**Summary:** Monte Carlo computer simulations have been performed for model polymers confined in slits of thickness comparable to the transverse diameter of the chains. The density of polymer within the slits is allowed to vary with the slit thickness in such a way that the content of the slits is always in equilibrium with a large reservoir of bulk polymer. The calculations reveal the presence of polymer-mediated attractive or repulsive interactions between the slit plates, oscillating with the slit thickness in good agreement with experimental results.

The base cell used in the simulations.
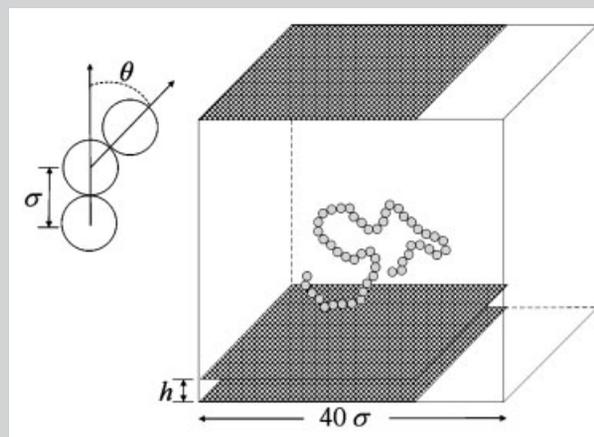
Monte Carlo Simulations of Polymers in Nanoslits

Michele Vacatello

Dipartimento di Chimica, Università di Napoli, Via Cinthia – 80126 Napoli, Italy
Fax: +39 81 674325; E-mail: vacatello@chemistry.unina.it

Introduction

Numerous computer simulations have been carried out with various methods in the last two decades in order to study the molecular arrangements and conformations of polymers in contact with solid surfaces; an exemplificative list, certainly not exhaustive, is given in refs.[1-45] In spite of the great diversity of the systems that have been studied (from cubic lattice models of totally flexible chains to coarse-grained or atomistic out-of-lattice models of semi-flexible chains near planar solid surfaces, in narrow slits, in the presence of spherical filler nanoparticles, etc.), there is general agreement that the interface between polymers and solids consists of densely packed and partly ordered layers in which the polymer segments tend to run preferentially parallel to the solid surface. For systems far from crystallization, this perturbation of density and order does not extend into the liquid more than two or three times the transverse diameter of the chains, while the consequent perturbation of size and shape of chains having segments in the interfacial layers extends into the liquid on a length scale on the order of at least the rms radius of gyration of the chains (R_g).

As a consequence, the molecular arrangements and conformations of polymers confined in slits of thicknesses smaller than $2R_g$ are expected to depend on the slit thickness. The situation of polymers confined in nanoslits (i.e. slits of thickness on the nanometer scale, comparable to the transverse diameter of the chains) is obviously quite special, since the perturbations of density and order due to the two solid surfaces may give positive or negative interference, depending on the thickness of the slit. This paper reports briefly on Monte Carlo simulations extending to relatively long chains analogous to calculations performed in the past for tridecane molecules confined in nanoslits,[15] and compares the results with experimental data available for systems of this kind.

Models and Methods

The model chains and the simulation methods are similar to those described in detail for polymers near a single structureless solid surface in a previous paper.[34] In brief, the simulated systems consist of three-dimensionally periodic arrays of orthorhombic cells with edges 40σ, $\approx 40\sigma$

and 60σ along the x, y and z axes, respectively. Two identical solid plates, modeled as planar arrays of hexagonally packed units of diameter σ, are placed perpendicular to the z axis at $z = 0$ and at $z = h$. In a way similar to that used for the tridecane simulations in ref.,[15] the two plates are infinitely extended along the y axis (for this reason, the actual edge of the cell along the y axis is 39.84σ), while they are only extended from $x = 0$ to $x = 30\sigma$ in the x direction (Figure 1). Calculations are performed for values of h ranging from 1.6σ to 3.8σ. The polymer chains are modeled as sequences of 50 isodiametric units connected by links of length σ. The distribution of angles between consecutive chain links is regulated by a bending potential of the form $E(\theta) = (1/2)k_\theta\theta^2$, with θ the angle between consecutive links ($\theta = 0$ for collinear links; see Figure 1). The chain units interact with other chain units and with the plate units through a truncated and shifted 12–6 Lennard-Jones potential $E(r) = \varepsilon[(\sigma/r)^{12} - 2(\sigma/r)^6 + 1]$, r being the distance between the interacting units; the minimum distance allowed between units is $r_{min} = 0.70\sigma$, and the interactions are truncated at σ in such a way to include only the repulsive part of $E(r)$. Calculations are performed with $\varepsilon/kT = 0.125$ and $k_\theta/kT = 1.00$ rad^{-2}, giving a softness of the polymer units and a chain stiffness comparable to those in real systems,[35] and with 1 840 chains in the base cell.

After initialization of the chains at random with the methods described in ref.[19] (i.e., considering the chain units and the plate units as rigid spheres of diameter 0.75σ), the systems are equilibrated in the *NVT* ensemble by Monte Carlo methods, using the reptation technique. Since molecular arrangements, conformation and mobility of chains of this kind having center of mass at more than $12-15\sigma$ from solid surfaces have been shown to be practically unperturbed,[34] the setup of the model is suc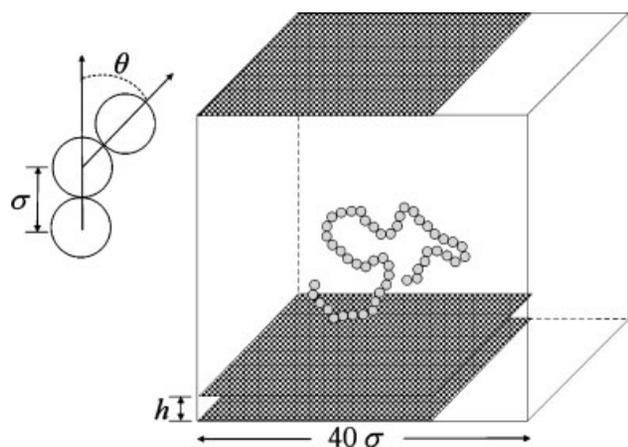h that the chains in the nanoslits are in equilibrium with a large reservoir of bulk unperturbed chains in the region $15\sigma < z < 45\sigma$. With 1 840 total chains, the equilibrium density in this region is equal to σ^{-3}. If the chain units are considered to be polymethylene isodiametric units (3.5 CH$_2$, $\sigma = 0.45$ nm),[46] this value corresponds to experimental values for long chain *n*-alkanes (890 kg·m^{-3}). Consequently, the density of polymer in the nanoslits is not fixed a priori, but is allowed to vary with the slit thickness in such a way that the content of the slits is always in equilibrium with a realistically dense polymer melt. After equilibration, the properties of the various systems have been calculated at the end of 150 consecutive MC cycles, a cycle being defined as consisting of $5 \cdot 10^8$ attempted reptations. Although the fraction of accepted moves is relatively small (3%) due to the high density of the simulated systems, the mobility of the chains is large enough that most of them are found in the nanoslits at some stages and in the central bulk-like region at others.

Results and Discussion

Figure 2 shows the content of the nanoslit with $h = 1.6\sigma$ (i.e. the situation with the lowest chain mobility among those studied) in two configurations separated by two consecutive cycles. For clarity, only chains that are totally contained in the slit are shown in the first configuration, and only the same chains are likewise shown in the second; regions that appear empty are occupied by chains having units inside and outside the slit, or by chains that partially entered and left the slit during the two cycles. Although the configurations shown are separated by two cycles only, the conformation and the location of the centers of mass of most of these practically two-dimensional chains are seen to be substantially different in the two cases. Considering that the average persistence of a chain in this slit is

Figure 1. The base cell used in the simulations and definition of symbols.
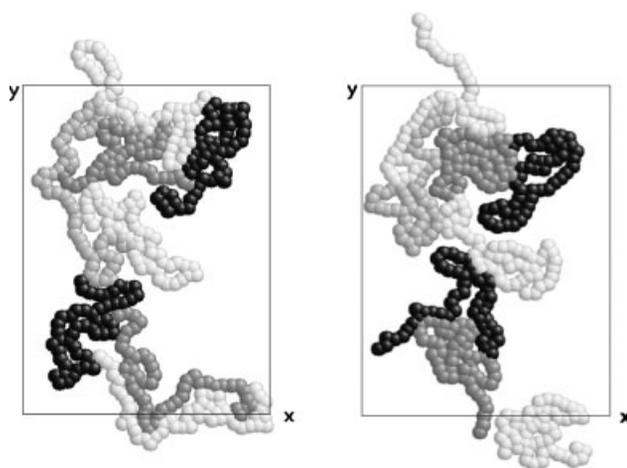

Figure 2. Snapshots of the nanoslit with $h = 1.6\sigma$ in two configurations separated by two consecutive cycles. Only chains totally contained in the slit in the first configuration are shown (see text).

20–25 cycles and that the content of the slit was totally renewed during the sampling cycles, one can assume that the calculations have also been long enough in this extreme case. The chain mobility is obviously higher in the other slits studied and much higher in the central bulk regions.

Since the attainment of an equilibrium condition between the content of the nanoslits and the bulk polymer is central for this work, some of the simulated systems (including those with $h = 1.6\sigma$ and $h = 2.0\sigma$) have been also initialized by forbidding the slit region to the chain units. At the completion of the first MC equilibration cycle the distribution of chain units within the slits was already very similar to that obtained at equilibrium in systems initialized at random, and after 50 cycles all properties of interest were practically indistinguishable in the two cases.

Figure 3 shows the normalized density of units (i.e. the density divided by the bulk density) in sublayers of thickness 0.1σ as a function of z for the system with $h = 2.4\sigma$. Here and in the following, the data have been collected in the region of x between $x = 5\sigma$ and $x = 25\sigma$, with the reasonable assumption that the situation in this region can be considered representative of the situation between plates infinitely extended in both the x and y directions. The curve in the left part of Figure 3 ($z < h$) plots the density within the nanoslit, while the curve in the right part ($z > h$) plots the density between the plate at $h = 2.4\sigma$ and the bulk polymer, i.e. the density of the polymer as a function of the distance from a single plate. Not unexpectedly, the latter curve is practically coincident, when properly shifted along the x axis, with the corresponding curves found for other values of h and with the curve shown in ref.[34] for the same model polymer near a single structureless solid surface.

The density profiles within the nanoslits are shown in Figure 4 as a function of the distance Δz_c from the center of the slits. As anticipated, the polymer chains are confined into one single layer of practically two-dimensional chains in the slit of thickness 1.6σ (see Figure 2). By increasing the slit thickness, the arrangement
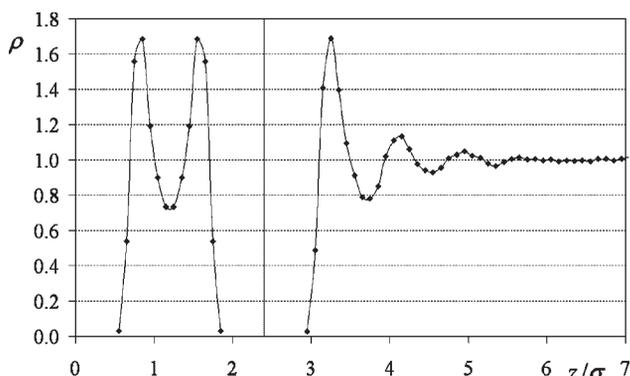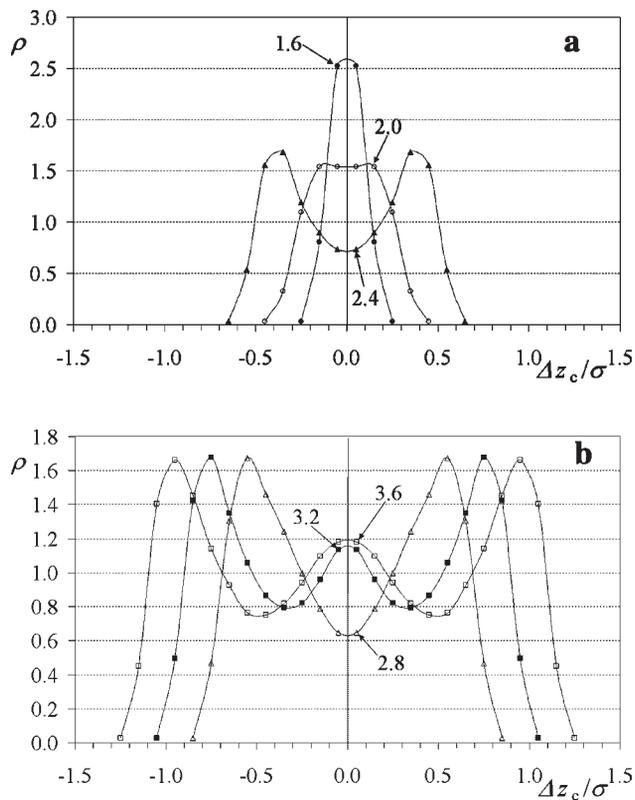

Figure 4. The normalized density of units in sublayers of thickness 0.1σ in as a function of the distance Δz_c from the center of the nanoslits in system with the indicated values of h; data for x between 5σ and 25σ.

Figure 3. The normalized density of units as a function of z in sublayers of thickness 0.1σ for x between 5σ and 25σ in the system with the second plate at $h = 2.4\sigma$ (vertical line).

evolves in such a way that two layer of units are formed for h between 2.4σ and 2.8σ, while a third intermediate layer appears for $h > 3.0\sigma$. It is interesting to remark that, whenever more than one layer of units is present, the layers of units are not layers of chains, in the sense that a given chain frequently steps from one layer to the other. In fact, the average length of the trains of units running in a given layer depends obviously on how a layer is defined, but is anyhow never greater than 4 units. The same conclusion is indicated by plots of the distribution of the centers of mass of the chains and by plots of the order parameter of the links between consecutive units along the z axis (plots not shown for brevity). In particular, the centers of mass are mainly located in the lower density regions between layers, while the order parameter of the links is negative within the layers (close to -0.5 for bonds near the plates) and is zero or positive for links located in the intermediate regions.

Figure 5 plots the difference $\Delta\rho$ of the normalized densities between sublayers of thickness 0.1σ within the nanoslits and near a single plate (the right region of Figure 2) as a function of the distance Δz of the considered sublayer from the closest plate. In sublayers immediately in touch with the plates, $\Delta\rho$ is seen to oscillate between
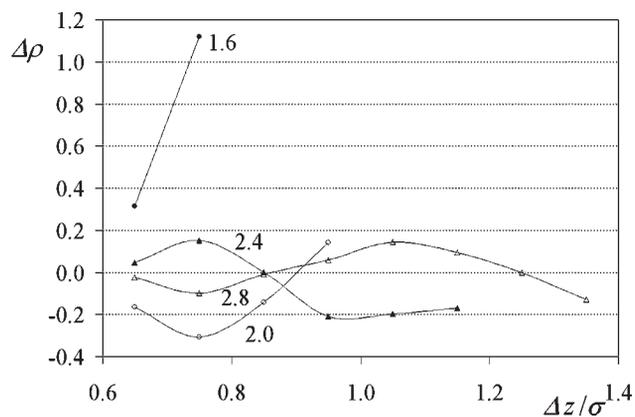
Figure 5. The difference of normalized density between sublayers of thickness 0.1σ within the nanoslits and near a single plate as a function of the distance Δz of the sublayer from the closest plate for systems with $h = 1.6$, 2.0, 2.4 and 2.8σ as indicated.

positive and negative values with increasing slit thickness, the entity of the oscillations decreasing with increasing h. In other words, with respect to the situation near a single plate, the units within a nanoslit are pressed against the plates in some cases and pulled out from the plates in others. Since each plate in the simulated systems then feels two different environments on the two sides, one may expect that the force exerted on the plates by the polymer within the slit be different from the force exerted by the polymer on the other side, resulting in a polymer-mediated net attraction or repulsion between the two plates.

The average net force acting on each plate has been determined from the various simulations performed and the resulting difference between internal and external pressures (i.e., the net force divided by the plate area) is plotted in Figure 6 as a function of the thickness of the nanoslit. The interaction between the two plates, mediated by the poly-
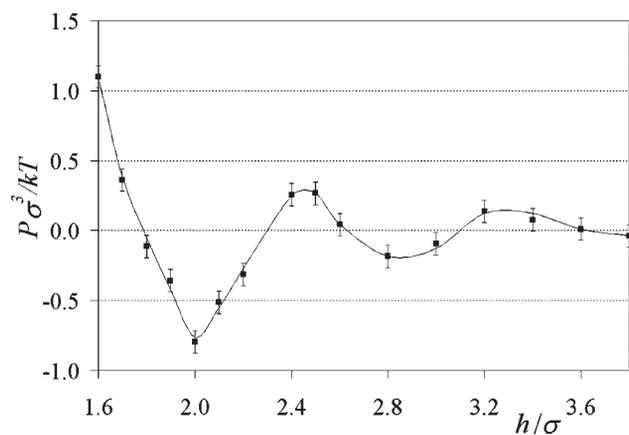
mer contained in the slits, is seen to oscillate between repulsive and attractive with increasing h; the distance between consecutive maxima or minima is slightly less than σ, and the entity of the oscillations decreases with increasing h in a way similar to that observed for $\Delta\rho$ in Figure 5. In particular, the interaction between the plates is repulsive when $\Delta\rho$ is positive in sublayers immediately in touch with the plates (i.e. for Δz less than 0.9σ), while it is attractive when $\Delta\rho$ is negative in these sublayers.

Of course, the actual values of the pressure shown in Figure 6 are scarcely significant, since they depend on various details of the simulations performed (structure of the plates, interactions between plates and polymer, truncation of all interactions at σ, etc.). However, considering that conformations and packing in polymer melts of the kind studied in this work (i.e. in the absence of particularly strong interactions between groups located in specific parts of the polymer chains or between these groups and the plates) are mainly dictated by the chain stiffness and by repulsive (excluded volume) interactions, it is quite interesting to compare the behavior suggested by Figure 6 with experimental results obtained for liquids of chain molecules in nanoslits. In particular, Christenson et al. have studied the force between two atomically smooth mica surfaces immersed in liquid alkanes as a function of the distance of the two surfaces.[47] When the surfaces are at less than 3 nm, the force shows an oscillatory behavior with a spacing between two consecutive maxima or minima approximately 0.4 nm, irrespective of the chain length.[47] These results are in very good agreement with those shown in Figure 6. In fact, if the simulated units are considered to be polymethylene isodiametric units ($\sigma = 0.45$ nm; see before), Figure 6 predicts a similar oscillatory behavior with a periodicity 0.4 nm, and suggests that the range of h for which these oscillations are observed should be not greater than 3 nm. A similar oscillatory behavior has been found by Horn and Israelachvili[48] for mica surfaces immersed in liquid poly(dimethylsiloxane) with an average chain length of approximately 50 monomer units, roughly comparable to the chains studied in the present work. In good agreement with Figure 6, the experimental spacing between consecutive maxima or minima is nearly 0.7 nm in this case, a value close to the transverse diameter of the poly(dimethylsiloxane) chains. Note that analogous experiments on branched alkanes[49] and polybutadiene[50] in nanoslits indicate that chain branching suppresses the oscillatory behavior of the forces, mainly because it destroys at least in part the tendency to form well packed layers near the solid surfaces.[49,50] The results shown in Figure 4–6 are also in good agreement with the dependence upon the normal pressure found for the apparent shear viscosity of hexadecane films by Van Alsten and Granick,[51] and with the exceptionally large increase of the apparent shear viscosity observed for film thicknesses less than 0.8 nm.

Figure 6. The net pressure acting on the plates of nanoslits in equilibrium with the bulk polymer as a function of the slit thickness h.

Lastly, as far as the polymer conformation is concerned, it is interesting to point out that the slit chains are obviously flattened parallel to the plates in all slits studied, the z component of the mean square radius of gyration ($R_{g,z}^2$) being as small as $0.03\sigma^2$ when $h = 2.0\sigma$ and $0.5\sigma^2$ when $h = 3.6\sigma$, to be compared with $6.8\sigma^2$ for bulk chains. However, R_g^2 departs significantly from the bulk value ($20.4\sigma^2$) only in the extreme cases of slits with h less than 2.0σ, where it is approximately $26\sigma^2$. These findings are then in good agreement with the SANS experiments of Jones et al. on polystyrene thin films,[52] showing that the value of the rms radius of gyration is not appreciably different from the bulk value ($R_{g,bulk}$) when the polymer is confined into films of thickness greater than $R_{g,bulk}/2$; they are also in good agreement with recent Monte Carlo lattice simulations performed by Muller[44] for polymers in thin film geometry, indicating relatively small changes for the radius of gyration of the chains in films of thickness $R_{g,bulk}$, while the principal effect of the confinement consists in a distinct reduction of their tendency to be entangled.

Conclusion

The simple calculations described here indicate that the experimentally observed oscillatory behavior of the force between smooth solid surfaces immersed in liquids of chain molecules is related quite obviously to the well established tendency of the chain units to a layered arrangement in contact with these surfaces. When the slit thickness is comparable to the transverse diameter of the chains, the arrangement and the density of chain units within the slit depend on whether the appropriate number of layers can be well accommodated or not. This gives rise to polymer-mediated attractions or repulsions between the slit plates, oscillating with the slit thickness with a periodicity equal to the thickness of the layers (i.e., slightly less than the transverse diameter of the chains).

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