

The structure of polymer chains in confinement. A Monte Carlo study

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Abstract A coarse-grained model of polymer star chains confined in two parallel impenetrable surfaces, which were attractive for polymer beads was studied. The flexible homopolymer chains were built of united atoms whose positions in space were restricted to vertices of a simple cubic lattice. The chains were modeled in good solvent conditions and, thus, there were no long-range specific interactions between polymer beads—only the excluded volume was present. The influence of the polymer density and the distances between the confining surfaces on the properties of star-branched polymers was studied. It is shown that the chains adsorbed on one surface could change their position so that they swap between both surfaces with frequency depending on the size of the slit and on the density of the system only. The increase of the polymer density diminished the frequency of jumps and caused that chains became only partially adsorbed. The analysis of structural elements of chains showed that the increase of the density of the system leads to increase of the number of bridges connecting the two adsorbing surfaces, thus, the frequency of jumps between them decreases.

Keywords Branched polymers · Confined polymers · Lattice models · Monte Carlo method · Polymer dynamics

Introduction

The polymers in confined geometries have been recently a subject of many experimental and theoretical works because of their practical importance, e.g., size-exclusion chromatography, polymer adhesion or lubrication [1–2]. The most of the theoretical studies were devoted to linear polymer chains in slits with pure repulsive surfaces [3]. A few works studied the polymers in slits with adsorbing surfaces using mean-field theoretical considerations [4–5], molecular dynamics [6–7] simulations and Monte Carlo off-lattice [8–11], and lattice [12–14] simulations. The distributions of polymer segments in the slit, as well as their changes with the attraction of walls were studied and the competition between this interaction and the intrachain attraction were investigated and some properties of such polymers were also determined. The presence of a surface changes the properties of a macromolecule dramatically even for the pure entropic reasons. The introduction of the second surface and thus the confinement of the entire chain and the polymer attractive interactions with the confining surfaces raises the question concerning the influence of these two factors on the structure on the single chain and a polymer solution. One should also expect that the chain's mechanism of motion would change.

The properties of branched polymers differ from those of their linear counterparts and this effect is especially visible at interfaces and in confinement. A simple model of a non-linear macromolecule is a star-branched polymer consisting of branches of equal length emanating from a common origin. Star-branched macromolecules can be synthesized and their properties can be studied experimentally but their model features are especially useful for theoretical considerations [15]. The coarse-grained models of star-branched polymer chains in a slit were recently extensively studied using the

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Monte Carlo simulation method [16–17]. The structure of confined branched polymer chains in a slit formed by two impenetrable surfaces was also studied there. It was shown that the changes of the size of a macromolecule were universal regardless of the chain lengths although the size did not change monotonically with the size of the slit (even for dense polymer melts). The changes in the mechanism of motion during the transition of a chain from a three-dimensional to a two-dimensional regime were discussed.

The above mentioned coarse-grained model was recently extended by the introduction of the interactions between the confined polymer chains and the surfaces of the slit [18]. The structure of single star-branched chains in such slits was determined and discussed. A different behavior of a polymer was found for an adsorbing slit: at low temperatures (a strong adsorption regime) and for sufficiently narrow slits (5–8 lattice units) the chains fully adsorbed on one surface but they were able to jump from one surface to another. The frequency of these jumps depended on the length of the chain, the strength of the adsorption and the width of the slit. In the present work we studied a polymer solution in an adsorbing slit using a similar model and the simulation method. The structure of a polymer film in the adsorbing slit was determined and the mutual motion of chains was shown and discussed.

The model and the calculation method

The model macromolecules used in our simulations were star-branched polymers. The arms which consisted n of identical segments were attached to a common origin (branching point). The number of arms f in the molecules was $f=3$. Each segment was treated as a united atom representing some number of monomers of a real polymer.

In order to make the calculations more efficient the positions of segments in space were restricted to vertices of a simple cubic lattice. The exclusion of the double occupancy of the same lattice site was introduced into the model what was equivalent to the effect of the excluded volume in the system.

The model chains were located in a slit formed by a pair of surfaces, which were parallel to the xy plane and the distance between the surfaces along the z -axis was d lattice units: one surface was located at $z=0$ and the second one at $z = d+1$ (see Fig. 1). The confining surfaces were impenetrable for polymer segments and an attractive square-well contact potential V was assumed between these surfaces and a polymer segment:

$$V = \begin{cases} \varepsilon_a & \text{for } z_i = 1 \text{ or } z = d \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

where z_i is the z -coordinate of the i th polymer segment.

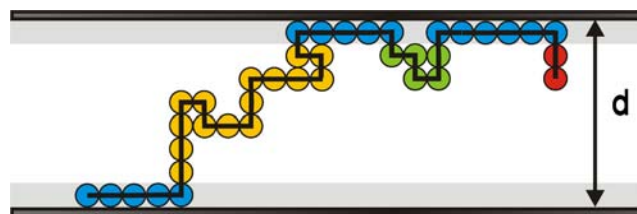


Fig. 1 A scheme of a linear polymer chain in the adsorbing slit. Grey area shows the attractive fragments of the slit, d is a distance between the surfaces. The structures are shown in colors: train (blue), loop (green), tail (red), bridge (yellow)

The segment that was touching a surface (in other words: was adsorbed on the surface) gained the energy $\varepsilon_a < 0$ [17].

In order to determine the properties of the model system the Monte Carlo simulations were performed using a sampling algorithm in which the chain's conformation was locally changed by the following set of motions: (i) 2-segment motion, (ii) 3-segment motion, (iii) 3-segment crankshaft motion, (iv) 1- and 2-segment end reorientations and (v) the branching point collective motions [18]. These changes of chain's conformation were accepted according to the Metropolis scheme with respect to the changes of the energy of the system:

$$P_{old \rightarrow new} = \min[1, \exp(-\Delta E_a/kT)] \quad (2)$$

where $P_{old \rightarrow new}$ is the probability of the transition from an old to a new configuration, ΔE_a is a difference of adsorption energy between the old and the new configuration, $k=1$ is the Boltzmann factor. An attempt of applying each micromodification (i-v) per one polymer segment is called a Monte Carlo step. A single Monte Carlo simulation run consisted of 10^7 – 10^8 Monte Carlo steps and the process was repeated 20–25 times starting from different system configurations. The initial configuration of the system was generated in a process of simultaneous growth of all chains and their equilibration [19]. The above Monte Carlo technique is called 'dynamic' which requires some comments. The first problem to which major attention should be paid is that we can discuss the dynamic behavior of the system in terms of the probability rather than the evolution in time. Thus, all the 'dynamic' results should be regarded as the path through the most probable sequence of states.

We studied star-branched chains that consisted of $n=67$ segments in one arm which means that the total number of segments in the chains was $N=199$. It was shown that for this chain length the influence of the lattice approximation is rather small and on the other hand the chain mobility is still considerably high [16–17]. The simulations were performed for various number of chains $m=1, 2, 3, 5, 10, 20, 30$ and 40 . The size of the Monte Carlo box along x and y axis was $L=50$ while the width of the slit was $d=5, 6$ and 7 . The density of polymer segments in the system was

defined as the fraction of lattice sites in the slit occupied by polymer segments:

$$\varphi = \frac{mN}{dL^2} \quad (3)$$

Therefore, the polymer density changed from $\varphi=0.011$ (one chain) to $\varphi=0.64$; for higher densities our algorithm was inefficient. The fraction of the effective local motions changed from 0.37 (2-bond moves) and 0.292 (3-bond moves) for 1 chain system to 0.024 and 0.025 for 40 chains in a slit of $d=5$ respectively. The highest number of chains used ($m=40$) is well over the number of chains which can totally cover both surfaces $m_{cov}=mN/L^2=25$. The choice of the width of a slit was done based on our previous finding in which we showed that the star-branched chains could execute the jumps between the surfaces of the slit [17]. In order to introduce the temperature in our study we defined the reduced temperature as $T^*=kT/\epsilon_a$. The reduced temperature was set to $T^*=1$ in order to provide a strong adsorption regime in which the chains perform the above mentioned jumps.

Results and discussion

The simulation results were obtained from the trajectories which were calculated during long computer runs as described above. In order to investigate the presented model first we analyzed the mean number of polymer chain-surface contacts (this number is proportional to the mean adsorbing energy of one chain) for different number of chains in the slit. Figure 2 presents the distribution of number of these contacts for different polymer densities. In a low density system the distribution of contacts is very

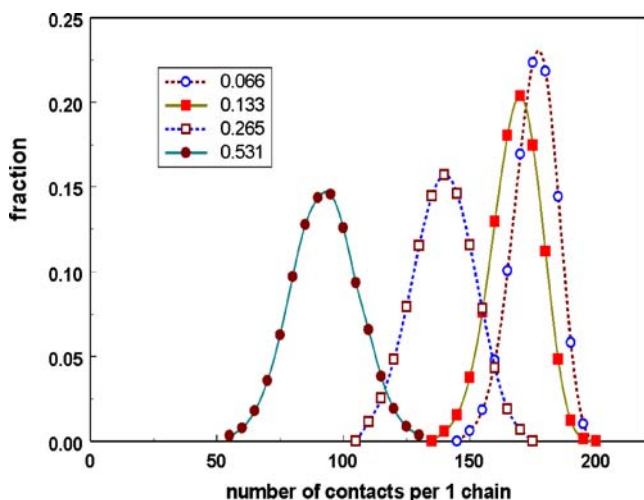


Fig. 2 The distribution of number of polymer-surface contacts for $d=6$ and variable density of the system (see inset for φ values)

narrow and close to the maximum value (199 contacts per one chain, in this case all polymer segments touch one of the surfaces). As the number of chains increases, the available surface is covered by other chains and thus only a fraction of polymer segments can approach it, this reduces the number of polymer-segments contacts, which can be seen well in Fig. 2. The lack of two maxima on the distributions curves suggests that at higher densities all chains are partially adsorbed. It means that for higher densities only one part of each chain is adsorbed and there are no chains totally non-adsorbed and located in the middle of the slit.

We found that for all systems under consideration one can observe that each chain was in contact with at least one surface. Then, after a certain number of MC steps the desorption of the chain is observed and then, after execution of some chaotic motions the chain can be adsorbed again on one of two surfaces. This motion of a chain in the slit can be monitored using the location of its center of mass. Figures 3a-c show flow-charts of the z coordinate of the center of mass for 3 chains randomly selected from system consisting of 3, 10 and 20 chains. For the system with small number of chains ($m=3$) the behavior of chains is shown in Fig. 3a. In the presented fragment of the flow-chart we can distinguish three chains. The green one is located predominately in the vicinity of the lower surface and from time to time it changes the position of the center of mass from the lower surface to the region located between $z=1$ and $z=2$. A similar behavior is observed for the second chain plotted in blue although this chain is located in the proximity of the upper surface. Quite different behavior can be observed for the chain plotted in red. After executing the motions similar to those of the blue chain one can observe the transition from the upper to the lower surface. The transition started near MC steps 13,000 and was completed at 14,000. One should also notice that during the jump the center of mass of the red chain oscillated at the distance from the surface as it was observed for the remaining chains. This behavior of the three-chain system is qualitatively the same as for the system consisting of a single chain [17]. The existence of the level of oscillations located between 1 and 2 units apart from the attractive surface corresponds to the case in which one arm of the star was desorbed and then adsorbed on the opposite surface. The translocation of the total chain to the opposite surface requires the subsequent desorption of two remaining arms. This is less probable than the return of the desorbed arm to the surface at which two remaining arms are adsorbed. Analyzing the fragment of the red chain trajectory one can see that after removing one arm from the upper surface the second arm was also desorbed and then, after some number of MC steps the third one was adsorbed on the lower surface. It should be pointed out that for this

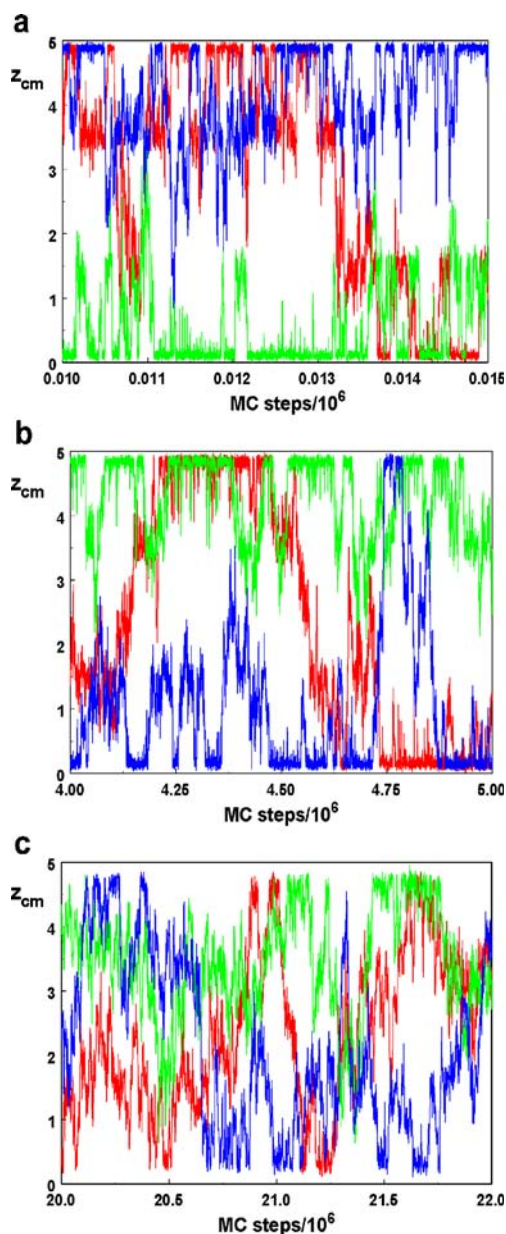


Fig. 3 The flow charts of the z coordinate of chains' center-of-mass z_{CM} for a system of $m=3$ (a), 10 (b), 20 (c) chains at $d=6$. For clarity reasons three chains of m are shown only (each in a different color)

system there were no chains that are not totally adsorbed ('totally' means that all segments interact with a surface with the exception of a few segments which from time to time formed a bridge between surfaces).

The fragment of the trajectory obtained for $m=10$ chains (Fig. 3b) shows, that the jumps were less frequent (please note, that the span is 1×10^6 MC steps, while for $m=3$ it was 0.005×10^6). Also the jumps were not as fast as for the previous example—the intermediate positions between the walls were visible. The fragment of the trajectory for $m=20$ chains (Fig. 3c) shows, that there were more intermediate states (located between the surfaces) than the adsorbed

ones. Also the changes of the positions of chains were slower (the span of the data is 2×10^6 MC steps). An interesting example of the existence of the intermediate states was a red chain, which 'tried' to execute the jump (e.g., for time = 20.5×10^6), but this motion did not lead to the 'full' jump and the chain returned to the previous (upper) position. The detailed analysis of the presented fragments of trajectories gives also the observation, that for more dense systems the centers of mass of the chains did not touch the confining surfaces, even if the chains under consideration were adsorbed (see Fig. 3c). As one can see, the behavior and the center-of-mass positions of the chains in our model depend strongly on the density of the system. Thus one can ask the question: how does the density of the system influence the structure of the adsorbed chains?

It was shown recently, that the dimensions of the chains decrease as the density of the system becomes larger (this behavior is similar to that observed for the unconfined polymer solutions and melts) [14], however, the description of the multi chain system should contain more information on the structure. Thus, we present the analysis of the structural elements which appear in confined adsorbed chain system. The following structures can be recognized for a chain located between two surfaces with respect to the polymer-surface contact: trains, loops, tails and bridges. The schematic definition of the possible structures for a single linear chain is presented in Fig. 1. The analysis of structures of star-branched chains is slightly more complicated—however the final investigation of structures is the same as for the case of a single linear chain. The difference in the approach for the star-branched chain is that the f -branched chain can be treated as a combination of $f^*(f-1)/2$ pairs of linear chains (each of them containing the branching point). The results of such analysis are averaged over the whole ensemble.

The analysis of the structure is shown in Figs. 4a–d, presenting the trains, loops, tails and bridges for different width of the slit as a function of the polymer density respectively. The fraction of trains in a system (Fig. 4a) was close to 1 for low polymer concentration φ —it means that most of chains stayed in contact with the surface. As the number of chains increased, the fraction of beads touching the surface decreases and this effect was obviously stronger for wider slits. In contrast to the trains' behavior, the fraction of loops increased (Fig. 4b) which was caused by the process of local desorption of some fragments of trains. The tails were the structures which could appear at the end fragments of the chains only and therefore their population for polymer in slits was low. The number of tails increases along with the increase of the number of chains (Fig. 4c). The number of bridges in a system was strictly connected with the slit's width—the wider the slit the less bridge structures were observed. The increase of the polymer density leads to the increase of the number of bridges. For

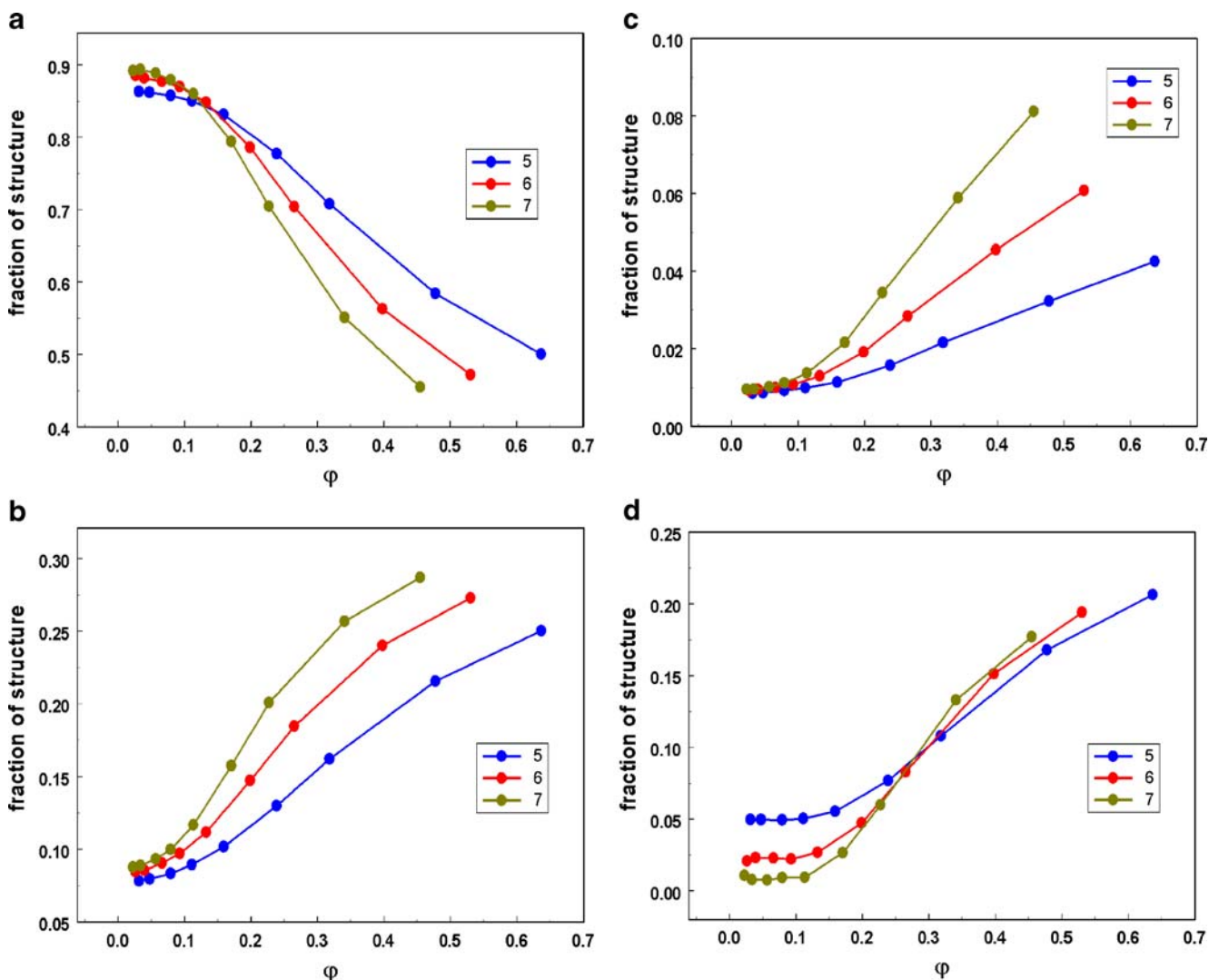


Fig. 4 The fractions of trains (a), loops (b), tails (c) and bridges (d) as a function of the system density φ for different slit's width (see inset for d values)

densities lower than 0.15 this effect depended on the slit's width because the probability of formation of a bridge depended as $\exp(-d)$, which was an Arrhenius-like dependence [17]. The formation of bridges in a crowded environment was no longer governed by this rule.

Conclusions

In this paper we present results concerning computer simulations of star-branched polymer chains confined to an adsorbing slit. The model macromolecules were built on a simple cubic lattice with the united atom representation of chains. The excluded volume was the only intra- and inter-chain interaction potential. The properties of the model system were determined using the Monte Carlo simulation method with a Metropolis-like sampling algorithm.

It was shown that the introduction of the confinement and the strong attractive potential of the confining surfaces changed significantly the size and structure of chains, which approached the two-dimensional objects. It was observed that for low densities of polymer segments the chains desorbed from one surface and then jumped to another one. The frequency of the jumps decreased as the polymer density was higher. In the latter case the chains were partially adsorbed and the number of structural elements (trains, loops, and bridges) was comparable while for low polymer densities trains prevailed over the remaining structures.

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