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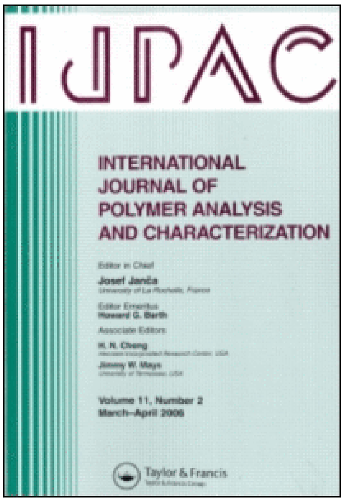

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Sikorski, Andrzej and Romiszowski, Piotr(2007) 'Computer Simulation Study of Polymer Dynamics in Adsorbing Slit', International Journal of Polymer Analysis and Characterization, 12: 1, 77 — 85

To link to this Article: DOI: 10.1080/10236660601060060

URL: http://dx.doi.org/10.1080/10236660601060060

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International Journal of Polymer Anal. Charact., 12: 77–85, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/10236660601060060

Computer Simulation Study of Polymer Dynamics in Adsorbing Slit

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Abstract: In this study, we investigated the properties of star-branched polymers confined to a slit. The polymer models used were rather idealized: they consisted of identical united atoms (segments) whose positions were restricted to vertices of a simple cubic lattice. The polymers were put into a slit formed by a pair of parallel and impenetrable surfaces. The system was at good solvent conditions, and, thus, the chains interacted with the excluded volume only. The force field used consisted of a simple contact potential acting between polymer segments and confining surfaces. The properties of the model chains were determined by means of Monte Carlo simulations with a sampling algorithm based on local changes of chain's conformation. The influence of the temperature and the size of the slit on the dynamic behavior of chains was studied. It appeared that, at certain conditions, chain jumps between the confining surfaces were observed.

Keywords: Adsorbed polymer; Confined polymer chain; Monte Carlo simulation; Polymer dynamics

INTRODUCTION

Properties of macromolecules located in confined space are important because of their practical applications like colloidal stabilization and lubrication.[1] The confinement of polymer chains is also interesting from the theoretical point of view as confinement dramatically changes the

Received 9 July 2006; accepted 29 September 2006.

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properties of the system when compared to free chains in solution and in melt. Theoretical considerations concerning confined macromolecules go back to the pioneering works of de Gennes.[2] Computer simulations were found to be a useful tool for studying confined polymer chains because it is still difficult to exactly solve analytical theories and to study these systems experimentally. Van Vliet and ten Brinke[3] carried out Monte Carlo simulations of lattice models of confined linear polymers and found that the size of a confined macromolecule exhibits a universal behavior disregarding its length and the width of the slit. Milchev and Binder[4] simulated off-lattice models of linear polymers, focusing their attention on polymer density profiles inside the slit. Cifra and Bleha[5] checked the influence of sort of the confinement (slit versus cylinder) on the properties of lattice polymer chains. Recently, properties of idealized confined models of star-branched and linear polymers were studied by means of the Monte Carlo method.[6,7] The universal behavior of the polymer size and of the dynamic properties was shown. Changes in the mechanism of a chain's motion when going from an unconfined solution or melt to a slit were suggested and discussed.

The aim of this article is to study the dynamic properties of star-branched chains confined in a slit formed by adsorbing surfaces. The studies of the changes of chain dynamics caused by both factors, adsorption and the presence of the confinement, seem to be especially interesting for branched chains. During the past decade, some theoretical and simulation works on adsorbing slits were published, but they concerned linear chains only.[8–11] For the purpose of these studies, simple cubic lattice models were developed.[7] The properties of both unconfined and confined (but without adsorption) star-branched chains were recently determined, and, thus, there is a good reference state.[6,7] The model chains under consideration were studied under good solvent conditions with the excluded volume potential only and with a simple contact attractive potential assumed between polymer segments and the surfaces forming the slit. The properties of model macromolecules were determined from Monte Carlo simulations that were performed employing a Metropolis-like sampling algorithm developed recently for studies of systems of star-branched chains.

THE MODEL AND THE METHOD

We used highly idealized models in order to study properties of polymer systems in a long time scale. For this purpose, all atomic details were suppressed, and, thus, the model chain was constructed as a sequence of identical united segments representing some real monomers. The positions of these segments were restricted to the vertices of a simple cubic

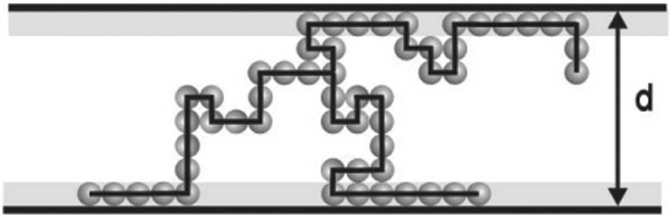

Figure 1. The scheme of a star-branched polymer chain trapped between two parallel impenetrable walls. The surfaces are located *d* apart. The gray layers indicate lattice sites adjacent to the surfaces where the adsorbing potential is effective.

lattice. It was assumed that all energetic contacts were the same, and, therefore, the system can be considered as under good solvent conditions. The model chains were put into a large Monte Carlo box (the edge of this box was $L = 200$ lattice units) with periodic boundary conditions set in x and y directions only. Two impenetrable surfaces were parallel to the xy plane and separated by d consecutive lattice sites. In Figure 1 we present a scheme of a star-branched macromolecule with three arms located in a slit formed by these confining surfaces. The surfaces interacted with polymer segments with a simple contact potential:

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

where z_i is the z-coordinate of ith segment and the interaction parameter $\varepsilon < 0$, which implied that the surfaces were attractive for polymer segments. The excluded volume was introduced into the system by forbidding the double occupancy of lattice sites by polymer segments. In the simulations, we used this potential in kT units $\xi = \varepsilon/\mathrm{kT}$ and the inverse of the potential served as a measure of the temperature of the system: $\mathrm{T}^* = 1/\xi = \mathrm{kT}/\varepsilon$.

The properties of the model system were determined using Monte Carlo simulations. The sampling algorithm was based on the classical asymmetric Metropolis scheme. The conformational space was sampled by a series of the following local modifications: 2-bond motion, 3-bond motion, 3-bond crankshaft motion, chain ends reorientation, and branching point collective motion.[12] The local moves were selected along the chain at random during the simulation process. One attempt of each motion per polymer segment defined a time unit. A new conformation obtained after such micromodification was accepted due to topological constraints, the excluded volume condition, and the Metropolis criterion. A single Monte Carlo simulation run consisted of 10^8 time units. Before

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this production run, an equilibration run was always performed consisting of 10^7 time units. In order to obtain the proper sampling for each model chain at a given distance between the surfaces and the temperature, the simulations were carried out 25–30 times starting from different chain conformations. We used three pools of initial conformations. The first one contained high-temperature random coil conformations built as self-avoiding walks for the shortest size of a slit ($d = 3$). The next simulation runs were made for distances d gradually increasing. The second pool contained elongated chains – each arm had the conformation of a linear rod. The third starting pool of conformations consisted of unconfined chains; the surfaces were imposed onto the system and the distance between them was gradually diminished.

RESULTS AND DISCUSSION

The calculations were carried out for star-branched chains consisting of $n = 17$, 34, 67, 134, and 267 segments in one arm; the total number of segments in the chain was $N = 49$, 100, 199, 400, and 799 respectively. The distance between the confining surfaces d was varied from 3 (the shortest distance for which the simulation algorithm works) to $d = 27$, i.e., the distance comparable to the mean diameter of the longest chains under consideration.[7] In order to make the data obtained for different slits comparable, we introduced the reduced parameter describing the relative size of the slit $d^* = d/(2 < S_o^2 >^{1/2})$, where S_o is the radius of gyration of an unconfined chain of the same length.[3,7] The reduced size of the slit d^* can be treated as a measure of the 'squeezing' of a macromolecule. The strength of the adsorbing potential was varied from $\xi = 0$ to $-1\,k\mathrm{T}$ because it was previously shown that within this range, the chains adsorbed on one surface underwent the transition from a weak to a strong adsorption regime.[13]

In order to study the long-term dynamic behavior of confined chains, we calculated the following autocorrelation function:

$$g_{cm}(t) = \left\langle [\mathbf{r}_{cn}(t) - \mathbf{r}_{cm}(0)]^2 \right\rangle \tag{2}$$

where $g_{cm}(t)$ stands for the center of the mass autocorrelation function and $\boldsymbol{r}_{cm}$ are the coordinates of the center of mass. The motion of chains confined in a slit is suppressed in the direction perpendicular to the confining surfaces, and thus we studied the autocorrelation function along the xy plane only. The self-diffusion coefficient was calculated from the center-of-mass autocorrelation function according to the Einstein formula $D_{xy} = g_{cm}(t)^{xy}/4t + \mathrm{const}$. The diffusion coefficient was calculated for a longer time, where the center-of-mass autocorrelation function scales as t^1. In Figure 2 we present the diffusion constant D_{xy} as a

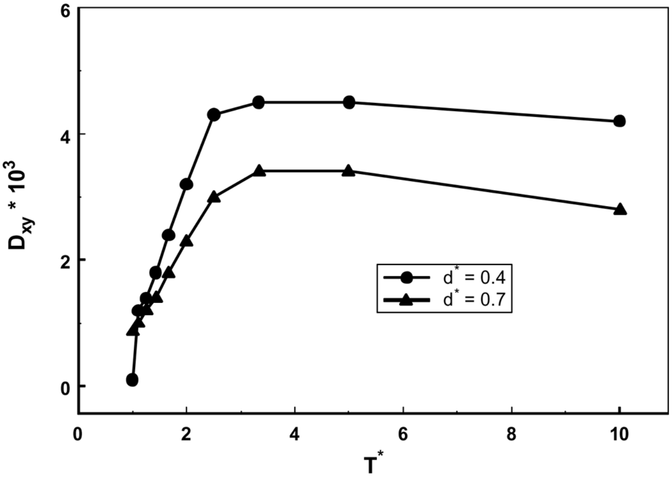

Figure 2. The self-diffusion coefficient D_{xy} as a function of the reduced temperature T^* for the chain consisting of $N = 199$ segments. The reduced widths of the slit d^* are given in the inset.

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function of the temperature for two different widths of the slit. One can observe that both curves have a similar shape: during the annealing process the diffusion coefficient slightly increases but below $T^* = 3.33$ it starts to decrease rapidly. This behavior can be explained by the fact that near this temperature a transition from weak to strong adsorption regime took place. The decrease of the slit width leads to the increase of the chain mobility. A similar behavior was found for chains in pure repulsive slits.[6] This effect is probably caused by two factors: the changes of the mechanism of motion and the differences in the disentanglement process.

In Figure 3 we present the dependency of the diffusion coefficient on chain length for two reduced sizes of the slit $d^* = 0.4$ and 0.7 and for two temperatures $T^* = 3.33$ and 1.67. In all cases, one can observe that for sufficiently long chains ($N \leq 199$), the diffusion coefficient roughly scales with the number of segments as N^{-1}. This scaling behavior is similar to that for free chains in diluted solutions and in pure repulsive slits.[6,7]

Figure 4 presents mean frequencies of contacts between polymer segments and the surfaces as a function of the segment number. In numbering the segments #1 was assigned to the branching point and #*n* to the arm's end. One can observe that for segments from the middle part of the arm, the reduced frequency of contacts with the adsorbing surfaces is almost constant regardless of the temperature and the size of the slit. In the vicinity of the branching point, one can observe a rapid decrease of the frequencies of contacts, although at low temperatures this decrease is limited to the branching point. For the very ends of arms,

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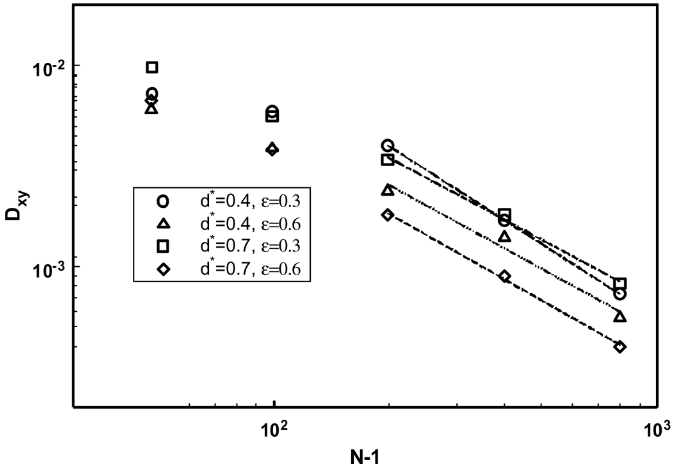

Figure 3. The self-diffusion coefficient D_{xy} as a function of the chain total length N. The reduced widths of the slit d^* and the reduced temperatures T^* are given in the inset.

the frequencies of contacts increase for high temperatures and decrease for lower ones. This can be explained by higher mobility of chain ends than for the rest of the chain.[7]

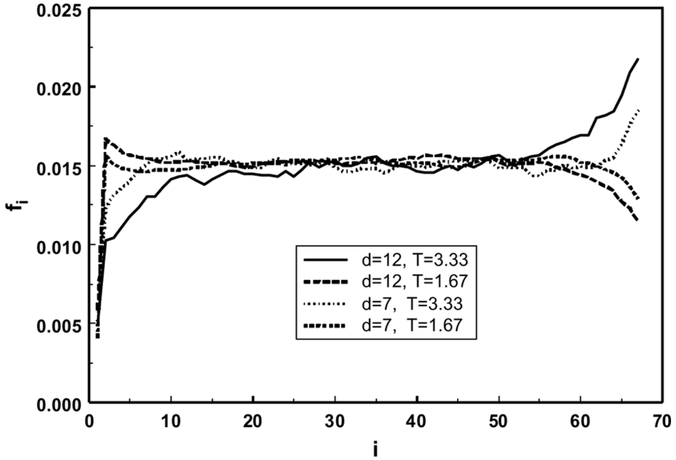

Figure 4. The frequencies of contacts between polymer segments and the confining surfaces f as a function of the bead number i (see text for details). The case of the chain consisted of $N = 199$ segments. The reduced widths of the slit d^* and the reduced temperatures T^* are given in the inset.

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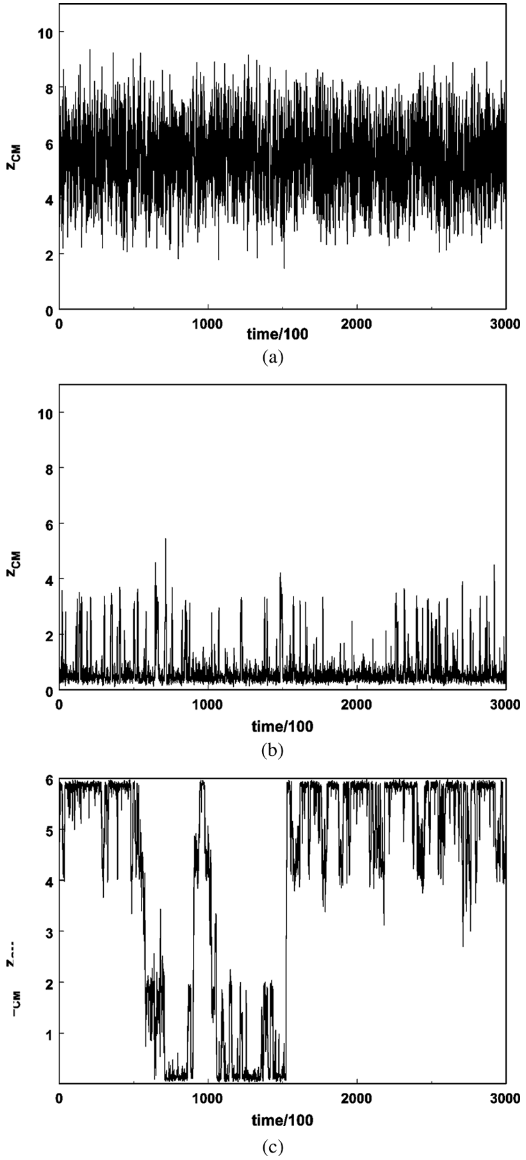

Figure 5. The flowcharts of the chain's center-of-mass position along the z-axis z_{cm} for the chain consisting of $N = 199$ segments; slit $d = 12$ and temperature $T^* = 3.3$ (a), $d = 12$ and $T^* = 1.67$ (b), and $d = 7$ and $T^* = 1.11$ (c).

At certain conditions an interesting new mechanism of chain motion appeared in the adsorbing slit. This motion took place at low temperatures $1.25 < T^* < 1$ and for moderate widths of the slit $6 < d < 9$, where the chains are almost fully adsorbed to one of the confining surfaces. For a certain period of time, the chain detached from that surface and became adsorbed to the second surface. This motion can be identified and shown by monitoring of the z coordinate of the chain's center-of-mass position. Figure 5 presents the flowcharts of this parameter z_{cm}. One can observe in Figure 5(a) that for wider slits ($d = 12$) and at higher temperatures ($T^* = 3.33$), the chain's center of mass remains near the middle of the slit. The decrease of the temperature to $T^* = 1.67$ (Figure 5(b)) led to the full adsorption on one surface – z_{cm} is close to 0. The further decrease of temperature to $T^* = 1.11$ and the size of the slit to $d = 9$ caused the characteristic changes in the z_{cm} flow chart. In the beginning, the chain is located close to one surface and then it rapidly jumped to the second one. This process was repeated many times and exhibited features of an all-or-none transition.

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CONCLUSIONS

In this work we studied the properties of a simplified model of branched polymer chains located in an adsorbing slit. The star-branched chains were represented as sequences of athermal segments forming a star with three arms of equal lengths. The lattice approximation of macromolecules was used. The properties of this model were determined using Metropolis-type Monte Carlo simulations. The main conclusion from this work is that the dynamic properties of the chain are highly affected by the adsorbing slit. For longer chains, the diffusion coefficient of chains scaled as for unconfined ones. It was found that for certain temperatures and widths of the slit the chains jumped between these surfaces.

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