

Structure of polymer films in adsorbing slit: A computer simulation study

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Abstract

The introduction of confinement has an impact on most properties of polymer chains. A coarse-grained model of branched polymers confined in a slit formed by two parallel impenetrable surfaces which were attractive for polymer segments was developed and studied. The model chains were regular stars consisted of three branches of equal length. The positions of chains were restricted to vertices of a simple cubic lattice. The chains were at good solvent conditions and, therefore, the excluded volume was the only interaction between the segments of the chain. The properties of the model systems were determined by means of dynamic Monte Carlo simulations with a sampling algorithm based on chain's local changes of conformation. The dependence of polymer density in the slit on a structure of the macromolecular film was studied. An interesting mechanism of the chain motion – jumps between surfaces – was also shown.

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1. Introduction

Structural properties of polymers under a geometrical confinement, i.e., in a slit, a tube or a sphere are quite different from those of a chain in a bulk and can be treated as an interesting and challenging theoretical problem [1,2]. Because of the practical importance of the polymer behavior in coating the surfaces, laminates, chromatography, colloidal stabilization, capillary electrophoresis, etc. such systems were recently a subject of many experimental and theoretical studies. From the theoretical point of view, the presence of the confinement limits the number of conformations of polymer chains when going from a bulk to a restricted space [3]. Many theoretical considerations and results of simulations concerning polymers in adsorbing confinement were recently published on this subject but they were concentrated predominately on single chains and dense polymer melts [4–15].

An idealized model of polymer chains in an adsorbing slit was recently introduced and studied by means of Monte Carlo simulations [16,17]. The chains were constructed in

the form of a sequence of united atoms restricted to a simple cubic lattice and put into a slit formed by a pair of impenetrable surfaces; the width of this slit was comparable with the chain's size. The model polymer chains were studied at good solvent conditions, where all polymer–polymer, polymer–solvent and solvent–solvent contacts were assumed to be the energetically identical. A simple contact attractive potential was introduced between polymer beads and both confining surfaces. The properties of the system were determined by means of the Monte Carlo simulations. The sampling algorithm used was based on the Metropolis scheme and the local changes of chain conformation. It was shown that the introduction of the attractive interactions between the confining surfaces and the polymer led to an interesting dynamic behavior of chains. For relatively short distances between the confining surfaces and at lower temperature the macromolecules, which are fully adsorbed at one of the surfaces jumps to the second surface [16]. The mechanism of the jumps was determined: the first two arms were detached from the surface starting from their ends while the third one moved in the opposite way and the frequency of jumps strongly depended on the size of the slit [17,18]. The main interest of this work was to study the structure of the film formed of the polymers in the slit. The structure of films formed by such com-

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pressed macromolecules would change if the polymer density increases.

2. The model and the algorithm

A simplified model of branched polymer chains was worked out for the studies of thin films of confined macromolecules. In this model a homopolymer was constructed as a sequence of identical united atoms (beads), each of them representing some real chemical monomers. The positions of these beads were limited to vertices of a simple cubic lattice. A model macromolecule consisted of three linear chains of equal length emanated from a common origin called the branching point. The polymers were studied at good solvent conditions and the system was athermal. The intra-chain and inter-chain interactions (bead–bead) were limited to the excluded volume only what was easily realized by forbidding the double occupancy of lattice sites by polymer beads. The chains were put in a Monte Carlo box and the periodic boundary conditions were set in x and y directions only. The size of the Monte Carlo box L was large enough to avoid the interactions of a chain with itself: in x and y directions $L_x = L_y = 50$. Two surfaces confining the polymers and parallel to the xy plane were introduced at $z=0$ and $z=d+1$. The walls were, therefore, separated by the distance d lattice sites and were assumed to be impenetrable for polymer segments. In Fig. 1 a scheme of star-branched polymers in the slit is presented. An attractive interaction between the walls forming the slit and polymer beads was also introduced:

$$V_i^a = \begin{cases} \infty & \text{for } z_i < 1 \text{ or } z_i > d \\ \varepsilon & \text{for } z_i = 1 \text{ or } z_i = d \\ 0 & \text{for } 1 < z_i < d \end{cases} \quad (1)$$

where z_i is the z -coordinate of i th bead. For our simulations we used this potential in kT units with the Boltzmann constant $k=1$. The inverse of the above potential of adsorption served as measure of the temperature of the system $T^* = |1/\xi| = |kT/\varepsilon|$. The total energy of the system was

$$E_a = \sum_{i=1}^n \sum_{j=1}^N V_i^a \quad (2)$$

The properties of the polymer system were determined by means of Monte Carlo simulations. The algorithm was based on the asymmetric Metropolis scheme with the local changes of chain's conformation. The set of these micromodification was previously developed for studies of simple cubic lattice chains and consisted of: one-beads motion, two-beads motion, two-beads crankshaft motion, chain's ends random reorientations and the branching point collective motion [20]. Polymer beads,

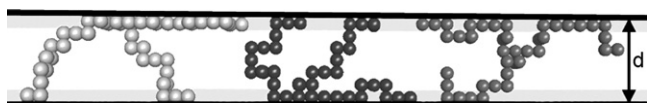


Fig. 1. The scheme of a star-branched polymer chains located in a slit formed by two parallel surfaces. The gray areas show the region in which the beads of chains are adsorbed.

which were to be moved, were selected at random and a new conformation obtained after a micromodification was accepted due to topological constraints, the excluded volume condition and the Metropolis criterion. One attempt of each type of a local motion per polymer bead defines a time unit. A Monte Carlo production simulation run lasted 10^9 time units while the equilibration run consisted of 10^8 time units. For each system, the simulations were performed 20–30 times starting from different configurations.

3. Results and discussion

The simulations were performed for the polymers consisting of $N=199$ segments (67 segment in 1 arm) because it was previously found that such chains in an adsorbing slit can rather frequently jump between the surfaces at these conditions [21]. The size of the slit varied from $d=5$ to $d=7$ lattice units and the reduced temperature $T^*=1$ (a strong adsorption regime for this model of polymer chains [22]) for the same purpose. The number of chains in the slit n was changed between 1 and 40, and therefore the density of polymer segments was also varied. The density of segments was defined as

$$\varphi = \frac{nN}{L^2d} \quad (3)$$

The size of the polymer chain is usually described by the mean-squared radius of gyration $\langle S^2 \rangle$. Previous studies showed that the size of the chain did not change monotonically when the size of the slit d decreased [19]. The size decreased approaching a minimum for the width of the slit comparable with the mean diameter of the macromolecule. Further decrease of d led to the rapid increase of the chain's size. This behavior can be explained by the fact that the polymer was changed from a three-dimensional to a two-dimensional structure. The question arises what was the influence of the number of chains (polymer density) on the size of macromolecules. Fig. 2 presents the changes of the mean-squared radius of gyration $\langle S^2 \rangle$ as a function of the density of polymer segments φ . The size of the chain decreases

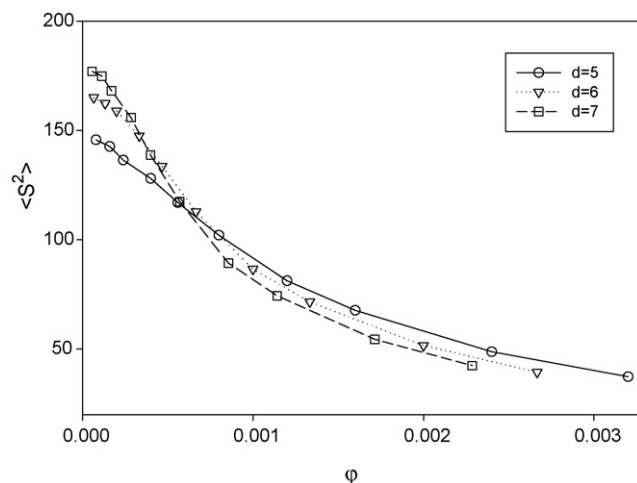


Fig. 2. The mean-squared radius of gyration $\langle S^2 \rangle$ as a function of the polymer density φ . The widths of the slit are given in the inset.

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