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Computer simulations of polymers in a confined environment

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Abstract

A coarse-grained model of star-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 consisting of $f = 3$ branches of equal length. The flexible chains were constructed of united atoms (segments) and were restricted to vertices of a simple cubic lattice. Good solvent conditions were modelled and, thus, the macromolecules interacted only with the excluded volume. The properties of the model chains were determined by means of Monte Carlo simulations with a sampling algorithm based on the local changes of conformation of the chains. It appeared that the strongly adsorbed chains located in slits of appropriate width could swap between both confining surfaces. The influence of the chain length, width of the slit and the temperature on the frequency of such jumps was studied. The mechanism of the chain motion is also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Macromolecules confined to a slit (nanopore) that is comparable with their size are the subject of many experimental and theoretical studies because of the practical applications of such systems in chromatography, colloidal stabilization, lubrication, etc [1]. The problem of confinement is also interesting from the theoretical point of view because the confinement dramatically changes the properties of polymers when compared with those in bulk. Computer simulations were found to be a useful tool for studying the confined chains because it is still difficult to study such systems experimentally [2, 3].

Most theoretical works have concerned slits built of repulsive surfaces and containing linear polymers. These studies have been recently reviewed [4, 5]. Only a few studies have been devoted to linear polymers in a slit with attractive (adsorbing) surfaces. Single chains and dense

polymer melts have been studied by means of mean-field theoretical considerations [6–12], off-lattice [13–17], lattice [18–21] Monte Carlo and molecular dynamics [22, 23] simulations. In these works the distributions of polymer segments across the slit, the competition between adsorption and intra-chain attraction and dynamic properties were determined. Such systems have also been studied in real experiments [24].

It was shown that the properties of branched chains differ from those of their linear counterparts, which was especially visible at interfaces and in a confined space. These star-branched polymer chains consisted of three branches of equal length emanating from a common origin. The star polymers can be synthesized and studied experimentally [25] and their model features are very useful for theoretical studies [26]. The simplified models of confined star-branched polymer chains were developed and studied by means of Monte Carlo simulations in order to study the influence of the confinement on the size and structure of the chains [27, 28]. It was shown that the changes of the polymer size could be described by a universal dependence regardless of chain lengths, although this dependence did not change monotonically with the slit's size. Moreover, a similar behaviour was found for the dynamic properties of confined macromolecules. The possible changes in the mechanism of chain motion when going from a solution to a slit have been suggested and discussed. Recently, some initial studies concerning star-branched chains in adsorbing slits were performed [29]. We studied the influence of the strength of the adsorption on the static properties of star-branched chains and on their internal structure. It was also shown that for strongly adsorbed chains, and for certain widths of the slit, jumps of chains from one surface to another took place. Simulations of more complicated models of confined heteropolymers (polypeptides) also showed the influence of the chain sequence on properties of the system [30]. This dynamic behaviour of polymers in the adsorbing slit has not been studied and confirmed experimentally yet, although the proper tools are available.

In this work we studied the influence of the confinement and the strength of the adsorption on some dynamic properties of a single star-branched polymer confined in a slit formed by a pair of parallel impenetrable surfaces. For this purpose we used an idealized model of polymer chains, where the chains were represented by united atoms located at vertices of a simple cubic lattice. The lattice approximation was sufficient for this kind of study because we considered parameters describing the entire chain, and the width of the slit was considerably larger than a single bead. The polymers studied were modelled at good solvent conditions, i.e. the excluded volume was the only polymer–polymer potential used. A contact square-well attractive potential between polymer segments and the confining wall was additionally introduced. The properties of model system were determined by means of Monte Carlo simulations. The sampling algorithm employed was of a Verdier–Stockmayer type with local micromodifications of the chain conformation, developed for studies of systems of star-branched chains.

2. The model

2.1. The representation of polymer chains

We used a simplified model of polymer chains, where all atomic details were omitted and each chain was constructed as a sequence of identical segments, each of them representing some real monomers [27, 29]. The chains under consideration consisted of $f = 3$ linear chains of equal lengths (arms). These arms consisted of a sequence of n identical segments and emanated from the common origin called the branching point. The total number of segments in the star-branched chain was therefore $N = f(n - 1) + 1$. The positions of these segments

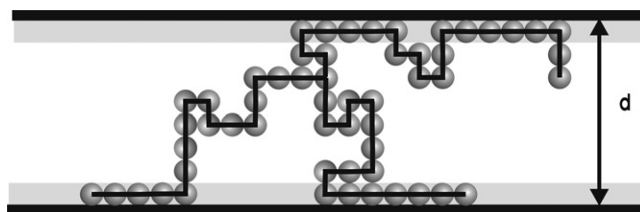


Figure 1. The scheme of a simple cubic lattice model of a star-branched chain in the slit. The layers adjacent to the surfaces forming the slit attractive for polymer segments are marked in grey.

were restricted to the vertices of a simple cubic lattice. It was assumed that segment–segment, segment–solvent and solvent–solvent interactions were identical and, thus, the system could be considered as being at good solvent conditions. The excluded volume of the chain was introduced by forbidding the double occupancy of lattice sites by polymer segments.

The calculations were carried out for a single chain which was put in a Monte Carlo box with periodic boundary conditions set in the x and y directions only. The size of the Monte Carlo box, $L = 200$ lattice units, was chosen to be large enough in order to minimize the influence of its size on the properties of the model chains. Two impenetrable surfaces confining the polymer were parallel to the xy plane and were separated by d lattice sites. Both surfaces interacted with an i th polymer segment with the same simple contact potential in a form of a square well [29]:

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

where z_i is the z -coordinate of the i th segment and $\varepsilon < 0$ is the single segment–wall interaction. The total energy of the system arises, therefore, from the contacts of the chain with both surfaces. In our calculations we used this potential in kT units $\xi = \varepsilon/kT$ with $k = 1$, and the inverse of this potential is a measure of the temperature of the system $T^* = |1/\xi| = |kT/\varepsilon|$. Figure 1 presents a scheme of a star-branched macromolecule in the adsorbing slit.

2.2. The simulation algorithm

In order to determine the properties of the model chains we carried out Monte Carlo simulations using an algorithm based on the classical asymmetric Metropolis scheme. A conformation of the chain underwent a series of the following local modifications: two-bond motion, three-bond motion, three-bond crankshaft motion and chain end reorientations, and branching point collective motion [31]. The segments to be moved were selected at random along the chain during the simulation and one attempt of each move per polymer segment defined a time unit. The position of a segment was changed, provided that the chain's connectivity as well as the excluded volume effects were preserved. The changes of the conformation were applied according to the Metropolis criterion with respect to the changes of the energy of the system. A single Monte Carlo simulation run consisted of 10^8 time units. Before the actual simulation run an equilibration run (10^7 time units) was always performed. In order to check whether the algorithm correctly sampled the phase space, we carried out 25–30 separate runs for each system under consideration starting from different chain conformations. In order to avoid a bias caused by the influences of initial conformations, the simulations started from different pools of initial states [29]. The first one was a high-temperature random coil conformation built as a

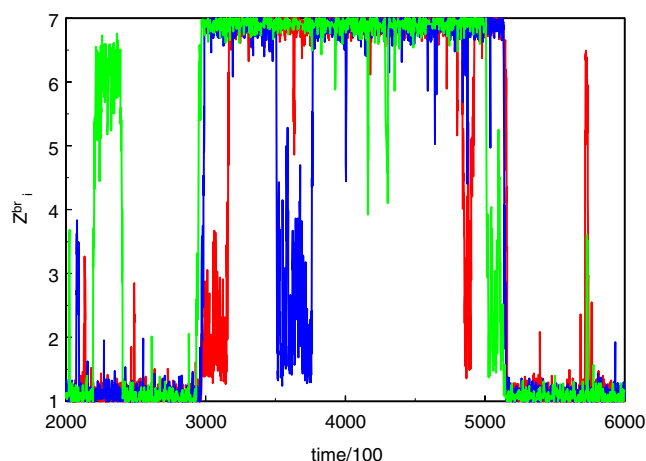


Figure 2. The changes of the arms' centre-of-mass positions across the slit, z_{cm} , as a function of time t . The chain consists of $N = 199$ segments, the width of the slit $d = 7$, and the temperature $T^* = 1$. The flowchart of each arm is marked in a different shade.

self-avoiding walk for the shortest size of slit, and then this distance was gradually increased. The second starting pool contained elongated chains forming long linear rods. The third pool of starting conformations consisted of unconfined chains with the impenetrable surfaces imposed with the distance between them being gradually diminished.

3. Results and discussion

The simulations were performed for star-branched chains consisting of $n = 17, 34, 67, 134$ and 267 segments in one arm, and thus the total number of segments in the entire chain was $N = 49, 100, 199, 400$ and 799 . These ranges of chain lengths were chosen similarly to those of previous simulations of similar models [28, 29, 31]. The simulation of longer chains even with a Metropolis-type algorithm is still beyond today's computer capabilities. Most of the calculations were carried out for a chain consisting of $N = 199$ segments. Because the size of the Monte Carlo box along the x and y axes is rather large ($L = 200$ lattice units), the maximum coverage of each surface by polymer segments in the case of strong adsorption did not exceed 3%, which implied that the system was well below the saturation of the surface.

The width of the slit varied from $d = 3$ lattice units (the shortest distance for which local moves of the chain's conformation could be performed) to $d = 16$ lattice units (the distance comparable with the mean diameter of the chain consisting of $N = 199$ segments) [29]. The lowest possible value of the z -coordinate of a polymer segment was 1, while the largest z -coordinate could not be greater than d , and the confining surfaces were put at $z = 0$ and $d + 1$ respectively. The selection of the width of the slit was based on the previous finding [27, 29]. The temperature was varied from $T^* = 2.5$ to 0.8 because it was previously shown that in this range one can find a collapse transition for a free star-branched chain on a cubic lattice and a transition from weakly to strongly adsorbed star chain on one surface [29, 32].

It was recently shown that in certain conditions polymer chains can jump from one surface to another [14]. This kind of polymer motion can be presented via the analysis of the chains' centre of mass. In figure 2 we present flowcharts of the centre of mass of each star arm for a relatively narrow slit ($d = 7$) at low temperature ($T^* = 1$). One can observe that in these

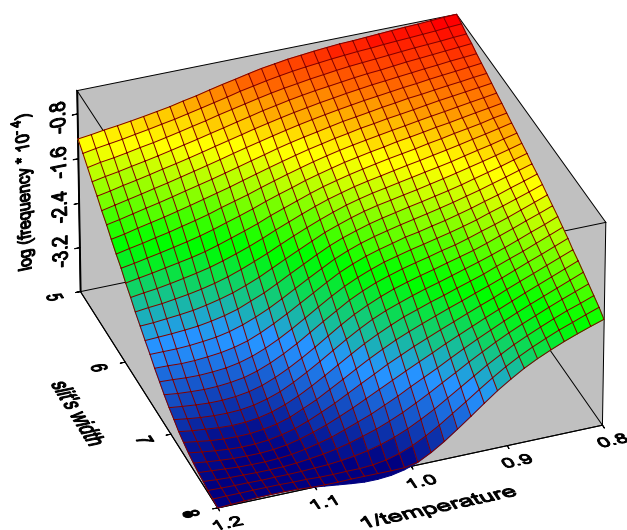


Figure 3. The log of frequency of chain jumps f as a function of the width of the slit d and the inverse of temperature T^* . The chain consists of $N = 199$ segments.

conditions for most of the simulation time the arms are almost fully adsorbed, i.e. their centres of mass are very close to the positions of the confining surfaces. From time to time one of the arms attempts to switch from one surface to another, although most of these attempts remain unsuccessful. Some attempts were successful: for instance, at the beginning of the simulation the arm marked by light grey (green in the electronic version) was close to the lower surface ($z = 0$) and for time $t = 290\,000$ it approaches the upper one ($z = d + 1$). The motion of this arm in the opposite direction can be observed for $t = 505\,000$. The jumps of the two remaining arms were also observed (see figure 2). The identification of these jumps was done by the analysis of the centre-of-mass position along the z -axis, z_{cm} . Based on our previous findings [29], we assumed that $z_{\text{cm}} < 0.5$ and that $z_{\text{cm}} > d - 0.5$ corresponds to a fully adsorbed chain at the lower and upper surface respectively. In a few cases one can observe that all three arms changed surface almost simultaneously (from the lower to the upper surface for $t = 295\,000$ and in the opposite way for $t = 510\,000$). This implies that the entire macromolecule switches the surface to which it was predominately adsorbed.

Therefore, having the definition of a jump, we can calculate the frequencies of the jumps at different conditions. Figure 3 presents the logarithm of frequencies of jumps for chains with $N = 199$ segments as a function of the width of the slit and the inverse of temperature. The size of the slit for which chains adsorbed at low and intermediate temperatures, i.e. for $T^* < 1.25$, can swap the confining surfaces are the same for all chain lengths under consideration: $5 \leq d \leq 8$. For narrow slits with $d < 5$ the chains during the entire simulation interact with both surfaces simultaneously, and it is difficult to define the criterion of the translocation from the first to the second surface. The plot was organized in a semi-logarithmic way in order to check whether or not the Arrhenius-type dependence of the jump frequency could apply. In fact, one can see that for the slit width $d = 8$ the frequency is linear for temperatures $T > 1$, whilst for lower temperatures the jumps were not observed. For wide slits with $d > 8$, chains are not able to reach the second surface, as the probability of the passage to another surface is negligible, because the formation of bridges between the distant surfaces is energetically unfavourable. At higher temperatures, $T^* > 1.25$, the chains interact with both

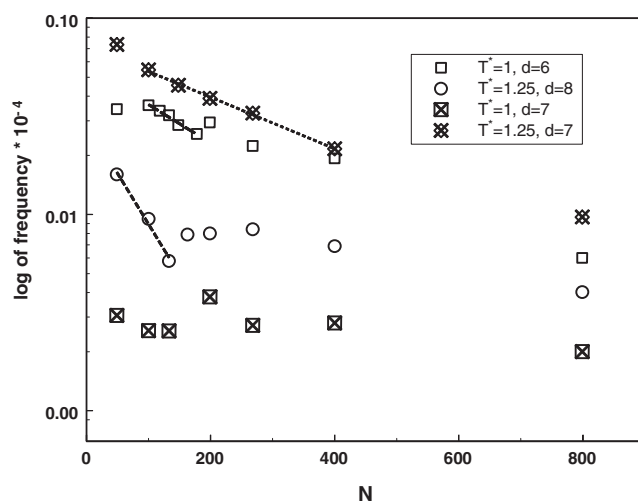


Figure 4. The frequency of chain jumps f as a function of the chain length N . The widths of the slit d and the temperatures T^* are given in the inset.

surfaces simultaneously, and the problem concerning the definition of a jump also appears. The mechanism of star-branched chains swapping was found to be as follows: one arm of the star was detached from the surface at which the chain was fully adsorbed, starting most frequently from the very end, and eventually it adsorbed on the second surface. Then, the next arm was transferred to the second wall according to the same mechanism. The third arm started the detachment in a different way, i.e. from the branching point.

The last question concerned the influence of the chain length on the frequencies of polymer jumps between the confining surfaces. In figure 4 we present the frequencies for different widths of the slit and for different temperatures. One can expect that the frequency does not depend on the chain length but only on the slit width and temperature. This would be the implication of the following assumption: the probability of the jump is proportional to the Arrhenius-type factor $\exp(-E_a/kT)$. The activation energy E_a corresponds to the energy loss by the adsorbed chain because a bridge connecting both surfaces has been formed and the length of that bridge is proportional to the width of the slit. Therefore, we present the data in figure 4 as semi-logarithmic plots. The linear dependence of the frequencies of jumps can be observed for short and intermediate chains, which means that the formation of bridges controls the jumps. It seems that for longer chains, and especially for lower temperatures, the formation of bridges between the surfaces is not the only factor that controls the process of jumps: most of the time is wasted in detaching a long chain from the first surface and attaching it on the second surface. For longer chains ($N > 400$) the frequencies of jumps observed for the slit with $d = 6$ are about seven times greater than those for $d = 7$. If we assume Arrhenius behaviour, this factor can be interpreted as the effect of bridging the surfaces by a few extra segments. One could argue that when the width of the slit is enlarged by one unit the length of the bridge should increase by m segments, where m is a small number close to 1. Therefore, the ratio of the frequencies for a slit with a different width is proportional to $\exp[-E_a(d)/kT - E_a(d+1)/kT] = \exp(-m\xi)$, and is constant for a given temperature. Thus, for $T^* = 1$ ($\xi = -1$) one can expect the ratio e^1 or e^2 , which is close to the obtained value, 7.

4. Conclusions

In this work a simple model of star-branched polymers confined by two parallel impenetrable and attractive surfaces was studied in order to understand the dynamic properties of the chains. Model chains used were built of united atoms and their positions were restricted to a simple cubic lattice. The excluded volume was the only intra-chain interaction in this model. The properties of the polymer system under consideration were determined by means of Monte Carlo simulations using a Verdier–Stockmayer-type sampling algorithm with local changes of chain conformation. The adsorption of the confining surfaces was realized by attractive interactions with polymer segments.

It was shown that a strongly adsorbed polymer chain in a slit can leave the surface on which it was adsorbed and then it can attach to the second wall. This process was observed for star-branched chains for certain widths of the slit and at some temperatures only. The chain had to be strongly adsorbed, but on the other hand the strength of the adsorption cannot be too strong, in order to allow the chain to detach. For the model branched chains under consideration (on a simple cubic lattice simulated by a Verdier–Stockmayer algorithm) jumps were observed for temperatures $1.25 \leq T^* \leq 0.8$. The width of the slit had to be within a defined range too: $5 \leq d \leq 8$ (in lattice units). In a wide slit the probability of a chain's jump was considerably lower. If the slit is too narrow the chains are adsorbed on both surfaces even at low temperatures and it would be difficult to define and identify a jump. The frequencies of chain jumps also depend on the polymer length. This especially concerns short and intermediate chains. One could expect that the behaviour of linear chains is qualitatively the same in similar conditions: the chains are almost adsorbed on one surface and sometimes perform a jump to the second surface. The frequency of these jumps is expected to be higher than for star-polymers and the changes of positions less rapid because the arms of a star move from surface to surface rather independently, while the properties of linear chains are almost the same along the chain contour.

Acknowledgments

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