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Simulation of polyethylene thin films composed of various chain lengths☆

Pemra Doruker

Department of Chemical Engineering and Polymer Research Center, Bogazici University, Bebek 80815, Istanbul, Turkey

Abstract

Polyethylene thin films are simulated using a coarse-grained on-lattice Monte Carlo technique. Properties of free-standing films, which are made up of either C_{50}, C_{100} or C_{316} chains, are analyzed in the melt phase at 509 K. As a result of increasing molecular weight, the following observations are made: (i) bulk density of the films increases; (ii) there is a higher degree of parallel orientation of bonds at the surface and a broader region over which this orientation survives; (iii) the decrease in the radius of gyration of the chains at the surface becomes more significant and (iv) parallel orientation of the chains at the surface is enhanced. Moreover, mixed films that contain both C_{50} and C_{100} chains are simulated. In these mixed films, the properties of C_{100} chains do not change, whereas the orientation of C_{50} chains and bonds is higher in the presence of longer chains. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Simulations are useful in analyzing polymer thin films that present free surfaces to vacuum. In a series of recent papers with Wayne Mattice [1–3], we analyzed the equilibrium and dynamic properties of free-standing polyethylene (PE) thin films, which were composed of linear and/or cyclic PE chains of constant chain length, namely C_{100}. We used a coarse-grained on-lattice simulation technique, which has been developed in Wayne Mattice's laboratory [4–7]. This Monte Carlo (MC) algorithm, which is called the second nearest neighbor diamond (2nnd) lattice simulation, can efficiently equilibrate large system sizes. As a result, local and global properties of PE films, which contain around 100 C_{100} chains, could be studied [1–3].

Earlier studies on free-standing polymer thin films were MC simulations [8,9] of flexible polymer chains. Madden [8] performed the first on-lattice simulations of a melt–vacuum interface using a film adsorbed on a solid surface. Later, off-lattice MC simulations of bead-spring homopolymer films were done by Kumar et al. [9]. Treatment of relatively short alkane systems (C_{10} and C_{20}) were carried out by molecular dynamics (MD) simulations [10] using a united atom model. Mansfield and Theodorou simulated a glassy atactic polypropylene (PP) surface by using a fully atomistic molecular mechanics technique [11] to determine local and global equilibrium properties. They also performed MD simulations [12] using equilibrium snapshots to study the short time dynamics.

Some important free surface properties compiled from the simulations mentioned above [1–3,8–12] are as follows: (i) depletion of middle beads and predominance of end beads, (ii) anisotropy in the orientation of bonds and chains, (iii) higher mobility at the scale of individual beads and chains and (iv) increase in the diffusion coefficient of the chains parallel to the surface.

Atomistic systems that contain single or a few longer chains have been studied by MD simulations [13,14]. Due to the system size limitations of MD simulations, only local properties and energetics of free surfaces have been considered in the studies so far. A compilation of the atomistic simulation studies of polymer melts confined between solid walls and/or free surfaces is given by Yoon et al. [15].

In a recent work [16], we showed that surface properties such as roughness and orientation of bonds are affected by the lateral dimensions of the periodic surface. These results are in conformity with the simulation studies of Werner et al. [17] on interfaces formed by binary polymer blends. They showed that the interfacial properties change with periodic dimensions as a result of capillary waves.

In the current study, the 2nnd lattice simulation technique will be applied to homopolymer films composed of various linear chain lengths (C_{50}, C_{100} and C_{316}). The films will contain either a single chain length or two different short- and long-chains. The effect of chain length on the local and global equilibrium properties of monodisperse films will be examined first. In the meantime, the consequences of varying the periodic surface dimensions will also be considered.

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Then, the properties of mixtures of short and long chains will be analyzed in comparison with the monodisperse films.

2. Simulation method

Simulations are performed on a coarse-grained lattice, which is formed by connecting every other lattice site on a diamond lattice. This resulting lattice corresponds to the hexagonal packing of hard spheres. It is possible to map different polymer chains on this lattice by the modeling the specific short- and long-range interactions according to the chemistry of each polymer chain, such as PE [5,6], PP [18–21] and polyvinyl chloride [20,21]. Efficient simulations of different polymeric systems, such as thin films [1–3] and nanofibers [22,23], can be performed and then reverse-mapped [7] back to the atomistic continuous space after equilibration.

Short-range interactions [5], which determine the local conformations of the specific chains, are modeled by the rotational isomeric state (RIS) formalism [24,25]. Long-range interactions [6] are obtained by coarse-graining the continuous Lennard-Jones interaction between two monomer units for the different shells on the lattice.

In this work, PE thin films are simulated at 509 K, i.e. well above the melting point of PE. Each lattice site accommodates an ethylene unit (monomer). The original RIS model developed for PE by Abe et al. [26] is modified to account for the short-range interactions. The long-range average interaction energies obtained for the first three neighboring shells on the lattice are 14.122, 0.526 and −0.627 kJ/mol, sequentially [1,6]. The attractive third-shell energy brings cohesion to the thin film systems formed on the 2nnd lattice. Surface energy calculated for PE thin films formed on the 2nnd lattice were found to be close to the experimental value [1].

Table 1 summarizes the film systems used in this study. First four films are monodisperse systems, composed of C_{50}, C_{100} or C_{316} chains. The last two films are polydisperse systems, which are binary mixtures of C_{50} with either C_{100} or C_{316}. f50-S and f50-L have different number of C_{50} chains and periodic lateral dimensions.

Table 1
Simulation systems

Film	Chain 1	Chain 2	Periodic lateral area[a]
f50-S	18 C_{50}	–	13 × 13
f50-L	72 C_{50}	–	21 × 22
f100	36 C_{100}	–	21 × 22
f316	25 C_{316}	–	28 × 28
f100/50	24 C_{100}	24 C_{50}	21 × 22
f316/50	20 C_{316}	30 C_{50}	28 × 28

[a] The simulation box is a slanted cube in x, y and z directions. The box is long enough in the z direction so that the free surfaces do not interact. Number of lattice sites in x and y directions is given here. The lattice spacing is 2.5 Å.

Films f100 and f316 are formed by increasing one of the periodic sides of an equilibrated bulk snapshot to a high value, so that the newly formed free surfaces do not interact with each other [13]. In the case of films f50/100, f50/316 and f50, the C_{50} chains are formed by dividing a portion or all of the long chains from a homopolymer system (either C_{100} or C_{316}) into short chains of required size. In both cases, the newly formed films are equilibrated for a few million Monte Carlo steps (MCS). Analysis of equilibrated films are performed over 1–2 million MCS.

3. Results and discussion

In the first part, the effect of chain length on local and global surface properties will be analyzed by comparing three monodisperse systems. In view of these results, the second part will focus on the properties of chains that are altered in the presence of other (shorter/longer) chains.

3.1. Monodisperse systems

Density profiles. Fig. 1(a) depicts the density profiles along the z direction (in Å), which is normal to the film surface. The center of mass of the film is located at $z = 0$. Films f50-L and f100 have comparable thickness and f316 is about 15 Å thicker than the others, in terms of the distance between free surfaces. The bulk densities in the center of mass of the films increase from 0.66 to 0.72 g/cm^3 with increasing molecular weight (refer to Table 2). The experimental density of PE is 0.75 g/cm^3 at 480 K, [27] and it can be extrapolated to approximately 0.73 g/cm^3 at 509 K.

In Fig. 1(b) the density profiles are superimposed by normalizing the results obtained for different chain lengths by the respective bulk density and by shifting the data to account for the different film thicknesses with the location of f100 kept as the reference. This scaling indicates that the concentration of end beads determines the variations in the bulk density and the interfacial profiles of the films composed of different chain lengths. Another important factor that influences the interfacial profiles is the lateral periodic dimensions of the film, as will be discussed below. Thus, the small variations in the interfacial profiles in Fig. 1(b) should result from the differences in the periodic dimensions, given in Table 1.

Table 2 lists the radius of gyration of the chains, R_g, which is averaged over all snapshots of the trajectory after equilibration. First column gives overall R_g that is calculated for all chains irrespective of their location in the film (at the surface or bulk region), whereas the second column considers only those chains located in the center of the film. Two ratios that relate the size of the chains to the thickness and the lateral periodic dimensions of the films are also given in the same table. Specifically, L refers to the length of one of the sides of the periodic surface area. Δh is the

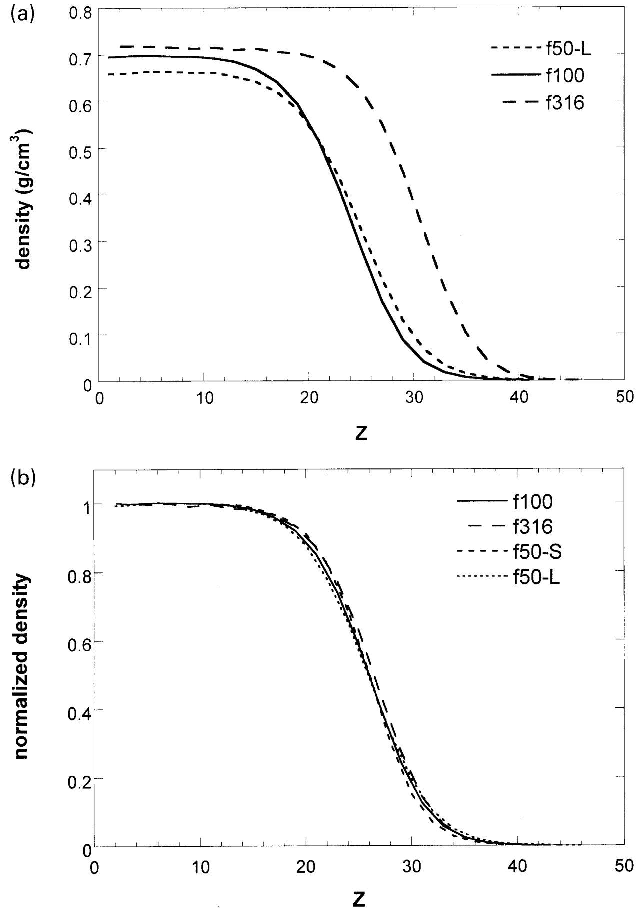

Fig. 1. (a) Density profiles of monodisperse PE films of different chain lengths as a function of distance from the center of mass in the z direction that is normal to the free surfaces. (b) Superimposed density profiles after normalization by the respective bulk density of the films and shifting the data to account for the different film thicknesses.

thickness of the films between the two free surfaces. The location of the free surface is taken at the point where the local density drops down to 0.1 g/cm^3.

In a previous work on thin films composed of linear C_{100} chains [1], the properties of the free surfaces were shown to be almost identical for two films that have same $L/R_g = 3.9$, but different thickness of $\Delta h/R_g = 4.2$ or 7.9. It can be stated that, at constant L/R_g, surface properties are independent of the film thickness for thin films, which have sufficient bulk density in the center. In another recent work [16], we dealt with C_{100} films of constant thickness $\Delta h/R_g = 4.2$, but varying periodic dimensions, namely $L/R_g = 2.5$, 4.9 and 9.9. It was found that the interfacial width and surface roughness increase as a result of increasing lateral periodic dimensions. These results are in conformity with the results of Werner et al. [17], on the interfacial profiles of coexisting phases of a binary polymer mixture in a confined thin film. Therefore, in the comparison of surface properties of films composed of different chain lengths, the L/R_g ratios of the films will also be taken into account.

Orientation of bonds. The order parameter, S, is used to determine the orientational preferences of coarse-grained bonds at the free surfaces.

$$S = \tfrac{1}{2}\langle 3\langle\cos^2\theta\rangle - 1\rangle, \tag{1}$$

where θ is the angle between any coarse-grained bond and the z axis (normal to the free surface). According to this definition, $S = 0$, -0.5 and 1.0 correspond to perfectly random, parallel and perpendicular orientations relative to the film surface, respectively. Fig. 2(a) displays order parameter as a function of z (Å) for the three films. In general, there is random orientation in the bulk region of the films. At the surface, the middle bonds prefer parallel orientation, whereas the end bonds tend to stick out to the vacuum. The net overall effect is that S goes through a minimum at the free surface. All these results are in accordance with previous simulations [1,3,9–11].

In Fig. 2(a), the interface of the f316 film is displaced by 8 Å, so that the location of the minima in S coincides in all films. With increasing chain molecular weight, there is a higher degree of orientation at the surface and a broader region over which this orientation survives. However, a direct comparison of these films could be uncertain, because the films have different L/R_g and $\Delta h/R_g$ ratios. In Fig. 2(b), the bond orientation in films f50-S and f100 are plotted, which have almost comparable L/R_g and $\Delta h/R_g$ ratios. In this case, the bulk region of f50-S is displaced so that the locations of the minima coincide. The parallel orientation in f50-S occurs in a narrower region compared to f50-L. Thus, the effect of increasing orientation with

Table 2
Properties of monodisperse film systems

Film	Bulk density (g/cm^3)	R_g (Å)[a] overall	R_g (Å)[b] at $z = 0$	L/R_g[c]	$\Delta h/R_g$[d]
f50-S	0.66	9.1	9.4	3.6	4.6
f50-L	0.66	9.1	9.2	5.8	6.6
f100	0.70	13.6	14.2	3.9	4.1
f316	0.72	24.3	29.4	2.9	2.9

[a] Average radius of gyration for all the chains in the film.

[b] Average R_g for the center (bulk region) of the film.

[c] L refers to one of the periodic lateral dimensions of the film.

[d] Δh is the distance between the two free surfaces of the film. Free surface is taken to be located at the point where the local density drops to 0.1 g/cm^3.

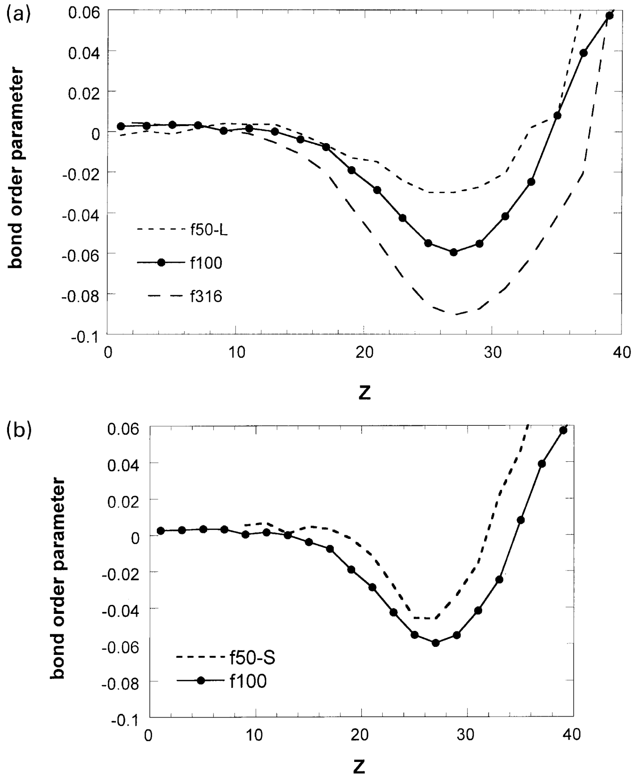

Fig. 2. Orientation of coarse-grained bonds with the z-axis (a) for monodisperse films that have different chain lengths and lateral periodic dimensions, (b) for f50-S and f100 that have almost same lateral periodic dimensions. The z position is defined as the midpoint of each coarse-grained bond.

molecular weight survives in the case of constant L/R_g and $\Delta h/R_g$, as well.

Chain properties. R_g of chains in different bins along z normalized by R_g value at the center bin of the film, $R_g/R_g(z=0)$, is plotted in Fig. 3. The bins over which averaging is performed have a thickness of 2 Å in f50 and f100, and 4 Å in f316, to obtain reliable statistics. In general, R_g decreases at the free surfaces over a range of about $2R_g$. This range, over which the global chain properties are affected at the free surface, was also indicated by Mansfield and Theodorou [11]. The decrease in $R_g/R_g(z=0)$, becomes more significant, as the chain length increases. The fluctuations in the outermost bins, which reflect poor statistics due to the few number of chains, are left there to designate the film thickness in terms of center of mass location. In f316, the distance between the outermost bin and film center is about 26 Å, which corresponds to R_g of C_{316}. Thus, f316 film is not thick enough to observe the entire surface range over which chain properties are affected.

To define the shapes and orientation of the chains, the eigenvalues (L_1^2, L_2^2 and L_3^2) of the radius of gyration tensor for each chain are calculated by converting to the principal axis system. The eigenvalues (principal moments) of the chains normalized by their squared radius of gyration in specific bins stay almost constant over the thickness of the films. This result is in conformity with previous simulations [1,3,11] and indicates that the overall shape of the molecules does not change at the interface. The greatest deviations are observed in f316, where L_1^2/R_g^2 changes between 0.68 and 0.75.

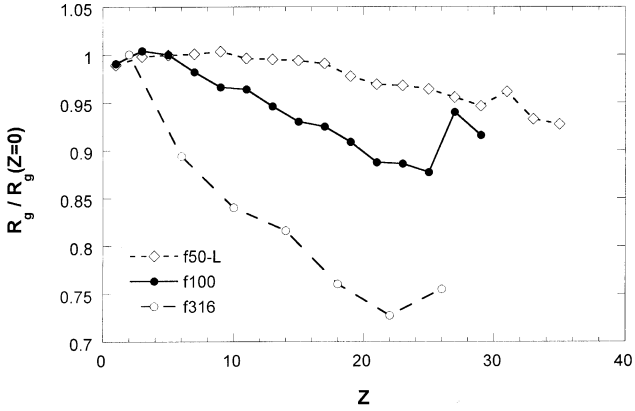

Fig. 3. Decrease in radius of gyration of the chains at the interface of monodisperse film. The z position of each chain is defined as its center of mass.

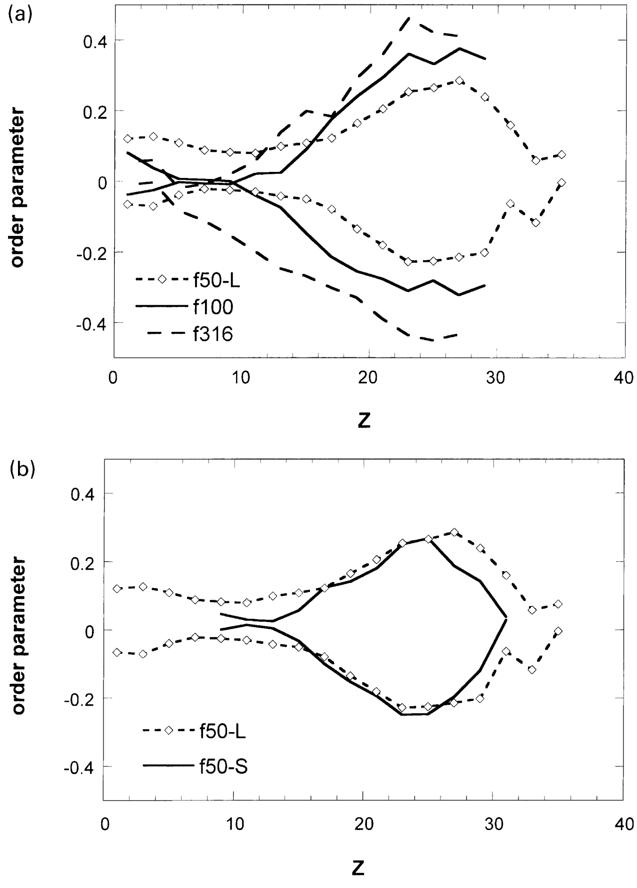

Fig. 4. Orientation of the first and third principal axis of the chains with the z axis, where z position represents the chain center of mass. (a) The long dashed lines, the solid lines and the dashed lines with diamonds correspond to films f316, f100 and f50-L, respectively. (b) The solid lines and dashed lines with diamonds refer to f50-S and f50-L, respectively.

Fig. 4(a) displays the orientation of the largest and smallest eigenvectors (principal axes) of the chains relative to the surfaces. Both axes are almost randomly oriented in the bulk region, whereas there is a strong tendency for the first (largest) principal axis to orient parallel to the surface and the third (smallest) axis normal to the surface. As the molecular weight increases, parallel orientation of the chains at the surface is enhanced. This result may also depend on L/R_g and $\Delta h/R_g$ ratios. Fig. 4(b) shows the difference between f50-S and f50-L systems, with f50-S being displaced by 8 Å so that the interface regions coincide for the two films.

Moreover, there is some preferred orientation in the bulk region of f50-L, which becomes more significant in mixed systems, as will be discussed in Section 3.2. This behavior is not observed in f50-S films, which have a smaller bulk region.

The alignment of the longest principal axis of the chains parallel to the free surface has been indicated in previous simulations as well [1,3,11]. Here, we observe that this orientation behavior diminishes at the gas side of the interface for C_{50} chains (films f50-S and f50-L), i.e. the order parameter for the largest and the smallest principal axes become zero at large z-values. However, the same behavior is not observed in the case of longer chains. As the chain radius of gyration increases, the random orientation of chains becomes unlikely at the surface. It should be noted that the orientation curves for longer chains stop at smaller z-values. This is a direct consequence of the chain center of mass behavior observed in Fig. 3, and not a result of poor statistics.

3.2. Mixed systems

Comparison of chain properties in film f100/50 with those in monodisperse films will reveal the effects of blending chains of two different molecular weights. Monodisperse systems f50-L and f100, which have the same periodic lateral dimensions with f100/50, will be used for comparison.

Fig. 5 displays the density profiles of the short and long chains in f100/50. As expected, the shorter chains are more predominant at the interface compared to the bulk region and the total bulk density in the middle of the film is 0.71 g/cm^3. The order parameter for bonds in f100/50 is shown together with those from monodisperse films in Fig. 6. Orientation of C_{100} bonds is the same in mixed and monodisperse films, whereas the orientation of C_{50} bonds is significantly enhanced in the mixed film f100/50.

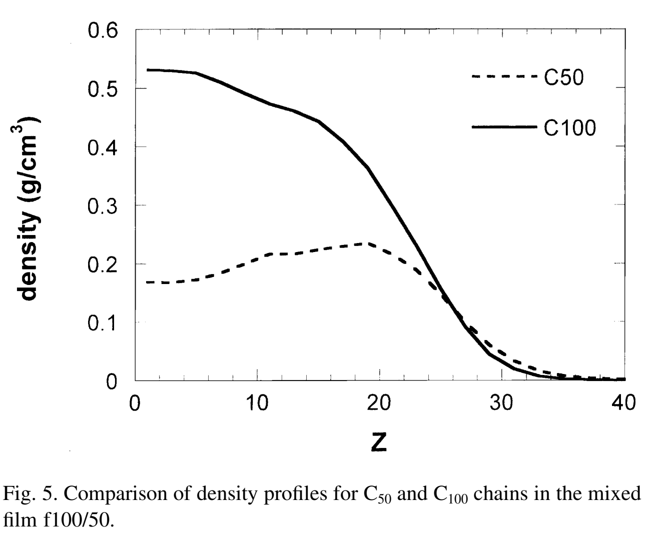

Fig. 5. Comparison of density profiles for C_{50} and C_{100} chains in the mixed film f100/50.

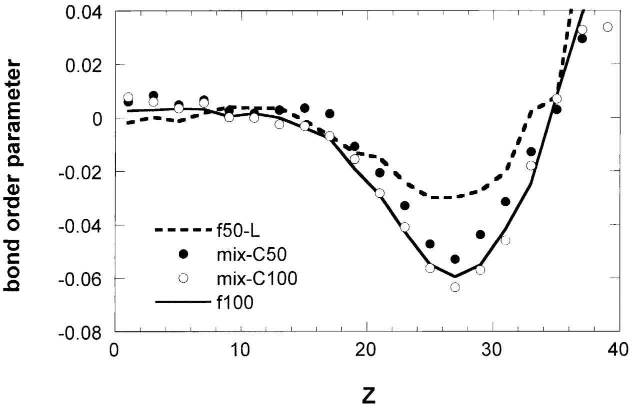

Fig. 6. Comparison of the orientation of C_{50} and C_{100} bonds in the mixed film f100/50 with the orientation in monodisperse films. The z position is defined as the midpoint of each coarse-grained bond.

Fig. 7 compares the orientation of the chains in mixed and polydisperse films. Again, the behavior of C_{100} chains is almost the same in mixed and monodisperse films. Only orientation of C_{100} chains in the mixed film is displayed here. Short dashed lines are from f50-L and dark filled circles correspond to the C_{50} chains in mixed system. The orientation of short chains is enhanced in the presence of long ones.

The non-random orientation of C_{50} chains in the bulk region is also enhanced in mixed f100/50 film. Further simulations are necessary to determine the source of this behavior, whether it is a consequence of short chain length

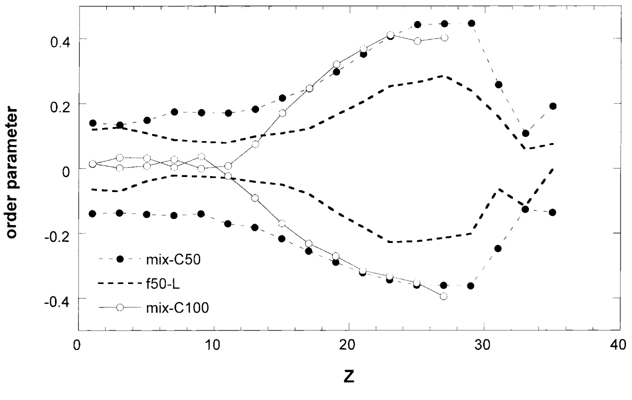

Fig. 7. Comparison of the orientation of C_{50} chains in mixed film f100/50 (dark filled circles) with the orientation in monodisperse film f50-L (short dashed lines). Behavior of C_{100} chains in f100/50 is indicated by open circles. The z position of each chain is defined as its center of mass.

or an artifact of the simulations. In thin film simulations of C_{100} mixed with shorter C_{20} chains (results not shown here), the escape of some C_{20} chains into the vacuum region is observed. Since the boiling point of C_{20} is 617 K at 1 atm, vaporization of some C_{20} chains may be possible at 509 K. Moreover, C_{20} chains that stay in the bulk region of the film exhibit even more enhanced orientation, with a magnitude similar that at the interface.

Preliminary results for f316/50 system indicate that the properties of C_{316} chains do not change in the presence of shorter chains. And the orientation of shorter chains is only slightly enhanced in the presence of C_{316} chains. However, the periodic lateral surface areas of f316/50 and monodisperse f50 films are not the same, so the comparison of C_{50} properties could be misleading in this case.

4. Concluding remarks

The effect of increasing chain length on the properties of free-standing PE films is studied using a coarse-grained on-lattice MC technique. The molecular weights and system sizes considered here (C_{50}, C_{100} and C_{316}) are much larger than those in previous simulations [10,14]. Local and global properties at the surfaces, such as orientation of bonds and chains, are enhanced in films composed of longer chains. Films that contain two different chain lengths (C_{50}–C_{100} or C_{50}–C_{316}) are also simulated. In those films, it is found that the longer chains possess similar properties in the monodisperse and mixed films. In contrast, shorter chain properties are affected due the presence of longer chains, displaying increased surface anisotropy in the mixture.

A more systematic approach at a higher level of coarse-graining could be used to study the free surface properties as a function of lateral dimensions, film thickness and chain length. A second generation of the 2nnd lattice simulations was shown to be promising [28] when every fourth backbone atom of PE is retained on the lattice. Further coarse-graining on the 2nnd lattice would make a more rigorous analysis possible.

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