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Simulated glass transition in thin polymer films: Influence of truncating the non-bonded interaction potentials

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ABSTRACT

NPT molecular-dynamics simulations have been carried out, using the Gromacs package, of the coarse-grained united-atom model of a polymer melt in the vicinity of the glass transition and confined between two crystalline substrates. The pair interactions between all united atoms are described with the help of the Lennard-Jones (LJ) potential. For a corresponding bulk polymer at fixed potential cutoff distance the temperature dependence of density is not influenced by different methods of shifting the potential but is affected by the long range energy and pressure correction. At the same time the shift to higher densities and higher glass-transition temperatures is observed upon increasing the LJ cutoff distance from 2.5σ to 5σ. Depending on the potential cutoff value the polymer-film density can be both below and above the corresponding bulk density at fixed temperature; these dependences are also very sensitive to modification of the potential at a fixed cutoff distance. The effect increases with decreasing film thickness, thus resulting in a different thickness dependence of the glass-transition temperature at different cutoff values.

1. Introduction

Thin polymer films are used nowadays for packaging, coatings, sensor and organic-electronics applications [1]. In these films polymer chains are subjected to the strong influence of different interfaces, as solid or free surfaces, for example. Despite numerous studies of polymer equilibrium and segmental-dynamic properties the understanding of their behavior at interfaces and in strongly confined thin films in particular is still an extensively debated subject. It is established, both in experiments and in simulations [2–12], that the presence of supporting surfaces and/or free interfaces may drastically change the behavior of macromolecules. Confinement effects play an even more important role when the film thickness becomes comparable to the gyration radius of the individual polymer coil. A change in glass-transition temperature has been observed for different polymer films (free-standing, supported or capped) upon the decrease of the film thickness below 100 nm, using ellipsometry [2], Brillouin light scattering [3], X-ray reflectivity [4], positron annihilation lifetime spectroscopy [5], neutron reflectivity [6], dielectric spectroscopy [7,8] and calorimetry [9]. As shown in all these experimental studies, the T_g shift is influenced tremendously by the subtle interplay between the strength of the polymer–substrate interactions, the film thickness, the existence of free interfaces, the film preparation method, the film annealing, and many other details. Clearly, the extensive literature exists on this subject; still the question about the influence of the spatial confinement on the glass-transition temperature in polymer melts is not yet resolved.

Numerous molecular-dynamics (MD) simulations of supported, free-standing and capped polymer films have been carried out as well and have provided important information about the effect of confinement on the polymer dynamics [10–14]. In these studies, the polymer segmental dynamics in the films have also been found to be thickness and substrate adsorption-strength dependent. In our recent studies [15,16] the dynamics of capped highly-densed polymer films were presented. It was shown that the thickness-dependence of the segmental dynamics strongly depends on the substrate attraction strength. The acceleration of the dynamics when decreasing film thickness was observed for films capped under energetically neutral substrates, although non-monotonic thickness-dependent behavior was shown for the case of strongly adsorbing substrates.

The main scope of the present study is to investigate the effects on the polymer density-temperature (ρT) behavior caused by different truncation distances and shifting methods of the substrate–polymer and polymer–polymer interaction potential which could be implemented in a typical MD simulation of thin films.

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Usually the non-bonded interactions between polymer segments separated by the distance r are described by the Lennard-Jones potential

$$V_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \tag{1}$$

where ε is the characteristic energy and σ is the characteristic length scale. The problem immediately arises how to treat efficiently all the pairwise interactions described by Eq. (1); their explicit calculation for a system with N interacting centers requires $O(N^2)$ operations per integration step and quickly becomes computationally unfeasible. Usually, to reduce the amount of calculations, a spherical cutoff to the pair potential $V_{LJ}(r)$ is implemented; this means setting this potential to zero for $r > r_c$, where r_c is the cutoff distance. The introduction of this cutoff is normally considered as a small perturbation to the attractive forces; in order to ensure this the cutoff distance should be large enough. Still, the thermodynamical properties of the model with the modified pair interactions will be different from those of the "non-truncated" polymer melt. As a consequence of the potential truncation, the attractive interactions between model particles i and j, separated by a distance $|\boldsymbol{r}_{ij}|$, are underestimated, and the pressure, which is normally calculated from the virial theorem [17],

$$P = \frac{2}{3V}\left(E_{kin} + \frac{1}{2}\sum_{i\neq j}\vec{r}_{ij}\cdot\vec{F}_{ij}\right) \tag{2}$$

is overestimated. Here V is the system volume, E_{kin} is the total kinetic energy and $\vec{F}_{ij}$ is the force between two particles. To repair these errors in pressure and energy calculations, isotropic long-range corrections both to potential energy and to internal pressure (and to any other thermodynamic quantity) are usually applied by integrating from the cutoff radius r_c to infinity, assuming that the radial distribution function $g(r)$ in this spatial range is equal to unity. With this approach, artifacts resulting from small (but computationally cheap) cutoff distances are compensated.

In systems with interfaces, the isotropic pressure correction is not recommended because the system itself is rotationally anisotropic. Therefore, the value of the cutoff distance can be important for the final structural and dynamical properties of the simulated systems. A main issue is the discontinuity of the potential and the forces at the cutoff distance. The importance of this effect has been shown in systems with liquid–vapor interfaces [18]. Moreover, the thickness and the surface tension in such systems sensitively depend on the truncation distance [19]. The effect on density of the absence of the long-range pressure corrections has been highlighted for alkanes as well [20]. A method was proposed recently to implement long-range pressure corrections in systems with interfaces (i.e liquid–vapor interface) and in this way the surface tension was recovered in Lennard-Jones fluids with small cutoff distances [21]. An alternative approach was suggested recently by Lagüe et al. [20]. The authors proposed to calculate internal pressure both at very short and very long cutoff distances, and determine the difference $\varDelta P$. The NPT simulation is carried out further at the short cutoff with the additional pressure correction $\varDelta P$. Based on this approach, Wu et al. suggested the so-called isotropic period sum (IPS) method, where the long-range interactions are calculated based on isotropic periodic images which represent remote structures [22]. Nevertheless, the validity of these methods for simulations of strongly inhomogeneous systems is not yet completely verified. Another general method relies on particle-mesh Ewald (PME) summation which replaces the long-range calculations by a sum of replicas of the central box [17,23]. This method has proved successful to avoid artifacts occurring from the truncation of the electrostatic forces [24,25].

In the present study we use a truncated Lennard-Jones potential and try to show the influence of the cutoff distance when studying the glass-transition phenomena in confined polymer melts. The effects of modification of the potential are also evaluated. We perform NPT molecular-dynamics simulations of a coarse-grained polymer film capped between two crystalline substrates. The take-home message of our study is that the potential truncations and modifications are of major importance in attempts to reproduce correctly the experimental temperature dependence of density in very thin polymer films. We show that this dependence is rather sensitive to the cutoff distance and to different ways of modifying the pair potential; such ways are implemented in the Gromacs package [26].

One widely used correction is a simple shift of the truncated LJ potential, Eq. (1), to be zero at the cutoff,

$$V_{LJ}(r) = \begin{cases} 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) - V_{LJ}(r_c), & \text{if } r \leqslant r_c \\ 0, & \text{if } r > r_c. \end{cases} \tag{3}$$

This shifted potential will be referred as PS in what follows.

Another way, which is implemented in Gromacs, is to modify the LJ potential by replacing it between an inner cutoff r_1 and an outer cutoff r_c with a cubic polynomial function, so that both the potential and its derivative smoothly decay to zero at the outer cutoff distance [26]. In the present study the inner cutoff was chosen to be $r_1 = 2.25\sigma$. Note that this modification of the potential leads to stronger attractive forces in the modified region. This Gromacs-specific potential shift will be referred as the Gromacs potential shift (GPS) in what follows. In the present study the simulations have been carried out for a non-shifted potential as well Eq. (1) that was truncated at different distances r_c. This potential is referred as the non-shifted (NS) potential.

The remainder of this paper is organized as follows. A short description of the simulated polymer model and equilibration procedure is given in Section 2. Our main findings are discussed in Section 3. Section 3.1 shows T-dependence of the bulk density upon different truncation distances and shifting methods of the potential. The later effects on the T-dependence of density of thin polymer films are discussed in Section 3.2 and the Conclusions are summarized in Section 4.

2. Model and simulation methods

We simulate coarse-grained thin polymer films that are capped between two attractive crystalline substrates using a bead–rod polymer model. Each chain consists of 50 monomers, with 80% monomers of type A and 20% monomers of type B, which differ in their sizes ($\sigma_B = 1.2\sigma_A$) and masses ($m_B = 1.2^3 m_A$) and are randomly placed along each chain. The reason for choosing two types of particles is to avoid immediate crystallization. Every film was made of 100 polymer chains. Each of two substrates consists of three layers of Lennard-Jones spheres in an HCP arrangement; the diameter of each sphere is $\sigma_s = 0.85\sigma_A$. This model can be used to mimic the interparticle polymer bridge between neighboring filler particles in filled elastomers; each substrate then represents the surface of a filler particle. In these systems, the polymer–substrate interaction strength can be very high and the consequences of truncating the potential will be more pronounced. More details about the simulated polymer model can be found in our previous publications [15,16].

All bonded monomer pairs are connected with rigid bonds and all non-bonded monomer pairs interact via a truncated (shifted or non-shifted) LJ potential, Eqs. (1) and (3), using different values of cutoff distance r_c, from 2.5σ to 5σ. In what follows all quantities are expressed in LJ units. The substrate–polymer interaction strength ε_{sp} was chosen equal to the polymer–polymer interaction