Molecular dynamics study of polyethylene under extreme confinement

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Molecular Dynamics Study of Polyethylene under Extreme Confinement

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Abstract. We present results concerning the dynamics and the structure of adsorbed layers of molten polyethylene (PE) between two graphite surfaces. The molecular weight of the monodisperse PE chains reaches the entanglement regime. We study three cases of interwall distances, equal to two, three and four times the unperturbed radius of gyration ($R_g$) of PE chains. The confined system is equilibrated by use of efficient Monte Carlo (MC) algorithms. Conducting molecular dynamics (MD) simulations, we reveal the distribution of relaxation times as a function of distance from the graphite walls at the temperature of 450 K. From the atomic-level stresses we calculate a realistic estimate of the adhesion tension, which is not affected significantly by the width of the pore. Although the distance between the two walls is comparable to the width of the adsorbed layer, we do not record the formation of ‘glassy bridges’ under the studied conditions. The diffusion of polymer chains in the middle layer is not inhibited by the existence of the two adsorbed layers. Extreme confinement conditions imposed by the long range wall potentials bring about an increase in both the adsorption and desorption rates of chains. The presented results seem to cohere with a reduction in the calorimetric (heat capacity step) glass transition temperature ($T_g$).

1. Introduction
Upon cooling polymer melts, before the liquid to solid transition is reached, the viscosity and relaxation times increase dramatically. In some cases, extreme confinement conditions, in which the interwall distance ($h_n$) is comparable to the chain dimensions, have been related to a non-Einstein-like decrease in viscosity [1]. Moreover it has been shown [2–6] that attractive confining walls introduce one more mechanism (in addition to the caging effect and intramolecular conformational barriers) for time scale separation of glass forming polymers. This mechanism is the slow desorption kinetics of monomers from the surface, leading to slow layer exchange dynamics on the length scale of (at least) the radius of gyration of the chains. Several experimental works [4,7] have supported the idea that the confined/bounded layer is immobilized above the major $T_g$, in such a way that finally it does not participate in the glass transition.

In most atomistic simulation studies (MD, MC etc.) [2,5,6] the size of $h_n$ has been considered much larger than $R_g$. Nevertheless, in polymer nanocomposite science much attention has been focused on the case where layers of polymer adsorbed on neighboring particles overlap. In this situation an undefined mechanism seems to affect the mechanical properties of nanomaterials. The phenomenon is usually explained by the formation of ‘glassy bridges’ between the nanoparticles [8,9]. Moreover, it is not clear how these enhanced mechanical properties of polymer nanocomposites are related to...
polymer diffusion in the interparticle layer [1,9]. Our study focuses on the characteristics of the overlapping opposite adsorbed layers at a temperature far above $T_g$. Also, for the most confined system we have studied two cases of higher pressure. We have used combined MD and MC simulations in order to overcome the significant barriers of sampling under extreme confinement conditions.

2. Simulation details
The confined polymer systems were studied at the temperature of 450 K and pressure of 0.1 MPa. They consisted of 79 polyethylene (PE) chains of 200 carbons each. We have investigated three cases of confinement between the two opposite graphite surfaces located perpendicular to the z-axis (capped systems). A case of $h_w$ equal to 100.0 Å (labeled as cap100), a case of $h_w$ equal to 80.3 Å (cap80) and a case of $h_w$ equal to 50.5 (cap50). In the case where one of the two solid surfaces of the cap80 system was replaced by vacuum, the supported system was labeled as sup80. The choice of the volume of the simulation box took into account the excluded volume of the graphite. In order to do so we have assumed that the density profile of the capped system near one of the substrates should be superposable with the density profile of the respective supported system [10]. In this way the middle layer has the density and the pressure of the bulk. The initial configurations of the confined polyethylene have been obtained by a MC builder capable of constructing polymeric chains of arbitrary geometry in heavily constrained environments [11], based on the quasi-Metropolis scheme of Theodorou and Suter [12]. Then, a MC equilibration of the initial configurations was carried out by use of connectivity altering moves, such as concerted rotation and double bridging [13,14]. All MD simulations have been conducted using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [15].

We have used a united atom model for the description of the PE chains. Each methyl (CH$_3$) and methylene (CH$_2$) group along the chain backbone is treated as one interaction site [5,16]. Nonbonded interactions were described by the TraPPE force field [17] and bonded interactions (bond stretching, bond angle bending and torsional potential) were implemented following the work of Nath et al. [18]. The potential energy of interaction between a polymer atom and a semi-infinite crystalline graphite phase was calculated by the implementation of an efficient and accurate Fourier summation method designed by Steele [19]. According to the methodology introduced by Mansfield and Theodorou [20], the 10-4 sum was performed explicitly over the first 63 underlying layers of graphite atoms, while the contribution of the remaining layers was accounted for by a 9-3 potential. The Lennard-Jones interaction parameters between a polymer united atom and a graphite carbon atom were estimated according to the Lorentz-Berthelot rule.

3. Results and discussion
The wall potential used efficiently incorporates both the long range field of the graphite and the roughness of its basal plane. In figure 1 we present results concerning the density profile of the capped system compared with the respective density profile of a supported film. Although an accurate estimation of the polymer concentration in the graphite pore would strictly require a grand canonical approach, we can verify that the density fluctuations close to the wall are in agreement with the ones of a supported film of commensurate thickness [5]. In the same figure we distinguish three layers. Layer I is defined by the first density minimum at 6.25 Å from the wall. In this region the wall potential severely restricts displacement along the z-axis. A chain having at least one atom inside layer I is considered adsorbed [5]. Layer II, extends from 6.25 to 15.25 Å, where the presence of the wall
field is weaker and so are the density fluctuations. Over the middle layer III, beyond 15.25 Å, density fluctuations almost vanish. The root mean squared radius of gyration $R_g$ of the studied bulk PE was calculated as 25.8 Å. On the other hand, the extent of the adsorbed layer exceeds this distance, reaching up to 70 Å from each wall [4] according to the volume fraction profile (not shown). The bond order parameter for all capped systems (figure 2) confirms a middle layer of no order. The alignment parallel to the surface at the distance of 3.25 Å is caused by the trains and the loops [21], while the first maximum at 6.25 Å is interpreted as an alignment vertical to the wall at the distance of the first density minimum [4,22].

![Figure 1](image1.jpg)  
**Figure 1.** Density profiles of the three capped and one supported thin films.

![Figure 2](image2.jpg)  
**Figure 2.** Bond order parameter of the three capped systems

An explanation of the observed structure in the adsorbed layer is possible if we measure the gradient in mobility in layers parallel to the wall. The results (figure 3) show that the displacement in the xy-plane (parallel to the graphite surfaces) is enhanced at distances where a significant suppression of the displacement along the z-axis (perpendicular to graphite surfaces) is present [5,10]. It is supported the idea that the small fraction of adsorbed chains which joins the decoupled layers I and II with different mobility in the xy-plane is stretched [22]. It is worth mentioning that a notable maximum peak in the volume fraction of chain free ends [23] is observed at a distance of 7 Å, inside the depletion layer of the density profile. The resulting density gradient seems to guide the first step from the non-adsorbed (free) state to the adsorbed state.
Figure 3. Mean square displacement (MSD) of the atoms based only on the $x$ and $y$ components of the displacement, parallel to the walls, for the cap80 system. The results are presented for six equal size layers (of 3.5 Å), parallel to the walls (region from 3 to 24 Å in $z$-axis) and the remaining middle layer. In the inset to the figure (a) we present results for short times while in the main figure (b) we present results for long times.

In the analysis presented in figure 3, an atom contributes to the displacement in a particular layer only if it is the same with the one the atom occupied at the time origin. At short times (lower than 1 ns, figure 3a) we have made the assumption that the atom should not escape the layer at intermediate times, while at longer times (figure 3b) in order to improve the statistics it is assumed that the displacement in the $z$-axis cannot exceed the width of the layer. The results indicate that although at short times, due to the wall roughness, the displacement in the second layer at 8.25 Å from the wall is faster, at longer times (several nanoseconds) it is the first layer at 4.75 Å that depicts the highest displacement in the $xy$-plane \[5,10\].

Chains adsorbed on both walls (bridges) are detected only in the case of the most confined system cap50. In the center of the cap50 system, the volume fraction of the observed bridges is 0.05, while the volume fraction of free chains is 0.47. Upon increasing the pressure in order to reach bulk densities of 0.81 and 0.84 g/cm$^3$, we do not observe a significant increase in the volume fraction of bridges. Efficient sampling at these high pressures was enabled by use of the MC algorithm. In our computational experiment, the used force field for PE at a temperature of 450 K and pressures of 0.1, 40 and 85 MPa did not confirm the formation of any kind of ‘glassy bridges’.

The stress profile especially in the systems cap100 and cap80 confirms the existence of a middle layer with an isotropic pressure equal to 0.1 MPa. Moreover, the surface tension of a respective free film (both walls have been replaced by vacuum) of PE with 200 carbons was found equal to $23 \pm 2$ mN/m. The calculated adhesion tension for capped PE films of 200 and 260 carbons was equal to $90 \pm 3$ mN/m and $85 \pm 2$ mN/m respectively. We estimated a decrease of the adhesion tension as a function
of the molecular weight [24], while under the studied conditions the adhesion tension was not affected by the interwall distance.

In figure 4 we depict the bond auto-correlation function (ACF). The results are presented for the layers defined in figure 1 and also for the loops and the tails of adsorbed chains. We observe that the increased decorrelation times are mainly attributed to layer I (trains). Also, tails decorrelate faster than loops. The same picture is supported by the torsional auto-correlation functions. In figure 5 we plot the decorrelation times of the torsion ACFs (fitted to the mKWW function [6]) as a function of the distance from the surface for the cap80 and cap50 systems. It is observed that the longest decorrelation time on the wall for the cap80 system is higher than the respective value for the cap50 system. In order to interpret this significant outcome, we have calculated the average time a chain lies adsorbed in each of the three capped systems. The residence times in the adsorbed state are 1.15 ± 0.05 ns, 1.21 ± 0.08 ns and 1.31 ± 0.09 ns for the cap50, cap80 and cap100 systems, respectively. The lower residence time in the cap50 system is justified by the high adsorption and desorption rates introduced by the bridges. It seems that, although the graphite wall establishes an adsorption/desorption process, under conditions of extreme confinement ($h_w < 3R_g$) the field of the opposite wall can cause an increase in the desorption rate [25].

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure4.png}
\caption{Bond autocorrelation functions (ACFs) for layers defined in figure 1 and also the loop and tail parts of the adsorbed chains for the cap80 system.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure5.png}
\caption{Comparison of the relaxation times estimated by the mKWW function for the cap80 and cap50 systems.}
\end{figure}

Finally using MD simulation trajectories of over 600 ns, we have calculated the diffusion coefficients of the centers of mass. The results are (MSD=1.5[MSD_x + MSD_y]): $3.5 \times 10^{-7}$ cm$^2$s$^{-1}$, $4.0 \times 10^{-7}$ cm$^2$s$^{-1}$ and $3.7 \times 10^{-7}$ cm$^2$s$^{-1}$ for the cap50, cap80 and cap100 systems, respectively. In all cases the diffusion coefficients were higher than the one in the bulk ($3.2 \times 10^{-7}$ cm$^2$s$^{-1}$) [5,16].

4. Conclusions
We have presented results from atomistic simulations of PE under extreme confinement conditions, far above $T_g$. The initial configurations were equilibrated at all length scales by use of an efficient MC algorithm and trajectories of over 600 ns were produced with MD simulations. Even in the case of high pressure we do not record the formation of ‘glassy bridges’ under the studied conditions. The
Decoupling between layers of different mobility creates a density gradient where the concentration of chain free ends is increased. Moreover, the introduction of an opposite graphite wall (capped systems) seems to increase the desorption rate of chains. Our results agree with previous investigations [5] on thin supported PE films that indicate acceleration in dynamics compared to the bulk.

References