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# Star-branched polymers in an adsorbing slit: A Monte Carlo study

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A coarse-grained model of star-branched polymer chains confined in a slit was studied. The slit was formed by two parallel impenetrable surfaces, which were attractive for polymer beads. The polymer chains were flexible homopolymers built of identical united atoms whose positions in space were restricted to the vertices of a simple cubic lattice. The chains were regular star polymers consisted of  $f=3$  branches of equal length. The chains were modeled in good solvent conditions and, thus, there were no long-range specific interactions between the polymer beads—only the excluded volume was present. Monte Carlo simulations were carried out using the algorithm based on a chain's local changes of conformation. The influence of the chain length, the distances between the confining surfaces, and the strength of the adsorption on the properties of the star-branched polymers was studied. It was shown that the universal behavior found previously for the dimension of chains was not valid for some dynamic properties. The strongly adsorbed chains can change their position so that they swap between both surfaces with frequency depending on the size of the slit and on the temperature only. © 2005 American Institute of Physics. [DOI: 10.1063/1.2018634]

## I. INTRODUCTION

The properties of confined polymer chains have been recently subjects of many experimental and theoretical works.<sup>1,2</sup> This was because of the practical importance of polymers at interfaces, such as size-exclusion chromatography, polymer adhesion, lubrication, and wetting.<sup>3</sup> Up to date most of the theoretical works were devoted to slits with purely repulsive surfaces confining linear polymer chains. The results of these studies were recently reviewed (see, e.g., Refs. 4 and 5) so we are not going to present and discuss them here. Only a few studies were devoted to linear chains in a slit with adsorbing surfaces. There have been mean-field theoretical considerations<sup>6–12</sup> and off-lattice<sup>13–16</sup> and lattice<sup>17–20</sup> Monte Carlo and molecular-dynamics<sup>21,22</sup> simulations. The distributions of polymer beads in the slit, as well as, their changes with the attraction of walls were studied. The competition between this interaction and intrachain attraction was investigated. Some dynamic properties of such polymers were also determined.<sup>13</sup> Besides, single polymer chains and dense polymer melts in the attractive slits were also studied.<sup>11,12,20–22</sup> Systems with one attractive wall only were also a subject of interest.<sup>14</sup> One has to notice that such systems were investigated in real experiments.<sup>23</sup>

The properties of branched chains differ from those of their linear counterparts and this is especially visible at interfaces and in a confined space. The simplest model of a nonlinear chain is a star-branched polymer consisting of three branches emanating from a common origin. These star-branched polymer chains can be synthesized and studied experimentally<sup>24</sup> and their model features are especially useful for theoretical considerations.<sup>25</sup> The simplified models of confined star-branched polymer chains were recently de-

signed and studied by means of Monte Carlo simulations.<sup>26–28</sup> These coarse models were used to study the size and the structure of confined star-branched polymer chains in a slit formed by two impenetrable surfaces. It was shown that the size of polymer chains is universal regardless of chain lengths although it did not change monotonically with slit's size. The mobility of chains described as the self-diffusion coefficient also did not change monotonically with the size of the slit. The possible explanation of this phenomenon was that the mechanism of motion can change when a chain passes from a three-dimensional to a two-dimensional state. It was also shown that fragments of star-branched chains were exposed to a different degree on the confined surfaces and this behavior was also universal for all chain lengths. The frequencies of these contacts were limited for the core region near the branching point, numerous for the very ends of arms and almost constant for the rest of the chain. The universal behavior of linear and star-branched chains in spherical pores was also found for distribution coefficients.<sup>29,30</sup>

In this paper, we introduced the interactions of polymer chains with the confining surfaces into the model. We studied the influence of the temperature (the strength of the adsorption) on the static properties of star-branched chains and on their internal structure. The main focus of this study was to show the main differences in chain's size and structure between the athermal case and the case when the confining walls became attractive. The paper is organized as follows. In Sec. II we outline the assumptions of our model and the simulation technique. In Sec. III the results concerning mostly the size and the structure of chains as well as its motion between the confining surfaces are presented. In Sec. IV the most important and concluding remarks are presented.

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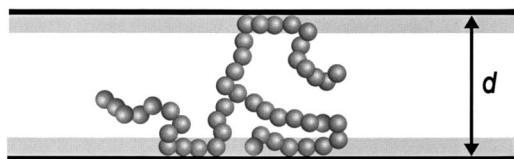


FIG. 1. The scheme of a star-branched chain located between two parallel impenetrable surfaces. The range of the adsorption potential is marked by the gray shade.

## II. THE MODEL AND THE SIMULATION ALGORITHM

The polymer chains under consideration were built of  $f=3$  linear chains (arms). These arms consisted of a sequence of  $n$  identical beads and emanated from a common origin (the branching point). Thus, the total number of beads in the star-branched chain was  $N=f(n-1)+1$ . Each bead was defined as a united atom and represented some monomers of a real macromolecular chain. The model chains were restricted to a simple cubic lattice in order to make the calculations more efficient. The ban of the multiple occupation of the same lattice site was introduced, providing the excluded volume effect in the system.

The model chain was confined between two parallel impenetrable surfaces. The surfaces were parallel to the  $xy$  plane. The distance between the surfaces was  $d$  lattice units, i.e., the lowest possible value of the  $z$  coordinate of the chain was 1, while the largest  $z$  coordinate could not be greater than  $d$ , thus the surfaces were placed at  $z=0$  and  $z=d+1$ , respectively. The scheme of the chain confined between the surfaces is presented in Fig. 1.

The adsorbing potential between the confining surfaces and an  $i$ th bead of the chain has the following form:

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

where  $\varepsilon < 0$  is the single bead-wall interaction. Thus, only the beads which were in contact with the surfaces contributed to the energy of the system. The total energy of the chain was therefore equal to

$$E = \nu_1 \varepsilon + \nu_2 \varepsilon, \quad (2)$$

where  $\nu_1$  and  $\nu_2$  are the numbers of polymer beads contacting with the surfaces 1 (at  $z=0$ ) and 2 (at  $z=d+1$ ), respectively. During the simulation, the chain was annealed from high to low temperatures. The reduced temperature of the system was defined as  $T^* = 1/\xi$ , where  $\xi = \varepsilon/kT$ . The annealing procedure was applied so that the quasiequilibrium conditions were maintained. The dynamic simulation of the system was performed according to the previously described procedure<sup>26,31</sup> during which the chain's initial (generated at random) conformation was changed with the use of micromodifications. The set of the micromodifications consisted of the local changes of the conformation applied to one or two chain beads. The micromodifications consisted of the following set of chain bead motions: two-bond motion, three-bond motion, three-bond crankshaft motion, one- and two-bond end reorientations, and branching point collective motions.

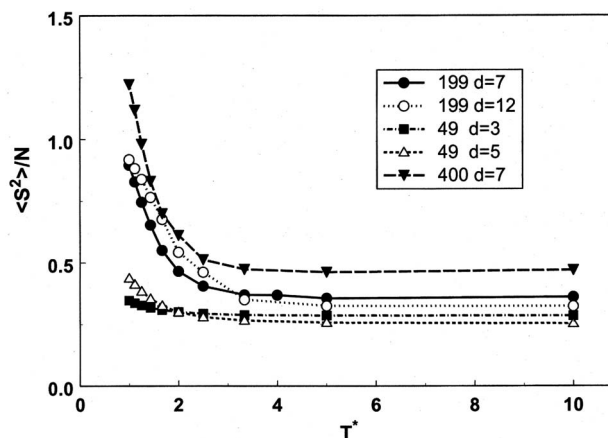


FIG. 2. The reduced mean-squared radius of gyration  $\langle S^2 \rangle / N$  as a function of temperature  $T^*$ . The chain lengths and the distances between the surfaces are given in the inset.

The position of a bead was changed provided that the chain's connectivity as well as the excluded volume effects were preserved. All the changes of the chain conformation were applied according to the Metropolis sampling algorithm with respect to the changes of the energy of the system  $E$ . The time scale was set as follows: during one time unit the number of attempts of each type of micromodifications was equal to the number of beads. The simulation runs consisted of  $10^8$ – $10^9$  time steps and were repeated 20–30 times. Each repetition of the simulation run started from a different conformation of the chain.

## III. RESULTS AND DISCUSSION

We studied star-branched chains with arms of the length  $n=17, 34, 67, 134, 267$ , and  $401$  beads and thus the total number of beads in the entire chain was  $N=49, 100, 199, 400, 799$ , and  $1201$ , respectively. This range of the chain length built on a cubic lattice is sufficient for the studies of the properties of long chains and the influence of branching. Because the size of the Monte Carlo box, along  $x$  and  $y$  axes,  $L$  was changed between 100 and 200, the maximum coverage of each surface by polymer segments did not exceed 3%. It means that the system was well below the saturation of the surface. The selection of the size of the slit was based on the previous finding for the same but athermal model system.<sup>27</sup> The distance between the confining surfaces varied between  $d=3$  (the shortest possible distance for which a chain confined chain can move) up to  $d=35$  which corresponds to the reduced distance  $d^*=0.7$  for the longest chain under consideration. The temperature  $T^*$  was changed between 10–1 because in this range one can find both: a collapse transition for a free star-branched chain on a cubic lattice and a transition from weakly to strongly adsorbed star chains on one surface.<sup>31,32</sup>

The size of the star-branched polymer can be described by the mean-squared radius of gyration of the entire chain  $\langle S^2 \rangle$  and the mean-squared center to end, i.e., the distance between the branching point and the end of an arm  $\langle R^2 \rangle$ . In Fig. 2, we present the dependence of the mean values of the squared radius of gyration on the temperature. The values of

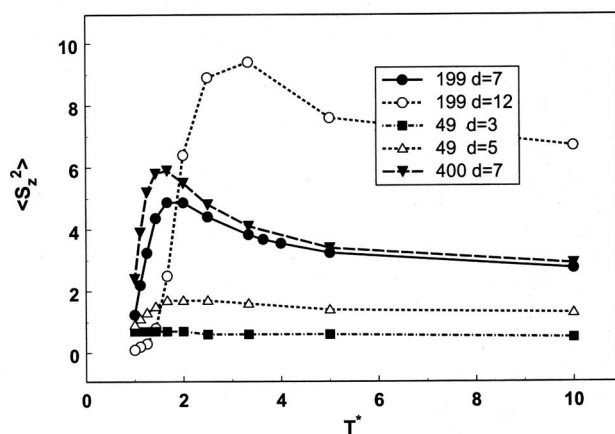


FIG. 3. The  $z$  component of the mean-squared radius of gyration ( $\langle S_z^2 \rangle$ ) as a function of temperature  $T^*$ . The chain lengths and the distances between the surfaces are given in the inset.

$\langle S^2 \rangle$  were divided by the total number of chain beads in order to make the results comparable to the whole set of the chain lengths. One can observe that for a wide range of temperatures above  $T^*=3$  the values of  $\langle S^2 \rangle$  are almost constant and close to values of an athermal system where no adsorption was present. In this temperature region, one can observe an effect of the compression of the chain in the slit: the values of  $\langle S^2 \rangle$  for a narrower slit are larger than those for a wider slit. It is caused by the expansion of the chain in the  $xy$  plane making a significant contribution to the total  $\langle S^2 \rangle$  value. Further annealing below  $T^*=3$  leads to the rapid and significant increase of the size of the chain, with the exception to the narrowest size of the slit ( $d=3$  and  $5$ ). At the lowest temperature under consideration ( $T=1$ ) the size of the polymer is more than twice of that in the high-temperature slit (for larger values of  $d$ ). The chains which are in narrow slits ( $d=3$  and  $5$ ) do not expand significantly during the annealing process since they are already almost two dimensional.

Further information about the chain structure can be elucidated from the behavior of the  $z$  contribution to the mean-squared radius of gyration ( $\langle S_z^2 \rangle$ ). The changes of this parameter with temperature  $T^*$  are presented in Fig. 3. The changes are not monotonic as in the case of the entire  $\langle S^2 \rangle$ . Significant maxima occur at the curves during the cooling of the system. This effect can be explained by the fact that the segments of the chain are adsorbed on both confining walls at the same time at intermediate temperatures. As the temperature decreases, the adsorption on one of the walls and the chain does not touch both surfaces simultaneously, resulting in a dramatic decrease of the  $z$  contribution to the dimension. In other words the one-wall adsorption leads to the minimum of the energy and no chain fragments connecting both sides of the slit (bridges) are observed. The above behavior of the  $\langle S_z^2 \rangle$  parameter correlates well with the number of contacts between the polymer beads and the confining surfaces. The detailed discussion concerning the structure of the chain and the contacts is given below (discussion of Figs. 8 and 9).

Figures 4(a) and 4(b) present the ratios  $\langle S^2 \rangle / \langle R^2 \rangle$  and  $\langle S_z^2 \rangle / \langle R_z^2 \rangle$  as function of the temperature. The values do not show almost any regularity, especially in the low-

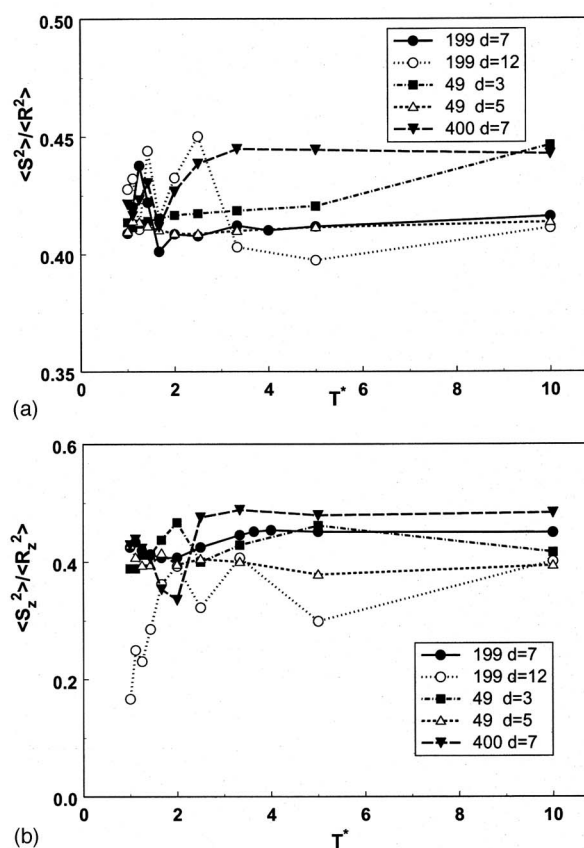


FIG. 4. The ratios  $\langle S^2 \rangle / \langle R^2 \rangle$  (a) and  $\langle S_z^2 \rangle / \langle R_z^2 \rangle$  (b) as a function of temperature  $T^*$ . The chain lengths and the distances between surfaces are given in the inset.

temperature region. One can notice that both ratios are within the range of 0.40–0.45, independent on the chain length, the size of the slit, and the temperature. The theoretical predictions for this ratio are 0.389 and 0.393 for star-branched chains without and with the excluded volume, respectively.<sup>31,33</sup> The simulation results for the star-branched chains in a slit with no attractive interactions with the surfaces showed that this ratio remained almost constant and close to 0.42 independent on the size of the slit and the chain length.<sup>28</sup> Thus we can conclude that the analysis of the  $\langle S^2 \rangle / \langle R^2 \rangle$  ratio does not enable one to locate the transition from the compressed three-dimensional chain to the fully adsorbed two-dimensional structures.

The total energy of the confined chains as a function of the temperature is presented in Fig. 5. In order to make the results comparable for all the chain lengths under consideration we present the energy per one polymer segment, i.e., the values  $\langle E \rangle$  were divided by the total number of the chain's beads  $N$ . One has to remember that the only contribution to the total energy comes from the interactions of polymer beads with confining surfaces. The energy of the chains decreases smoothly during the annealing process but a more rapid decrease starts below  $T^*=3$ . There are no qualitative differences in the energy behavior for chains of different lengths and for different sizes of the slit, except the most compressed case ( $N=49$  and  $d=3$ ), which shows a visible decrease of the curve in the intermediate temperature region. One can observe that for the lowest-temperature region the



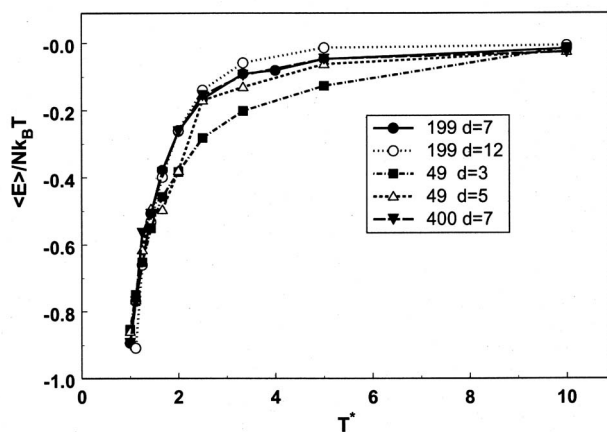


FIG. 5. The reduced mean energy  $\langle E \rangle / N$  as a function of temperature  $T^*$ . The chain lengths and the distances between the surfaces are given in the inset.

reduced energy values are close to  $-0.9$  which means that in all cases, independent of  $N$  and  $d$ , almost 90% of the entire star-branched chain beads are adsorbed on the confining surfaces.

Figure 6 presents the heat capacity as a function of the temperature for the same systems as in Figs. 2–5. We observed the  $C_p$  peaks on the curves for all cases under consideration. The presence of the maxima suggests that there is a phase transition while the system is annealed. Despite difficulties with the quantitative description of the location of the phase-transition temperature, one can conclude that for smaller slits the phase transition is observed at lower temperatures. It is difficult to determine precisely the location of the transition temperature  $T_c$ , but in all cases it took place at temperatures between 1 and 2. Our results show, however, that the larger slit caused the transition temperature to be higher than for a narrower one of the same chain length. This can be explained by the fact that in a narrow slit the star-branched chain is significantly flattened even at high temperatures.

The changes of the distribution of polymer segments across the slit are presented in Fig. 7. In order to make the comparison of the results obtained for the systems of differ-

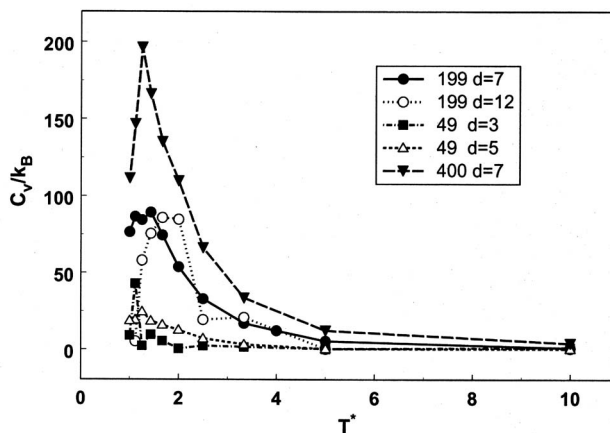


FIG. 6. The heat capacity  $C_p / k$  as a function of temperature  $T^*$ . The chain lengths and the distance between the surfaces are given in the inset.

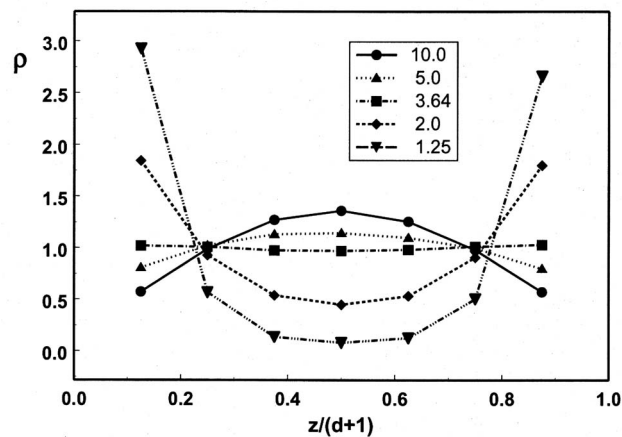


FIG. 7. Density profiles of polymer segments across the slit for the chain with  $N=199$  beads at  $d=7$ . The temperatures are given in the inset.

ent sizes possible, we normalized both the number of beads and the width of the slit. One has to remember that the noticeable asymmetry of the curves for small slit sizes is caused by the lattice effect. One can notice that the shape of the density profiles depends strongly on the temperature. For the system at high temperatures (a weak adsorption case) the density profiles are parabolic with a maximum at the middle of the slit and the depletion zones are at positions closest to the confining surfaces. The decrease of the temperature led to the lowering of the maxima and the entire curve became flatter. At a certain temperature a plateau was observed which means that there is a uniform density of polymer beads across the slit. Further annealing of the system changes the density profiles to a parabolic-like form with the minimum in the middle of the slit. This behavior was found for all the chain lengths under consideration. Similar density profiles were found by Allegra and Collombo who calculated them using the matrix method.<sup>6</sup> At an intermediate temperature besides the constant density across the slit, they found depletion in the layers at the sites adjacent to the surfaces.

The above discussion of the results was based on the ensemble averages which do not give any insight into the instantaneous structure of the system as well as into the mechanism of motion of the chain in the slit. Therefore, we prepared flowcharts of the number of contacts between polymer chains and each of the surfaces. The contacts with each of the surface are denoted by points of different colors. A series of figures presents flowcharts of the number of bead-surface contacts for  $N=199$  and for the lowest temperature  $T^*=1$  for different sizes of the slit  $d$  [Figs. 8(a)–8(c)]. For the slit  $d=6$  the points are distributed not uniformly so that a gap with significantly smaller number of points is visible. The gap is located in such a way that it encompassed approximately one third of the number of contacts (in a middle part of the y values). The points in the upper and the lower areas of the plot are distributed in forms of separated areas of different colors. These areas persist for a certain time and the changes of colors representing two different surfaces are periodical. Further expansion of the slit results in more pronounced areas in the upper region of the plot while the intermediate gap appears almost empty with a few points only.

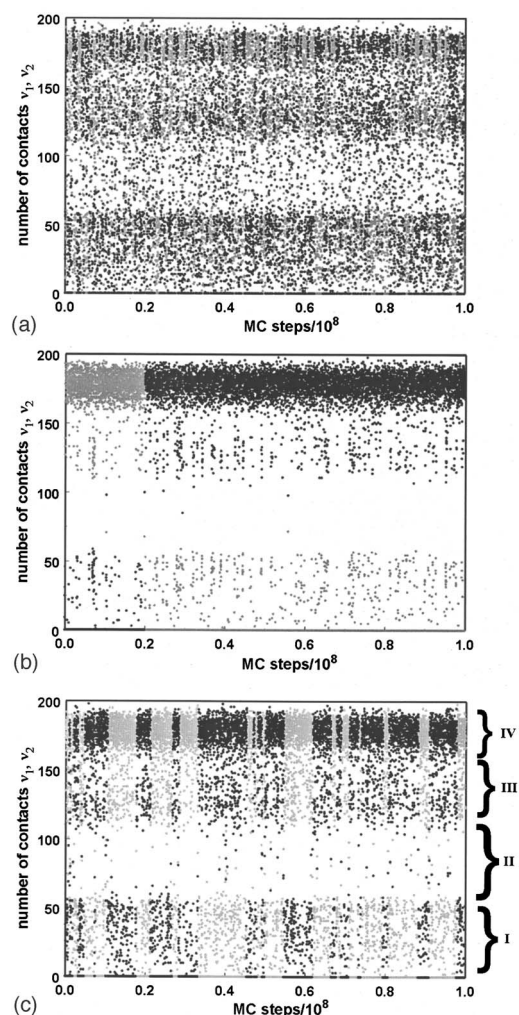


FIG. 8. The flowcharts of the number of contacts between polymer segments and each of the surfaces for the chain with  $N=199$  beads. The colors of the points are gray (for the surface at  $z=0$ ) and black (for the surface at  $z=d+1$ ). The case of the chain with temperature  $T^*=1$  and distances  $d=6$  (a), 8 (b), and 7 (c).

One can also observe that the number of color swaps decreases significantly: at  $d=8$  there is only one swap between the colors in the upper region of the plot while for  $d=7$  there are 17 of such swaps. As the system is warmed up, one-colored areas disappear and at  $T^*=1.67$  the number of chain-surface contacts decreases and its distribution does not exhibit any regularities in time. The plots in Fig. 8 can be explained in the following way. We can suppose that the chain is fully adsorbed on one surface so that all the beads are in contact with one surface. This situation is represented by a point located in the uppermost position of the plot. As the chain beads lose the contact with the surface, the total number of contacts decreases. In case of a strong adsorption, most beads touch one of the two surfaces. Since this situation persists for a relatively long time (in time steps), one observes many points grouped in a form of the intensive colored area at the top of the plot—see, for example, Fig. 8(c) ( $d=7$  and  $T^*=1$ ). After the certain time the colors in the plots change which means that the chain jumped from one surface to another. The swaps between the surfaces were rather fast so the intermediate states, in which the chain beads are located be-

tween the surfaces, are represented by few points only (for a given time step). These points are assembled in three distinguishable regions: two of them are sparsely populated, while the middle one is almost emptied. We can now name the regions [going up along the y axis as follows: I, II, III, and IV, see Fig. 8(c)]. First one should notice that regions I and III have opposite colors, so it means that they represent the beads adsorbed on two different surfaces. The number of contacts suggests that, as for example, one arm of the chain is adsorbed on one surface, while the rest of the chain is adsorbed on the second surface. This state is however not stable, since the number of points in region IV is evidently larger than in region III. It means that the most populated is the state in which the number of contacts approaches the total number of beads (in the case presented in Fig. 8 it was  $N=199$ ) which means that the chain becomes adsorbed to one surface only.

Therefore one can notice that the universal behavior of confined chains which was previously found for the behavior of chain dimension and structure is no longer valid. The distances between the confining surfaces for which fully adsorbed chains (at low and intermediate temperatures, i.e., for  $T^* < 1.25$ ) can swap the walls are actually the same for all chains lengths under consideration:  $5 < d < 9$ . This behavior can be explained by the fact that for strongly adsorbed chains almost all the beads are in contact with one of the surfaces. The translocation of the entire chain from one to the second surface takes place for certain values of the size of the slit only. For narrower slits ( $d < 6$ ) the chain always interacts with both surfaces simultaneously and irrespective its length the translocation from one to the second surface cannot occur. For larger slits ( $d > 8$ ) the chains cannot reach the second surface being fixed on one surface and the probability of the passage to another wall is negligible. This is because the formation of longer bridges between the surfaces is energetically unfavorable. For higher temperatures ( $T^* > 1.25$ ) one can find similar jumps of the chains between the surfaces. The only difference between jumps at low and intermediate temperatures is the higher frequency in the latter case.

Figure 9 presents snapshots of typical star-branched polymer conformations during the jump of the strongly adsorbed chain from one surface to another. One can observe that in the first stage of the swapping the end of one arm is detached from the surface at which the chain was fully adsorbed. Most of such detachments were unsuccessful, i.e., the end of the arms usually went back to the surface at which it was adsorbed. But in some cases the detached fragment of the chain reached the second surface. Then, usually almost the entire arm promptly detached from the first surface and adsorbed on the second one. The process of the swapping was repeated with the second arm starting from the end of the arm. The next stage was the detachment of the branching point from the surface and its translocation to the second surface. Then the entire remaining part of the arm followed the rest of the branching point and thus the entire macromolecule was adsorbed on the new surface. The detachment of the first two arms by their ends is in agreement with our previous findings where the highest frequencies of the contacts between these parts of the arms with the confining sur-

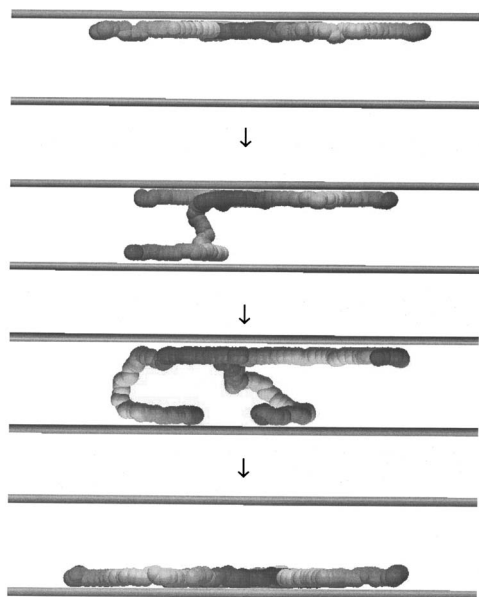


FIG. 9. A sequence of snapshots of the chain during the jumps from one surface to another. The case of the chain with  $N=199$ , distance  $d=7$ , and temperature  $T=1$ .

faces were found.<sup>27</sup> The jumps of the chains at intermediate temperatures were realized in a similar way; the only difference appeared in the mechanism of detachment of the arms. In some cases, an arm detaches not from the very end but in its middle part forming a bubble that reaches the second surface. Then, the end of the arm leaves the first surface and attaches to the second one.

#### IV. CONCLUSIONS

In this paper, we present the results of the calculations carried out for a simple model of the star-branched polymer chains confined by two parallel impenetrable and attractive surfaces. A coarse-grained model of polymer chains was employed using a simple cubic lattice and the united atom (polymer segment) representation. The chains were assumed to be at good solvent conditions and thus, the excluded volume was introduced into the model as the only intrachain interaction. The properties of this model were determined by means of the Monte Carlo simulations using a Metropolis-type algorithm.

It was shown that the introduction of the adsorption potential of the confining surfaces changed the structure of the chains at lower temperatures. This influence was more pronounced for the chains, which were not fully compressed, i.e., for the larger size of the slit. The transition to two-dimensional chain was described and discussed. It was also

shown that even a strongly adsorbed polymer chain can leave the surface on which it was fully adsorbed and attached to the second surface. This process was observed for certain distances between the surfaces only. For the model under consideration the slit of the width of  $5 < d < 9$  (in lattice units or in polymer segments) was required. The mechanism of these jumps of the strongly adsorbed star-branched chain between the both confining surfaces was determined too. It appeared that the first two arms detached starting from their ends while the third one moves in the opposite way. The dynamic description of the translocation process as well as the thermodynamic description of the confined star-branched polymer chains in the adsorbing slit are underway.

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