring [55] has proposed that in order for plastic deformations to be accommodated in amorphous polymers there must be an excess space near each atom (bead). It was observed earlier that each atom explores a volume $\mathbf{V}_c$ but this is not all the space available for it to move without violating the excluded volume condition. For studying plastic deformations in amorphous metals Spaepen [22] used the concept of free volume, a quasi-defect with the required space to accommodate the deformation imposed by external loads. By taking into account the number of nearest neighbors of every bead in the specimen, a measure of the local volume assigned to each one of them can be obtained; this local measure of the volume is termed the Voronoi volume, $V_V$ [56]. In the present work a Delaunay tessellation is performed at each equilibrated configuration at the prescribed strain level by using atomic equilibrium positions as node points. The local volume of each bead is computed by adding contributions of all the tetrahedra converging to its spatial location. One fourth of the volume of each tetrahedra is assigned to each one of its vertices. Distributions of $V_V$ were also obtained by using the code voro++ with very similar results [57,58].

The free volume, $V_V$ of each bead can be computed as the difference between $V_V$ and $V_c$. During the study of shear softening in amorphous metals Li and Li [59] used the core volume of each atom $V_{atom}$ instead of $V_V$ to quantify $V_V - V_{atom}$ related to the effective range of the repulsive forces between atoms. Such a volume is constant for a given force field. Values of $V_V$ are significantly smaller than those of $V_{atom}$, a trend also identified by Li and Li [59]. Even though $V_V \ll V_c$ the $A_x$ component shows a clear maximum around $\varepsilon_{xx} \approx 13\%$ identifying a signature characteristic of the local dynamics toward the overshoot in the axial stress—strain curve.

Sastry et al. [60] defined free volume in a system of $N$ rigid spheres as the volume over which the center of a given sphere can translate, given that the other $N-1$ spheres remain in their positions. The model used to describe the system relies on the existence of a core diameter which defines an exclusion sphere. This parameter unambiguously sets a minimum separation distance between particle’s centers. However, the model used in the present work does not have this property and the material does not behave as a group of unstructured particles. In the present work non-bonded interaction are modeled by a 12-6 Lennard Jones potential that does not set such inter-penetrability restriction. The method used in [60] also relies on the construction of the Voronoi polyhedra to compute the approximation of the free volume. In this case one of the rigid spheres has to be removed and the Voronoi polyhedra reconstructed without the removed point. The volume of the formed cavity is computed and its value set as the free volume corresponding to the removed particle.

For the structured polymer melt studied herein we assumed that $V_V$ can be found from the amplitude of oscillations of each particle around its mean position as explained above.

Table 2 shows p.d.f.’s of $V_V$ at prescribed strain levels. The p.d.f curves seem to be very similar to each other but differences in distributions are clear in the variation of the corresponding expected values (Fig. 5(a)) and standard deviations (Fig. 5(b)). Even though variations in these two quantities are very small their changes reflect to great extent changes in the local structure of the material and therefore in the internal distribution of forces (see Section 6 for the distribution of local stresses). Both quantities show an increasing trend and have an inflexion point at $\varepsilon_{xx} \approx 13\%$. The
Fig. 4. For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, variation with uniaxial strain of the expected values of the pervaded volume (a), p.d.f.’s of the pervaded volume at different strain levels (b), expected values of the atomic displacements along the x, y, and z directions (c), and p.d.f.’s of the axial displacement (d) at different axial strains. Curves are coloured in the web version of this article.

Fig. 5. For the local atomic volume ($V_v$) in the stepped uniaxial tensile loading of bulk amorphous PE at 100 K and axial strains ranging from $\varepsilon = 0$% to $\varepsilon = 30$%, variation of the expected value (a), variation of the standard deviation (b), and probability density functions (p.d.f.’s) (c). Curves are coloured in the web version of this article.
mean value is almost constant and equals 27.8 Å³ at the end of the stress softening regime. Its variation with the axial strain resembles that of the strain energy density. The standard deviation is almost constant up to ε_{xx} ~ 3% and keeps increasing showing a linear variation toward the end of the softening regime. Expected values of V_v remain in a small range between 25 and 28 Å³ while the standard deviation has a slightly wider range between 3.4 and 4.5 Å³. The total volume of the simulation experiences a maximum change of ~5% with respect to the undeformed configuration, and stays constant during the stress-softening regime.

4.2. Intra- and inter-chain interactions

4.2.1. The number of contacts

During local explorations around V_v each bead perturbs the local environment of its neighbors. A measure of how much the volume explored by each bead is affecting dynamics of the conforming chains is related to the number of contacts a chain can have with itself and with other chains in the specimen. To determine if two beads are in contact, the relative distance between them has to be small enough to generate a repulsive force, i.e., the two monomers start to indent the core region described by the LJ potential (excluded volume). This region is a sphere of radius 2^{1/6}σ, where σ is the length parameter of the LJ potential (see Table 1). At this distance the force between the two interacting beads is zero.

Fig. 6(a,b) shows the variation with the axial strain of the number of inter-chain and the intra-chain contacts. The number of inter-chain contacts decreases and reaches a minimum at ε_{xx} ~ 13% and remains almost constant during the stress-softening regime. The number of intra-chain contacts also decreases but reaches a local minimum at ε_{xx} = 30% exceeds 715 found at ε_{xx} = 0. It is important to note that the minimum value of the number of intra-chain contacts is attained at almost the same strain level as that where the axial stress is the maximum (ε_{xx} ~ 13%).

4.2.2. Entanglement

As observed from the number of contacts within V_p, beads that belong to the same chain can come close enough to interact with each other and with beads of other chains. A part of these interactions restricts the mobility of a polymer chain, known as entanglement. Entanglements have been identified as the key factor behind many properties of polymeric materials such as viscosity, toughness, and strength [61]. Jancar et al. [12] have stated that the exact dynamical evolution of the entanglement process has not been elucidated.

The concept of entanglement used in the present work is related to the description of the structural complexity in polymeric materials and its quantification by the number of bond overcrossings on the three Cartesian planes. In polymeric materials there are two classes of entanglements: topological and geometrical. Entanglements of the former type are permanent and have a conceptual equivalence with mathematical knots. The entanglements observed in linear polymers are geometrical and can be removed, i.e., they can change with time. We believe that these temporary obstacles play a significant role in the kinematics of deformation of amorphous polymers during yielding and stress softening. The quantifier for the level of entanglement used in the present work is similar to the mean overcrossing number proposed by Edvinsson [62].

A measure of entanglement using the Primitive Path Analysis (PPA) was proposed by Everaers et al. [63]. In this method the shortest path connecting two ends of a polymer chain is determined while the intra-chain constraints are deactivated. The contour length computed from the PPA is an indirect measure of the constraints imposed by the entanglements but eventually this measure does not discriminate between the excluded volume condition coming from beads of the same chain or beads of different chains. We believe that in order to have a complete picture of the kinematics of deformation the un-crossability constraint has to be considered in intra and inter-chain constraints. The deactivation of the internal constraints allows beads to occupy same positions in space canceling the possibility to perform such discrimination in the analysis of the system toward yielding where changes in the intra-chain degrees of freedom are very subtle.

In order to describe interactions among chains, the total entanglement has been divided into interactions among bonds of the same chain, self-entanglement, and interactions among bonds of different chains, inter-chain entanglement. Geometrically, bonds are considered as linear segments conforming to the backbone of each polymer chain. In order to get a quantitative estimate of these two contributions to the total entanglement, linear segments are projected on each one of the three Cartesian planes (xy-, xz-, yz-) and the number of crossing segments in these projections for two different chains i and j computed. The self (self) and inter (interch) chain entanglements of a chain i are given by

\[
\text{self}\text{Ent}^{(i)} = \sum_{j=1}^{N_{ch}} \frac{C_{xy}^{(i)} C_{yz}^{(i)} C_{xz}^{(i)}}{n_i n_j},
\]

\[
\text{interch}\text{Ent}^{(i)} = \frac{C_{xy}^{(i)}}{n_i n_j},
\]

where C_{xy}, C_{xz}, C_{yz} are number of crossings segments between chains i and j on the xy-, xz- and yz- coordinate planes, respectively; n_i, n_j and N_{ch} are number of beads in chain i, number of beads

Fig. 6. For the stepped uniaxial tensile loading of bulk amorphous PE at 100K, (a) variation with axial strain of the inter-chain contacts (a), and intra-chain contacts (b).
in chain $j$ and the total number of chains in the specimen, respectively. Fig. 7a and b depict variations with $\varepsilon_{xx}$ of the expected values of inter-chain entanglement $\langle \text{ent}_{\text{inter}} \rangle$ and self-entanglement $\langle \text{ent}_{\text{self}} \rangle$, respectively. The variation of $\langle \text{ent}_{\text{self}} \rangle$ does not show a coherent pattern. One can think of it as an almost constant value during the deformation regimes under study. In contrast, the variation of $\langle \text{ent}_{\text{inter}} \rangle$ showed two distinct tendencies before and after the yield point. These values can be approximated by straight lines as shown in the Figure. Even though changes in magnitude of this parameter are small the slopes of the straight lines are clearly different. During yielding the inter-chain entanglement decreases faster than the intra-chain entanglement. This tendency clearly decreases after reaching the yield point at an axial strain of $\sim 13\%$. At $\varepsilon_{xx} \sim 13\%$ the slope of the linear fit changes by $\sim 85\%$.

Table 3 summarizes observations from the geometrical parameters used to describe yielding and stress-softening regimes. Parameters influencing most the yielding (stress-softening) process are highlighted in blue (orange). A scrutiny of the geometry of deformations showed that as the axial stress approached its maximum value, a bead loses contact with both beads of the same chain and beads of other chains when $\varepsilon_{xx}$ is increased from 0 to 13%. Increasing values of $A_x$ also support this observation. At the same time the molecular structure of each chain does not show substantial changes (see the small variation of $\langle \text{ent}_{\text{self}} \rangle$). At the studied strain levels the deformation is accommodated by chains in the specimen sliding relative to each other. This observation is reflected in the decreasing value of $\langle \text{ent}_{\text{inter}} \rangle$. Once in the stress-softening regime, beads belonging to the same chain start to increase the number of contacts, thus interfering with intra-chain movements (decreasing $A_x$). At the same time the number of contacts and the interference in the motion of beads belonging to different chains remains almost constant.

At the yield point, and based on the parameters utilized to analyze strain-induced structural changes in the material, the following observations can be highlighted. (i) The mean value of $V_c$ saturates and remains almost constant over the stress softening regime. (ii) The amplitude $A_x$ of the axial displacement reaches a maximum and decreases during the stress softening regime. (iii) The mean value of $V_c$ has an inflexion point and starts increasing at a smaller rate. (iv) The number of inter-chain contacts saturates and stays almost constant during the softening regime. (v) The number of intra-chain contacts reaches a minimum and starts to increase during the softening regime. (vi) The mean value of the inter-chain entanglement quantified by the number of over-crossings decreases at a smaller rate.

It is clear from these observations that in order to accommodate the deformation imposed by the boundary conditions the system has to increase the volume available for the beads (particles) to move. Such behavior is evidenced by the continuously increasing mean value of $V_s$ and the continuously increasing mean value of $V_v$. This extra volume is created mainly in the axial direction as evidenced by the increasing value of the mean axial amplitude $A_x$ of beads vibrations. Amplitudes in the transverse directions also increase but at a smaller rate than that of $A_x$. At the yield point the core volume saturates and the Voronoi volume has an inflexion point. Looking at material’s structure the generation of this extra volume can only be possible due to the relative motion between chains. Substantial changes of intra-molecular degrees of freedom (stretching, bending and torsion) are postponed to additional deformations. However, during yielding, such structural rearrangements have no effect on the global geometry of each chain. Furthermore the mean values of geometrical quantifiers such as the pervaded volume $V_p$, the end-to-end radius $R_{ee}$ and eigen-values of the inertia tensor (or the radius of gyration) remain almost constant prior to the yield point. A detailed explanation of chains dynamics’ based on the analysis of the normal modes computed by the Empirical Orthogonal Functions method is given in section 5. The number of intra-chain and inter-chain contacts decreases as the specimen approaches yielding but once at this point the number of inter-chain contacts saturates while intra-chain contacts reach a minimum. Decreasing values of the number of contacts are in agreement with the generation of extra volume observed in variations of $V_c$ and $V_v$. Once the system reaches the yield point the relative motion between chains slows down momentarily as evidenced in an almost constant number of the inter-chain contacts and also in the substantial change in the rate at which inter-chain entanglements decrease.

The slow-down in dynamics of the inter-chain relative motion can be explained by the fact that the amount of available volume required to accommodate plastic deformations has reached a critical point. This is also evidenced by the substantial decrease in the rate at which the number of points with local negative pressure emerge after the yield point. Details of the local stress distributions will be given in Section 6 (Fig. 18).

5. Analysis of local vibrations

Upon equilibration, Cartesian coordinates of each bead in the system were saved for a subsequent time period of 5 ps. In order to study dynamical behavior of the polymer and capture the spatial and time variations of these signals in terms of statistical

---

**Fig. 7.** For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, variation with axial strain of the inter-chain entanglement (a), and intra-chain entanglement (b). Solid red curves correspond to polynomial curve fits by the least squares method of MD simulation results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
correlations, the method of Empirical Orthogonal Function (EOF) was utilized [36]. The EOF method is similar to harmonic analysis, but harmonic analysis uses predetermined family of orthogonal functions. In the EOF method values of orthogonal functions are determined directly from the data. The normalized correlation matrix $C$ was obtained and its eigenvectors and eigenvalues computed by the Single Value Decomposition (SVD) method [64]. The matrix $C$ is given by $D^T D$, where $D$ is the data matrix. $D$ contains the time variation of the three Cartesian components of beads' positions ($x_i(t), y_i(t), z_i(t)$). The normalization process includes subtracting the mean value of the time variation of each signal and dividing the result by its standard deviation. Even though the system has reached a global steady state (constant kinetic energy, constant potential energy, and constant values of components of the virial stress tensor) it was found that the wide distribution of eigenvalues emphasizes the fact that each bead in the system is moving randomly around its equilibrium position. Under these conditions it is not plausible to describe the behavior of such a system by only using a few eigenmodes for the data representation. In the present study, the first 100 eigenmodes have been used for signal reconstruction. The contributions of these eigenmodes capture the overall trend in the amplitude and phase for the displacements of each bead. Higher modes correspond to higher frequencies and are believed to capture the local aspects related to the stiffest structural components, i.e., the bond energy terms.

In Fig. 8 we have plotted the spatial distribution of the x-displacement in the 1st, 5th and 25th eigenmodes of $C$ at $\epsilon_{xx} = 0$. The displacement fields given by the eigenmodes are continuous along each polymer chain but do not have any inter-chain compatibility. Thus chains in the system slide and move relative to each other exploring the space around their equilibrium positions. The volume of this space decreases for high frequency modes (see the magnitude of the normalized displacements in the adjacent color scale in Fig. 8). The first few modes, the modes with higher eigenvalues, contain most of the information regarding the dispersion of the displacement signals. It is important to emphasize that the first 100 eigenmodes represent a very small set of the family for a system having $6 \times 10^4$ d.o.f.'s.

To explore differences and similarities of the eigenmodes at different strain levels the participation ratio of each eigenmode was computed. The participation ratio, $P_k$, of mode $k$ is a measure of its localization, i.e., the number of beads that are effectively involved in a given modal displacement [65]. $P_k$ is given by

$$P_k = \left(\frac{N}{\sum_{i=1}^{N} |\mathbf{w}^{(k)}_i|^4}\right)^{-1},$$

(2)

where $N$ is the total number of particles in the system and $\mathbf{w}^{(k)}_i$ is the displacement vector of bead $i$ in mode $k$, i.e., $\mathbf{w}^{(k)}_i = (v^{(k)}_i v^{(k)}_i v^{(k)}_i)$. $P_k$ takes values around 1 when the mode extends over the whole system and values proportional to $1/N$ for completely localized modes. In Fig. 9 we have exhibited distributions of $P_k$ for the first 100 modes at strain levels ranging from

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**Table 3**

Summary of the geometrical parameters used to describe the yielding and the stress-softening regimes.

<table>
<thead>
<tr>
<th>Expected values</th>
<th>Yielding</th>
<th>Stress softening</th>
</tr>
</thead>
<tbody>
<tr>
<td>free volume</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Axial displacement</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>Intra-chain contacts</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>Inter-chain contacts</td>
<td>↓</td>
<td>↔</td>
</tr>
<tr>
<td>Self-entanglements</td>
<td>↔</td>
<td>↔</td>
</tr>
<tr>
<td>Inter-chain entanglements</td>
<td>↓</td>
<td>↑↔</td>
</tr>
</tbody>
</table>

Increases (↑), decreases (↓), constant (↔).
Differences at high frequency modes are more significant but still follow a regular trend. For strain levels from \( \varepsilon_{XX} = 0 \) to \( \varepsilon_{XX} = 3\% \) the torsional energy content in all modes does not differ significantly.

The principal components (PCs) of the reduced group of eigenvectors were also computed. The PCs are the time variation of the eigenmodes corresponding to matrix \( C \). For strain levels ranging from \( \varepsilon_{XX} = 0 \) to \( \varepsilon_{XX} = 25\% \), results plotted in Fig. 11(a, c, e) show the time variation of the 1st, 5th and 25th PC, respectively. To help compare different PCs, the Fast Fourier Transform (FFT) of each signal was found. In Fig. 11(b,d,f) we have exhibited the power spectra (periodogram) corresponding to the 1st, 5th and 25th PC, respectively. The time variation of the first mode at different axial strains has almost the same amplitude but with differences in phase; the power content in the signal increases slightly with the strain level and peaks around 0.5 THz. For the 5th mode time variations of the PCs are very similar in amplitude and are in phase. The maximum power for this mode is attained at 1.3 THz. The time variation of the PC corresponding to the 25th eigenmode shows similar frequencies but differences in energy content are evident from the amplitudes (see Fig. 11(e)). The power peaks around 5 THz for \( \varepsilon_{XX} = 0 \) but maximum values strongly depend upon strain levels.

In Fig. 12(a,b) we have shown the frequency at which the maximum value in the power spectra is attained and the corresponding value, respectively. The frequency where the maximum value of the power is attained shows a linear variation with the mode number. The power (energy content) of the PCs decreases with an increase in the mode number, i.e., the energy content of low frequency modes is higher than that of high frequency modes. It is important to note that the distribution of power among PCs is almost independent of the axial strain level.

From the analysis of the energy contributions in eigenmodes and the time variation of PCs one infers that the deformation process during yielding and stress-softening regimes takes place mainly by the activation of non-bonded interactions with minimum changes in the intra-molecular structure. At a given strain level and upon equilibration of the system, the non-bonded forces hold the structure in the equilibrium position while vibrations are determined by movements related to the faster intra-molecular d.o.f.’s. In this sense eigenmodes of \( C \) do not suffer significant changes during early stages of deformation of the linear amorphous polymer being studied.

**6. Distribution of local stresses**

Approximate values of the local stress tensor were obtained following Hardy’s formalism [39]. In this procedure the local stress tensor \( \sigma \) at a given spatial position, \( \mathbf{R} \), has contributions from two parts: a kinetic contribution due to particle’s linear momentum in which the velocity \( \mathbf{v} \) relative to the macroscopic velocity at the point of interest \( \mathbf{v}(\mathbf{R}, t) \) is weighted by a window or localization function \( \psi(\mathbf{R} - \mathbf{R}) \); a configurational part which is given by the weighted contribution of the tensor product between the bead–bead interaction forces \( f^{(ij)} \) and the relative position vectors \( \mathbf{R}^{(ij)} \) among beads (see Eq. (3a)). The weighting factor in the configurational part is known as the bond function \( B^{(ij)}(\mathbf{R}) \).

\[
\sigma(\mathbf{R}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} f^{(ij)} \otimes B^{(ij)}(\mathbf{R}) + \sum_{i=1}^{N} \sum_{j=1}^{N} f^{(ij)} \otimes \psi(\mathbf{R} - \mathbf{R}).
\]
The bond function is given by
\[
B_{ij}(\mathbf{R}) = \int \psi \left( \lambda \mathbf{r}_{ij}^{(j)} + \mathbf{r}_{ij}^{(j)} - \mathbf{R} \right) d\lambda,
\]
where \(\lambda\) is an integration variable (see Fig. 13 for details of the vector geometry involved in this computation). The kernel function used in the weighting process localizes the computation favoring contributions of the nearest particles to the local stresses. In the present work a cubic spline with a characteristic smoothing length of 5 Å was used in computations. The same cubic spline has been utilized for computation of local stresses in gold nanowires [66,69].

Values of the cubic spline kernel function are zero for arguments greater than twice the smoothing length. This local approximation of the stress tensor is obtained at each bead for a time period of 5 ps. The time averaged values of this tensor, equivalently approximate values of the Cauchy stress tensor, are assigned to each bead.

For materials with internal structure Adamal and Tadmor [3] showed that Eq. (3a) derived by Hardy under the assumption of pair-wise interaction forces can also be extended to cases in which these interacting forces come from many body potential functions. They proved that any particular inter-atomic force can be expressed in terms of central pair-wise forces to obey the principle of equal and opposite reaction to a given action. In the present work many body interactions arise from bending and torsional components of the total potential energy. Forces due to two-body and many-body terms of the total potential energy were computed by using a fourth-order finite difference scheme to approximate the derivative of an energy term with respect to bead’s position vector, i.e.,

\[
\mathbf{f}_{ij}(\mathbf{R}) = \lambda \mathbf{r}_{ij}^{(j)} + \mathbf{r}_{ij}^{(j)} - \mathbf{R}.
\]

For different values of the axial strain Fig. 14(a,c,e) shows p.d.f.’s of the axial component of the time-averaged local stress tensor, \(\sigma_{xx}\), the equivalent von Mises stress, \(\sigma_{eq}\), and the local pressure, \(p\). Variations of the corresponding expected values are exhibited in Fig. 14(b,d,f). The expected value of \(\sigma_{xx}\) is negative at \(\varepsilon_{xx} = 0\%) as are those for the other two transverse normal stresses. This compressive stress state in
Fig. 11. For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, time variation and power spectra of the 1st (a,b), 5th (c,d) and 25th (e,f) principal component of the displacement field at different axial strains. Curves are coloured in the web version of this article.

Fig. 12. For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, frequency at the maximum value of the principal component of power spectra (a), and maximum values of the power spectra (b), at axial strains ranging from $\varepsilon_{xx} = 0\%$ to $\varepsilon_{xx} = 30\%$. Points are shown in coloured circles in the web version of this article.
the initial configuration contrasts with the zero values of the normal components of the global virial \((-P_{xx}, -P_{yy}, -P_{zz})\). We note that the virial stress tensor is the limiting case of the computed local stress tensor when dimensions of the system under consideration tend to infinity (a volume corresponding to the given simulation box with PBC). It can be seen that \(\sigma_{xx}\) continuously increases and peaks at \(\varepsilon_{xx} = 13\%\) reaching a maximum value of 42 MPa. Stress-softening is also observed in this variation; the expected value of \(\sigma_{xx}\) decreases and stays constant at 25 MPa during the stress-softening regime (see Fig. 14(b)). Substantial changes are observed in the p.d.f.'s for \(\sigma_{xx}\) at different strain levels. The p.d.f.'s move toward positive values as the deformation proceeds. Note that the expected value of the axial stress becomes zero at \(\varepsilon_{xx} = 13\%\).

In Fig. 15(a–f) we have shown distributions of \(\sigma_{xx}\) at \(\varepsilon_{xx} = 0\%, 5\%, 10\%, 12\%, 15\%\) and \(20\%\). A small region of high stress gradients can be seen at \(\varepsilon_{xx} = 0\%\) with stress levels ranging from \(-300\) MPa to \(300\) MPa. This region with localized stresses persists for all strain levels.

Fig. 13. For the computation of the local stress tensor at spatial position \(\mathbf{r}\) (green dot) using Hardy’s method, geometric parameters included in the computation of the bond function \(\mathbf{B}_{ij}(\mathbf{r})\). Points \(a_i\) and \(a_j\) correspond to atomic positions (green dots) with position vectors \(\mathbf{r}^{(i)}\) and \(\mathbf{r}^{(j)}\), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 14. For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, probability density functions and variation of the expected values at different axial strains of \(\sigma_{xx}\) (a,b), \(\sigma_{xy}\) (c,d) and \(p\) (e,f).
levels. From results exhibited in Fig. 15(a,b) the contrast between the $\sigma_{xx}$ distributions at $\varepsilon_{xx} = 0\%$ and $\varepsilon_{xx} = 5\%$ is evident with predominance of positive local stress in the latter. From this local distribution of stresses it is clear that relaxation times ought to be larger in order to achieve uniform stresses in the initial configuration.

The expected value of $\sigma_{vpM}$ does not change noticeably during yielding and stress-softening regimes. Even though the volume average of $\sigma_{vpM}$ peaks also at $\varepsilon_{xx} = 13\%$ its value changes only 0.7% in going from $\varepsilon_{xx} = 0\%$ to $\varepsilon_{xx} = 13\%$ (see Fig. 14(d)). The local distributions are very similar at different strain levels (see Fig. 16(a–f)). These results agree with the observations of other authors [42] where a pressure modified von Mises stress ($pmvM$) was presented as the macroscopic yield criterion for polymer glasses. Egami et al. [37] employed the atomic level stress tensor averaged over different number of beads in a local domain to compute the

![Fig. 15](image_url)

For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, distribution of $\sigma_{xx}$ at axial strains of $\varepsilon = 0\%$ (a), $\varepsilon = 5\%$ (b), $\varepsilon = 10\%$ (c), $\varepsilon = 12\%$ (d), $\varepsilon = 15\%$ (e), and $\varepsilon = 20\%$ (f).
stress distributions, and concluded that the global yield criterion has no conclusive predictions about plastic deformations in subdomains containing a few beads.

The expected value of \( p \) starts at 35 MPa at \( \varepsilon_{xx} = 0\% \) and continuously decreases toward a minimum value of 8 MPa at \( \varepsilon_{xx} = 13\% \) (see Fig. 14(f)). The local pressure increases again to 14 MPa at \( \varepsilon_{xx} = 20\% \) and remains almost constant until \( \varepsilon_{xx} = 30\% \). It is clear from the local variation of \( p \) that the most influencing factor in the nucleation of local plastic events is the local mass density of the material (increasing free volume) as evidenced by an increase in the number of atomic positions attaining negative values of the local pressure (see Fig. 18). The number of these loosely packed

Fig. 16. For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, distribution of \( \sigma_{xx} \) at axial strains of \( \varepsilon = 0\% \) (a), \( \varepsilon = 5\% \) (b), \( \varepsilon = 10\% \) (c), \( \varepsilon = 12\% \) (d), \( \varepsilon = 15\% \) (e), and \( \varepsilon = 20\% \) (f).
regions (defects) continuously increases with an increase in the strain and peaks at $\varepsilon_{xx} = 13\%$. Subsequently, the number of these quasi-defects decreases in the stress-softening regime.

Three regimes can be identified in the generation of local quasi-defects (the three linear sections in Fig. 18): $\varepsilon_{xx}(0\%\text{–}5\%)$, $\varepsilon_{xx}(5\%\text{–}13\%)$ and $\varepsilon_{xx}(13\%\text{–}30\%)$. The first regime has the highest rate of defect nucleation. It shows that plastic events in this amorphous material might be present since the very beginning of the deformation process. In the second regime the rate of nucleation decreases and finally reaches the smallest nucleation rate during the stress-softening regime where the increasing trend is reversed.

Distributions of these loosely packed regions having negative pressure are almost uniform (see Fig. 17). It is important to note how the number of points with a negative pressure decrease after the over-shoot in the axial stress–strain curve. The density of these points increased rapidly during the early stages of deformation but toward the overshoot in the axial stress curve a few additional points were required to accommodate the imposed axial deformation. Once in the stress-softening regime the density of points with negative pressure decreases considerably while the axial stress–strain curve presented a small plateau as if the specimen had reached a steady-state in the nucleation of quasi-defects.

Fig. 17. For the stepped uniaxial tensile loading of bulk amorphous PE at 100 K, distribution of $p$ at axial strains of $\varepsilon = 0\%$ (a), $\varepsilon = 5\%$ (b), $\varepsilon = 10\%$ (c), $\varepsilon = 12\%$ (d), $\varepsilon = 15\%$ (e), and $\varepsilon = 20\%$ (f).
It has been shown that the local dynamics and interactions among conforming chains are very complex. This is also reflected in components of the local stress tensor fluctuating with considerable amplitudes at each atomic location. Changes in local structures are also reflected in changes of the local mass density (local free volume). We recall the correlation between changes in the local mass density and values of the local pressure. A local negative pressure, possibly a local cavitation event, will indicate the presence of free volume available for the neighboring beads to move. This motion is restricted by the inherent structure of the polymer and also by the non-bonded interactions among beads; see the variation in self and inter-chain entanglements. As beads in the specimen explore this extra space the deformation imposed by the boundary conditions is progressively accommodated by irreversible local events.

7. Remarks

There are still many issues to be investigated in order to unveil additional details of plastic deformations in glassy polymers; we plan to address some of these issues in future works. One needs to carefully study the quenching process and the effect of the cooling rate on the density of points with negative pressure in the undeformed configuration at different temperatures for fully relaxed specimens with different degrees of polymerization. This should help correlate the initial density of quasi-defects with the magnitude of the maximum stress and subsequent values of the softening modulus. Secondly, the effect of the axial strain rate during the stepped uniaxial test on the rate of nucleation of quasi-defects and changes in the mass densities after unloading from different strain levels should be investigated. This will help determine whether the nucleated quasi-defects persist or the material will heal to a certain extent. Thirdly, deformations under different loading conditions or levels of triaxiality should be analyzed to ascertain their influence on the rate of nucleation and distribution of quasi-defects, and find a criterion for the occurrence of shear local plastic events.

8. Conclusions

Deformations of bulk amorphous polyethylene (PE) during stepped uniaxial tests have been analyzed using molecular dynamics (MD) simulations with energetics described by a united atom force field in order to elucidate the origins of irreversible plastic events. Three complementary criteria have been used to delineate internal structural changes in the material: (i) distributions of free volume, bead contacts and entanglements, (ii) modal analysis around equilibrium positions using the Empirical Orthogonal Functions (EOF) method, and (iii) distribution of local stresses. Salient conclusions from the present study are summarized below.

A. Global stress–strain curves and kinematics of deformation

(i) Values of different components of the total potential energy are not indicative of significant changes in the structural parameters of the polymer.

(ii) Free volume increased with an increase in the axial deformation up to the point of the maximum axial stress. The expected value of the local mass density decreases at a smaller rate during the stress-softening regime.

(iii) During the initial linear elastic and the non-linear regimes prior to the overshoot in the axial stress–strain curve deformations occur by a decrease in the value of the inter-chain entanglement. No substantial changes in the self-entanglement values were observed.

At early stages of deformation structural rearrangements not related to significant changes in the internal d.o.f. of polymer chains can fit in the general deformation pattern of macro-molecular bodies.

B. Modal analysis:

(i) The localization of the orthogonal modes of the displacement correlation matrix is unaffected by the global axial strain level.

(ii) The energy components of the orthogonal modes related to the molecular degrees of freedom differ only for high frequency modes.

(iii) The power spectra of the principal components change with the axial strain but the frequency and the value of the maximum power in the periodograms exhibit an almost identical trend.

Chain straightening does not significantly affect yielding and stress-softening regimes.

C. Local stress analysis:

(i) Even though the virial stress indicates a completely stress-free initial undeformed configuration, there were local compressive normal stresses at most atomic locations.

(ii) The expected value of the local von Mises stress and the local axial stress peak at the same strain level.

(iii) The number of atomic positions with a negative pressure (local cavitation) increases with an increase in the axial strain up to the overshoot in the axial stress–strain curve.

Plastic deformation in amorphous polymers at temperatures well below Tg commences with the nucleation of small scale (local) stress-induced defects. This is consistent with Argon et al.’s [1,2] work on the analysis of plastic deformations in amorphous materials. They proposed that stress-induced small-scale defects, termed shear transformation zones (STZ), are carriers of plastic deformation. For macro-molecular bodies chain straightening processes play a role later on during the strain hardening regime.

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Appendix A. Method for the construction of relaxed specimens

Once a specimen with N monomers per chain has been relaxed the Cartesian coordinates of each bead are scaled by a factor of \(2^{1/3}\). Subsequently N new beads are placed between two existing beads. The position of a new bead is given by the vector \(r_{p/o} = r_{s/o} + \mathbf{u}\), where \(r_{s/o}\) is obtained by adding the vector that locates the midpoint between beads \(k\) and \(i\), \(r_{s/o} = \frac{1}{2}(r_{k/o} - r_{i/o})\), and a vector \(r_{p/s}\) perpendicular to the previous one.

The objective is to generate at random a position vector for the new bead \(p\). The magnitude of \(r_{p/s}\) is set to \(h = \frac{1}{2} \| r_{k/i} \| \tan \left( \frac{\pi - \theta_{\text{bond}}}{2} \right) \), where \(\theta_{\text{bond}}\) is the equilibrium value for the bond-angle (1.92 rad). Components of the unit vector \(\mathbf{u}\) are obtained by enforcing its perpendicularity to \(\mathbf{u}\), the unit vector along the line joining beads \(i\) and \(k\). A component of \(\mathbf{u}\) is chosen at random by using a parameter \(a(n)\) for each bead where \(0 \leq a(n) \leq 1\). Coordinates of \(\mathbf{u}\) are given by

\[
p_x = a_x y, \quad p_y = \frac{1}{(1 + a^2)} \left( n_x + a n_z \right)^2, \quad p_z = \frac{1}{(1 + a^2)} \left( n_y + a n_z \right)^2.
\]

Once all new beads have been placed the torsional energy of each chain is minimized. Keeping bond lengths and bond angles constant components of the vector \(\mathbf{u} = \{a_x(n), a_y(n), \ldots, a_z(n)\}\) are changed by a pattern search global minimization algorithm with mesh adaptive search (MADS) implemented in the Optimization Toolbox of Matlab [67]. This minimization process is performed for each polymer chain separately. Energy terms other than the torsional energy are excluded in the minimization process.

Appendix B. Volume fraction and potential energy density variations in the quenching process

After the relaxation process at 500 K specimens with different degree of polymerization were quenched from 500 K to 100 K using quenching rates of 1 K/ps, 0.1K/ps and 0.01 K/ps under zero pressure. Even though the quenching rates cover three orders of magnitudes, differences in the total potential energy density and the volume fraction are not significant.

Figures B1(b,d,f) depict the variation with temperature of the total potential energy density for specimens with degree of polymerization of 125, 250, and 500, respectively. Irrespective of differences in the degree of polymerization and the quenching rates the potential energy density at 100 K equaled \(W(100K)\). Figures B1(a,c,e) depict the volume fraction \((U_{100K}/U_{500K})\) for specimens with degree of polymerization of 125, 250, and 500, respectively. Values of \((U_{100K}/U_{500K})\) for the three degrees of polymerization and the three quenching rates are in the interval 0.82 < \((U_{100K}/U_{500K})\) < 0.86. No substantial changes in \((U_{100K}/U_{500K})\) were observed in going from 500 to 1000 monomers per chain.
Fig. B1. For the quenching of bulk amorphous PE from 500 K to 100 K at temperature rates of 1 K/ps, 0.1 K/ps and 0.01 K/ps, variation with temperature of the volume fraction for specimens with 125 (a), 250 (c), and 500 (e) monomers per chain, and variation with temperature of the potential energy density for specimens with 125 (b), 250 (d), and 500 (f) monomers per chain. Curves are coloured in the web version of this article.