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The Structure of Star-Branched Chains in a Confined Space

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Summary. We studied the properties of a simplified model of star-branched polymers confined in a slit formed by two parallel and impenetrable surfaces. The chains were built of identical united atoms (segments) whose positions were restricted to vertices of a simple cubic lattice. The polymer excluded volume and polymer segment-surface contact interactions were also introduced into the model. The properties of the model chains were determined by means of Monte Carlo simulations with a Metropolis-type sampling algorithm based on local changes of chain's conformation. The structure of star-branched chains was investigated and the influence of the confinement and the temperature on the chain dimensions and structure was studied. It was shown that for chains in the adsorbing slits their sizes do not exhibit a universal behavior contrary to confined athermal polymers. The polymers in narrow slits at higher temperatures still exhibited features of a three-dimensional chain. It was also shown that chains in small slits and at low temperatures were fully adsorbed at one of the surfaces but could also switch the surface rapidly.

Keywords. Confined polymers; Lattice models; Monte Carlo method; Polymer adsorption; Star-branched polymers.

Introduction

The problem of confinement of macromolecules in a slit is interesting since the presence of the impassable surfaces changes dramatically the properties of such polymers when compared with the free (unconfined) chains in solution. This problem is also important due to its practical applications which can be met in modern technologies, like nano-materials, lubrication, production of thin polymer films, and colloidal stabilization [1]. The properties of macromolecules under confinement were extensively studied by means of computer simulation. Numerous Monte Carlo simulations of lattice and off-lattice models of linear chains were recently carried out [2, 3]. It was shown that the size of a linear chain in a slit exhibits a universal behavior disregarding its length and size of the slit. The

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structure and some dynamic properties of such systems were also determined [3–6]. The dimension of linear polymers confined in slits with adsorbing surfaces were also studied [7–15].

Recently, some intensive simulations concerning lattice models of single star-branched polymers were done [16–18]. These models were coarse: polymers were represented by identical beads embedded to a simple cubic lattice. The studies of linear and star-branched chains showed the existence of a universal behavior of the polymer size regardless the macromolecular architecture. The short-time dynamic properties (relaxation processes) and long-time dynamic properties (self-diffusion) were also examined. The resulting differences were explained by the possible changes of the chains' mechanism of motion.

In this paper we also studied a simple model of single star-branched polymers in a slit formed by two parallel and impenetrable surfaces but an attractive contact polymer-wall potential was additionally introduced. The main purpose of this work was to find out to what extent the presence of the adsorption changes properties of star-branched chains. We investigated the influence of the temperature (the strength of the adsorption), the size of the slit, and the chain length on the polymer dimension and the structure.

The Model and the Simulation Algorithm

Single star-branched polymer chains were studied – this model corresponded to an infinitely diluted solution. Star-branched polymer molecules consisted of three linear chains (branches) starting from a common origin (the branching point). Each branch consisted of the same number of identical units (beads). The locations of polymer beads were restricted to vertices of a simple cubic lattice. In the model there was no long-distance interaction potential between polymer beads what implied that the model polymer system was at good solvent conditions or high temperatures [17]. The double occupancy of lattice sites by polymer beads was forbidden, thus in this way we introduced the excluded volume. The model system was put into a Monte Carlo box with periodic boundary conditions set in x and y directions only. The Monte Carlo box contained two surfaces parallel to the xy plane that confined the polymer chain. Each surface was impenetrable for polymer beads. The distance between the surfaces was d lattice units. The following attractive potential U_i was introduced between the beads of the chain which were in contact with any of the confining surfaces. The value of the potential depended on i^{th} bead's z-coordinate as follows (Eq. (1)) where the parameter ε is negative.

$$U_i = \begin{cases} \infty & \text{for} \quad z_i < 1 \quad \text{or} \quad z_i > d \\ \varepsilon & \text{for} \quad z_i = 1 \quad \text{or} \quad z_i = d \\ 0 & \text{for} \qquad 1 < z_i < d \end{cases} \tag{1}$$

Thus, the total interaction energy of the system was given by Eq. (2) where ν_1 and ν_2 were the numbers of contacts of the chain with the lower and upper surfaces, respectively.

$$E = \nu_1 \cdot \varepsilon + \nu_2 \cdot \varepsilon \tag{2}$$

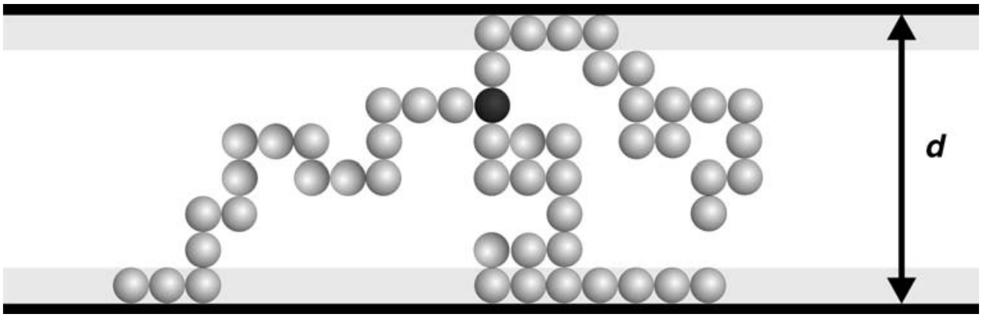

Fig. 1. Scheme of the star-branched chain confined between two adsorbing surfaces

Figure 1 presents a scheme of a star-branched polymer chain located between two surfaces. The gray shaded areas in the vicinity of the surfaces depict the regions in which the adsorption of the beads on the surface was effective.

The polymer systems were studied by means of the Monte Carlo method. In the simulations, we started from a random conformation of the chain and then the conformation was modified randomly. The following set of micromodifications was used: 2-bond move, 3-bond move, 3-bond crankshaft move, chain's ends move and the branching point collective move [19]. A number of attempts of all micromodifications per one polymer bead was defined as a time unit. A new conformation of the chain obtained as a result of such a local move was accepted due to topological constraints and the Metropolis criterion. Each Monte Carlo simulation run consisted of 10^8–10^9 time units. The simulations for each model system were carried out 30 times starting from quite different conformations [19]. The series of simulation runs were carried out for each chain length and the size of the slit with the contact potential varying from the weak adsorption to the strong one. The reduced temperature of the system was defined according to the relation $T^* = kT/\varepsilon$. The temperature T^* was changed between 1 and 10 because in this range a transition from weak to strong adsorption was found for a similar model but with one surface only [20].

The above presented model of a confined chain and the simulation algorithm as well as the code implementation were developed by the authors [16–18].

Results and Discussion

The Monte Carlo calculations were performed for a star-branched chain with $n = 17$, 34, 67, 134, 267 and 401 beads in one arm what corresponded to the total number of beads $N = 49$, 100, 199, 400, 799, and 1201, respectively. We studied properties of our model chains for distances between two parallel impenetrable surfaces varying from $d = 3$ to $d = 35$. This selection was based on our previous finding: the smallest possible distance for which all the changes of polymer conformations can be performed is $d = 3$. On the other hand, for the large slit with width $d = 35$ the longest chain under consideration ($N = 1201$) was still affected by the presence of the confining surfaces [16]. Since we investigated the system changing some parameters in simulations there was a necessity to find such description of the results that the data from the different simulations could be compared. In order

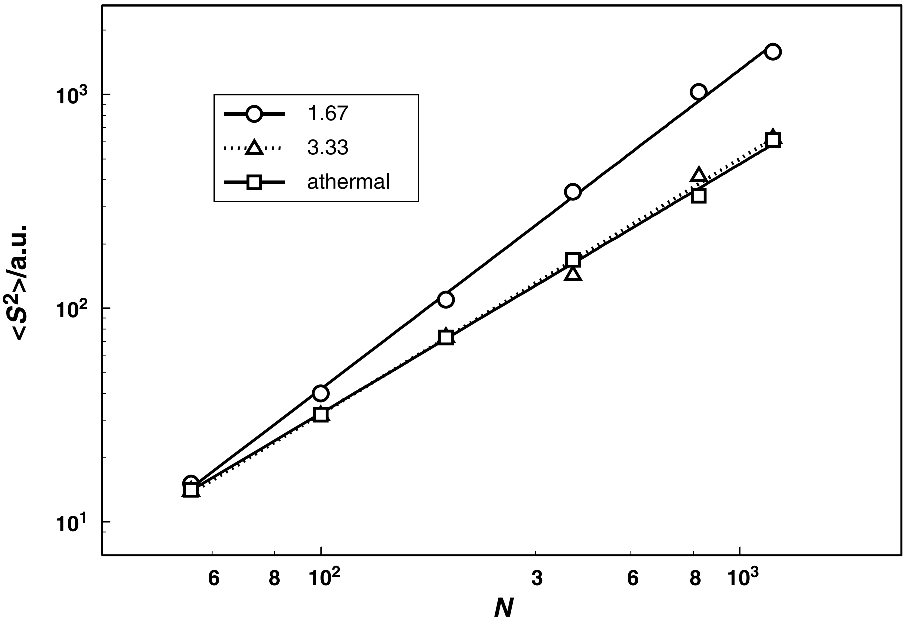

Fig. 2. Plot of the mean-square radius of gyration $\langle S^2 \rangle$ as function of chain length N for the reduced slit size $d^* = 0.4$; the values of the temperatures are given in the inset

to compare the results the reduced parameter describing the relative size of the slit, such as $d^* = d/\delta$, where δ is an estimation of the chains diameter and $\delta = 2\langle S^2 \rangle^{1/2}$ [4, 16].

The size of polymer chains was described by the radius of gyration. We studied the behavior of this parameter for chains consisting of different number of beads but deformed to the same degree. For this purpose we carried out the simulations using the same value of the reduced size of the slit $d^* = 0.4$ for some temperatures [18]. Figure 2 presents the log–log plot of the mean-square radius of gyration $\langle S^2 \rangle$ *versus* the total number of polymer segments N.

The presented simulations concerned star-branched chains for the temperatures $T^* = 1.67$, 3.33, and ∞ (the athermal system). The first temperature corresponds to the case of strong adsorption and the second one to a weak adsorption [20]. One can observe that in all cases presented the radius of gyration scales as $\langle S^2 \rangle \sim N^\gamma$. The scaling exponents were found $\gamma = 1.44$, 1.23, and 1.19 for $T^* = 1.67$, 3.33, and for the athermal system, respectively. Thus, one can see that in the case of a strong adsorption ($T^* = 1.67$) the chains' dimensions scale as the 2-dimensional objects where the exponent $3/2$ is predicted. This suggests that the strongly adsorbed macromolecules apparently form flat structures adsorbed on one of the walls of the slit. On the other hand, in the athermal case the exponent found was exactly the same as for the free (unconfined) three-dimensional chain. This means that chains that are squeezed by the confining surfaces to 40% of their original size are still exhibiting the scaling that is characteristic for three-dimensional polymer chains.

It was shown previously that properties of athermal confined polymer chains depend on the ratio of the size of the slit to the mean dimensions of the polymer. In our previous papers [17] we found that there is a uniform master curve that de-

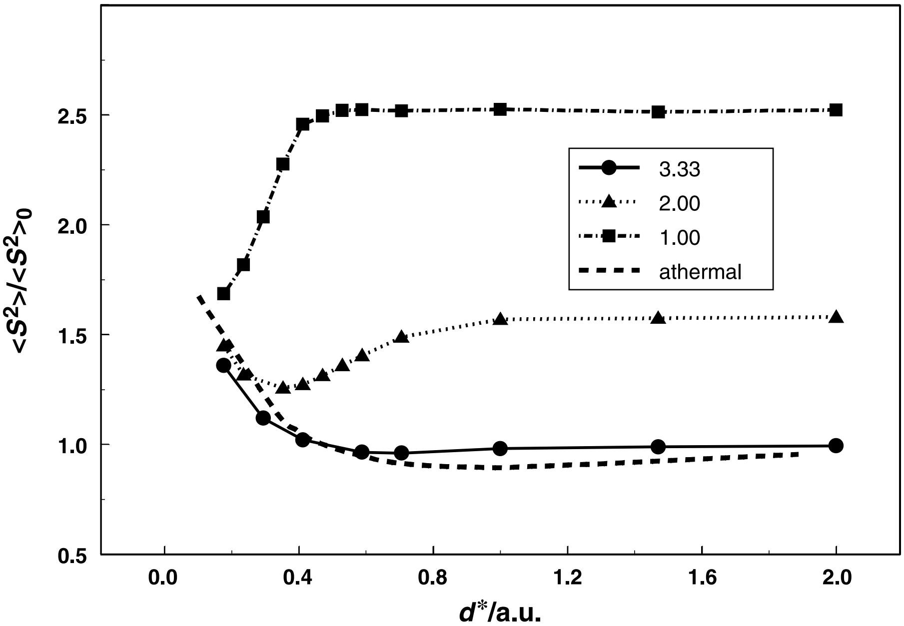

Fig. 3. Plot of reduced square radius of gyration $\langle S^2\rangle/\langle S^2\rangle_0$ as a function of the reduced slit size d^* for chains consisting of $N = 199$ beads; the values of temperature are given in the inset

scribes the dimension of athermal macromolecules in non-adsorbing confinement regardless their lengths and internal macromolecular architectures (linear and star-branched chains). In order to compare the case of non-adsorbing confinement with the results of this study we plotted in Fig. 3 the reduced size of the chain as a function of the reduced size of the slit d^*.

The reduced size of a chain was defined as the ratio $\langle S^2\rangle/\langle S^2\rangle_0$, where $\langle S^2\rangle_0$ is a mean-squared radius of gyration of the free (unconfined) athermal chain of the same length. The universal curve obtained for athermal but confined polymer systems is added to the plot for comparison. The curves concern the chains containing $N = 199$ beads and for different temperatures $T^* = 1$, 2, and 3.33. The results show that for strong adsorption ($T^* = 1$) the radius of gyration remains almost constant for $d^* > 0.5$ and then, when the size of the slit becomes smaller one observes a rapid collapse of the chain. One should also notice that for the strong adsorption the ratio $\langle S^2\rangle/\langle S^2\rangle_0$ is much larger than in weak and intermediate adsorption cases at relatively wide slits – these results will be discusses later. In the case of intermediate adsorption ($T^* = 2$) one observes that the dimensions of the chain become smaller as the slit size is reduced. Then, after a minimum is reached one observes that the values of radius of gyration expand. This expansion is caused by the increase of the xy components of the radius of gyration between the surfaces of the slit. For weak adsorption ($T^* = 3.33$) the curve is very similar to that in the athermal case, *i.e.* with a minimum near $d^* = 1$.

The results presented above suggest that at low temperatures (a strong adsorption case) the chains are adsorbed on one of the confining surfaces only. If this hypothesis is true then one should confirm it by observing the position of the center-of-mass of the chain during a simulation run. In Fig. 4 we present the set of

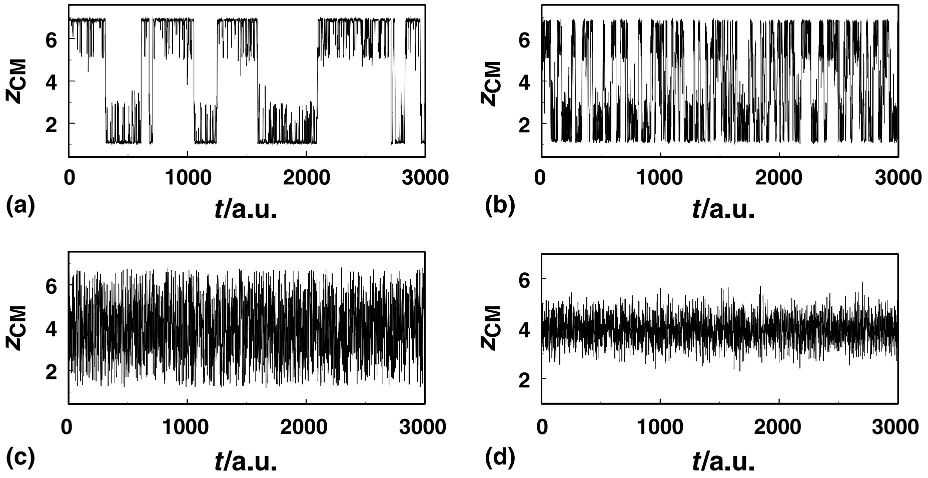

Fig. 4. Flowcharts of the z-component of the chain's center-of-mass position during a simulation run; the data were collected for $N = 199$ and $d = 7$ at the temperatures $T = 1$ (a), $T = 1.25$ (b), $T = 1.67$ (c), $T = 5.0$ (d)

flowcharts showing the position (namely, its z coordinate) of the center-of-mass of the chain taken from simulation trajectories.

The presented cases are obtained for the slit size $d = 7$ taken at different temperatures $T^* = 1$, 1.25, 1.66, and 5. In the case of strong adsorption ($T^* = 1$) the chain remains almost fully adsorbed on one of the confining surfaces. After a certain time it moves from one to another surface. These changes of the position are rapid and can be characterized as "all or none". For a slightly weaker adsorption case ($T^* = 1.25$) the switching from one surface to another is more frequent than in the previous case, however the nature of this process is similar to the previous one. As the strength of the adsorption further diminishes ($T^* = 1.66$) the center-of-mass of the macromolecule fluctuates between two surfaces without any visible preference to any of them. For a very weak adsorption ($T^* = 5$) the center-of-mass remains almost in the middle between the confining walls.

More insight into the structure of a confined chain can be obtained from the curves showing the number of polymer beads ν_i located on one of the surfaces of the slit. The data were collected from the long trajectories. Figure 5 presents the distribution of the number of polymer-surface contacts for the different temperatures and for the different slit sizes – all curves are calculated for chains consisting of $N = 199$ beads.

The curve for $d = 7$ (Fig. 5a) and $T^* = 1.67$ shows a broad maximum at $\nu_i \approx 50$. At lower temperatures there is a gap from $\nu_i = 50$ to $\nu_i = 100$ with three maxima located approximately at $\nu_i = 50$, 110, and 160. This suggests that the adsorption of one, two, or three almost entire arms is most probable (each arm consisted of $n = 67$ beads). At the temperature $T^* = 1$ the curve shows a sharp maximum visible for $\nu_i = 180$, what means that in this case adsorption of the almost whole chain prevails. It suggests that most contacts take place for the number of beads that form one or two chain's arms. At the temperature $T^* = 1.0$ the shape of the plot depends strongly on the size of the slit. For a narrow slit ($d = 5$) the effect of the adsorption is quite different: there is a well exposed maximum in the vicinity of the total

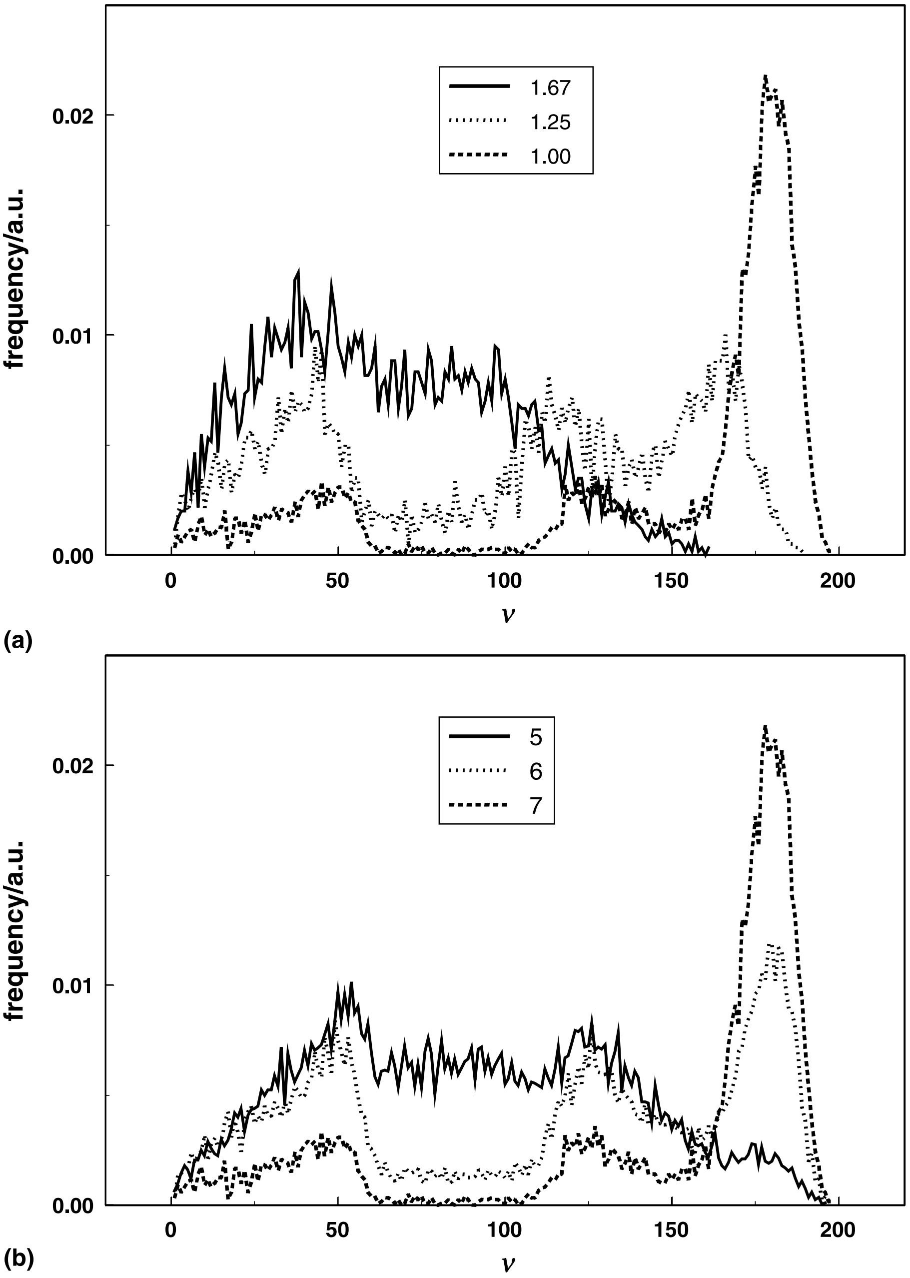

Fig. 5. Plots of the distribution of number of beads adsorbed on the confining surfaces for $N = 199$; the slit size was $d = 7$ and values of the temperatures are given in the inset (a); the temperature was $T = 1$ and values of d are given in the inset (b)

number of beads N what means that almost all beads of the macromolecule contact the surfaces. One should note that there are also well defined maxima in the vicinity of 50 and 130 with a visible gap between 60 and 120. It seems that such a behavior shows that there is a certain amount of contacts of one or two whole arms with the surfaces. The number of contacts between them is negligible what means, that this is an 'all-or-none' type switch of the molecules from one surface to another.

Conclusions

We studied the properties of a simplified lattice model of polymer chains confined in a slit formed by a pair of parallel and impenetrable surfaces in the presence of an adsorbing potential between the chain and these surfaces. The properties of model chains were determined using Metropolis-type Monte Carlo simulations. The results obtained enable one to conclude about some interesting features of the system, mainly the presence of the 'all-or-none' switching of the macromolecules between the walls. This process was present only at special conditions: the size of the slit should be relatively small and the temperature should be low (the strong adsorption regime). The chains squeezed in a narrow slit but at higher temperatures still exhibit features of three-dimensional polymers. It was also shown that for polymers in the adsorbing slits the size of chain does not exhibit a universal behavior like confined athermal polymers do.

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