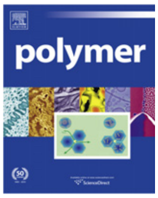
Polymer 51 (2010) 581–586

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Diffusion of polymer chains in porous media. A Monte Carlo study

Andrzej Sikorski*, Piotr Adamczyk

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

ARTICLE INFO

Article history:
Received 11 August 2009
Received in revised form
14 December 2009
Accepted 14 December 2009
Available online 22 December 2009

Keywords:
Branched polymers
Porous media
Monte Carlo method

ABSTRACT

In order to determine the structure and the dynamical properties of branched polymers in a random environment an idealized model was developed and studied by means of the Monte Carlo method. All atomic details were suppressed and the chain was represented as a sequence of identical beads. The model chains were star-branched with three arms of equal length. The chains were embedded to a simple cubic lattice and the polymer systems were confined between two parallel surfaces. The confining surfaces were attractive for polymer segments. A set of irregular obstacles was also introduced into the slit which can be viewed as a model of porous media. A Metropolis sampling algorithm employing local changes of chain conformation was used to sample the conformational space. It was shown that the mean dimensions of the chain depend strongly on the strength of surface's attraction and the concentration of obstacles. It was found that the size of the chains scales with the exponent close to the 2-dimensional case rather than to the 3-dimensional system. The long-time (diffusion) dynamic properties of the system were studied. The differences in the mobility of chains depending on the confinement, on the filling of the slit and on the internal macromolecular architectures were shown and discussed. The possible mechanism of chain's motion was shown: during the migration of the chain in the obstacles dense environment it can be trapped in the region of local lower density of obstacles (a 'cavity') and after some time it can leave the place moving into another cavity.

1. Introduction

The studies of structure and dynamic properties of polymer chains in a random environment like porous media present an interesting and challenging problem and therefore, it was recently a subject of many experimental and theoretical studies [1,2]. The reason is the practical importance of such systems, like polymer behavior in capillary electrophoresis, coating the surfaces, laminates, chromatography, colloidal stabilization etc. [3]. The confined polymer chains were extensively studied by theoretical considerations and by means of computer simulations but we are not going to discuss them in detail here as excellent reviews on this subject were recently published [4,5]. Simple lattice models of linear and non-linear (cyclic, star-branched) polymer chains confined between two impenetrable surfaces were a subject of many computer simulation studies [6]. The universality of the confinement's influence on the size and the structure of polymer chains regardless their internal architecture like linear, star-branched and cyclic chains was found and the mechanism of motion of chains was also discussed [7–9]. The influence of the interactions of macromolecules with the environment on chain's mobility was presented [1]. The introduction of obstacles into the slit containing a polymer chain can be treated as a crude model of macromolecules in porous media [1]. The scaling of parameters describing the chain's size and the density distributions across the slit was determined for such systems [1]. Computer simulations and theoretical considerations concerning macromolecules in a system containing impenetrable obstacles (rods, spheres) in three and two-dimensional space were recently frequently performed [11–26].

In this work we studied the influence of the confinement and the presence of obstacles on the structure and dynamic properties of a single star-branched polymer located in a slit formed by a pair of parallel impenetrable surfaces and filled with rod-like impenetrable obstacles. The introduction of obstacles into a slit should additionally affect the properties of chains and, thus, the results can be compared with previous findings for similar models but without obstacles [6]. For this purpose we used an idealized and coarse grained model of polymer chain on a simple cubic lattice. The lattice approximation was sufficient for this kind of studies because the considered parameters described the entire chain and the width of the slit was considerably larger than the lattice unit. The polymers were modeled at good solvent conditions because the excluded volume was the only polymer–polymer potential

---

* Corresponding author. Tel.: +48 22 822 0211; fax: +48 22 822 5996.
E-mail address: sikorski@chem.uw.edu.pl (A. Sikorski).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.12.018

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 the Monte Carlo simulations with the sampling algorithm of a Verdier–Stockmayer type with local micromodifications of chain conformation.

2. The model and the simulation algorithm

The model chains were constructed as sequences of N identical beads. The positions of polymer beads in space were limited to vertices of a simple cubic lattice. The chains consisted of $f = 3$ linear chains of equal lengths (arms) emanating from the common origin called the branching point. The excluded volume was introduced into the model, and, thus, macromolecules were studied at good solvent conditions. This model, although quite coarse, was found to be sufficient for the study of properties of a chain as a whole [5]. Polymers are put in a slit formed by two parallel and impenetrable surfaces: the first one at $z = 0$ and the second one at $z = d + 1$ (the slit width was d lattice units). Such confinement could mimic the real systems which could be found, for example, in friction phenomena or in biological systems ('macromolecular crowding'). Some rod-like obstacles impenetrable for polymer beads were also introduced into the slit. The obstacles pointed along the z-direction through the entire slit from one surface to another. Their positions were chosen at random and were also restricted to vertices of a simple cubic lattice. The confining surfaces interacted with an ith polymer bead with a simple contact potential in a form of a square-well:

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

where z_i is the z-coordinate of ith segment and $\varepsilon < 0$ is the single bead–wall interaction. The total energy of the chain came from the contacts with both surfaces. In the calculations, we used this potential in k_BT units, $\xi = \varepsilon / k_BT$ with $k_B = 1$ and the inverse of this potential was as usual a measure of the temperature of the system $T^* = |1/\xi| = |k_BT/\varepsilon|$. The scheme of the model system is presented in Fig. 1.

The properties of the polymer systems were determined by means of the computer simulation using a Monte Carlo algorithm based on local changes of chain conformations. The set of these local motions consisted of: 1-bead motion, 2-bead motion, 2-bead crankshaft motion, 1-bead end of chain reorientations, 2-bead end of chain reorientations and branching point collective motions [7]. A polymer bead was picked at random and an attempt of a local motion was performed. Each attempt of a local conformational change was accepted due to geometrical constraints and the Metropolis criterion. All types of elementary moves were employed with the same frequency because it was shown that such a procedure was efficient and provided the correct time scale in the simulation [27]. The time unit consisted of one attempt of each type of local motions per polymer bead on average.

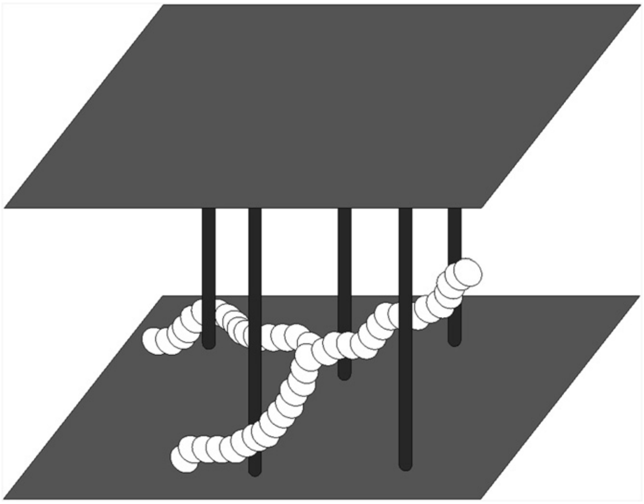


Fig. 1. The scheme of a star-branched polymer chain with $f = 3$ arms confined in a slit formed by a pair of parallel surfaces. The rod-like obstacles were perpendicular to the surfaces, extended from one surface to another and distributed randomly.

Initial configurations of chains were constructed in a process of the simultaneous growing and equilibration in the slit and two different procedures were employed. In the first one the obstacles were introduced before the chain was generated while in the second case obstacles were added into the slit with the polymer chain already set. For each system under consideration 25–30 independent Monte Carlo simulation runs were used. Each run consisted of 10^8–10^9 time units and it started from a different initial configuration of chains and different sets of obstacles. At the start of the each simulation run the equilibration run was performed, which lasted 10^7 time units. The criterion of the equilibration of the system was the stability of some time-mean parameters of the system, such as radius of gyration, energy and the mean-squared displacement.

3. Results and discussion

The simulations were performed for star-branched chains built of $f = 3$ arms of equal length n beads. Thus, the total number of beads was $N = f \cdot (n - 1) + 1$. We have chosen $N = 199$ beads for simulations because properties of this chain length were thoroughly examined [7,8,10]. The size of the slit, *i.e.* the distance between the confining surfaces d was chosen to be 6 (in lattice units). This choice is based on our previous findings where we showed an interesting chain dynamic behavior: strongly adsorbed chains for certain widths of the slit jumped from one surface to another. If the chain consisting of $N = 199$ beads was investigated these jumps were frequent and well defined in the slit with $d = 6$ [10]. The density of obstacles ρ was defined as a fraction of the slit's sites occupied by impenetrable rods, *i.e.*

$$\rho = \frac{m \cdot d \cdot l \cdot l}{L \cdot L \cdot d} = \frac{m}{L^2} \tag{2}$$

where m is the number of obstacles, L is the size of the Monte Carlo box in x and y direction and $l = 1$ is the lattice unit. The density of obstacles was changed between $\rho = 0$ and 0.25, *i.e.* in the range where the sampling algorithm is still efficient. The size of the box L was chosen to be considerably larger than the diameter of the macromolecule: $L = 200$ lattice units. The strength of the attractive interaction changed between 0 (both surfaces were neutral) and -1 k_BT (both surfaces were attractive – a strong adsorption regime). For narrower slits, higher obstacle densities and the lower temperature the simulation algorithm we used became inefficient [10] and, thus, studies concerning static properties of such systems using the PERM algorithm are in preparation.

The size of a star-branched polymer chain is usually described by means of the mean-squared radius of gyration calculated as:

$$\left\langle S^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \left\langle \left(\mathbf{r}_i - \mathbf{r}_{CM} \right)^2 \right\rangle \tag{3}$$

where $\mathbf{r}_i$ is a vector denoting a position of a ith bead and $\mathbf{r}_{CM}$ denotes the position of the chain's center-of-mass position. The second parameter is the mean-squared center-to-end distance:

$$\left\langle R^2 \right\rangle = \left\langle (\mathbf{r}_1 - \mathbf{r}_n)^2 \right\rangle \tag{4}$$

where $\mathbf{r}_1$ is a vector denoting the position of the branching point and $\mathbf{r}_n$ is the position of the vector denoting the last (nth) bead in the arm. Fig. 2a presents the mean-squared radius of gyration $<S^2>$ and the reduced mean-squared center-to-end distance of the chain $<R^2>^*$ as a function of the temperature T^* for the system without obstacles and with the obstacles. Instead of values of $<R^2>$ we used the parameter $<R^2>^* = 7/18\ <R^2>$ in order to make both parameters comparable – for an ideal (no-excluded volume) star-branched chain $<S^2>/<R^2> = (f/6)(3 \cdot f - 2)/f^2$, what for $f = 3$ arms gives 7/18. One can observe in Fig. 2a that the annealing of the chain led to the continuous increase of the chains' size what is explained by the fact that the polymer tended to maximalize the number of its contacts with the confining surfaces. This in turn makes the chain almost a two-dimensional structure for the strong adsorption regime [10]. There are no essential differences in the influence of the temperature on the size of chain with and without obstacles although the latter is considerably smaller. The z-contribution to both size parameters as a function of the temperature presented in Fig. 2b behaves in a different way. A maximum value of $<S^2>$ and $<R^2>^*$ appears for the temperature near 1.5. The introduction of obstacles into the system shifts this maximum towards lower temperature. This non-monotonic behavior of the polymer size perpendicular to the confining surfaces can be explained in the following way. The initial annealing of the system leads to the increase of polymer–surface contacts with both surfaces and thus, the chain forms bridges between the surfaces. The further annealing (the increase of the strength of the adsorption) causes that fragments of chains that form bridges become also adsorbed.

The long-time dynamic properties of macromolecules are usually expressed as the self-diffusion coefficient. As the motion along the z-axis is highly suppressed we studied this coefficient along the xy plane only. The diffusion coefficient D_{xy} was calculated as:

$$D_{xy} = g_{cm}(t)/4t \tag{5a}$$

where t is time. $g_{cm}(t)$ is the center-of-mass autocorrelation function:

$$g_{cm}(t) = \left\langle [r_{cm}(t) - r_{cm}(0)]^2 \right\rangle \tag{5b}$$

where $\boldsymbol{r}_{cm}$ stands for the center-of-mass vector. The diffusion coefficient was determined for longer displacements where g_{cm} scaled as t^1 [10]. In Fig. 3 the diffusion coefficient D_{xy} was plotted against the temperature for the same systems as discussed above. The weak adsorption regime is clearly visible here for temperatures $T^* > 1.67$, where the mobility of chains is rather constant. For lower temperature the differences in dynamics of the macromolecule without and with obstacles arises. The further annealing of the system without obstacles led to the unexpected and significant increase of the diffusion coefficient. This behavior can be explained by the fact that a fully adsorbed two-dimensional chain moves via different mechanism of motion. The motion of weakly adsorbed chains is hindered due to the Metropolis criterion: the fraction of accepted moves decreases when the attractive energy is introduced. On the other hand, strongly adsorbed chains can move along the plane next to the adsorbing surface almost without energetic losses. This is possible because of the model and algorithm used (lattice approximation, Verdier–Stockmayer set of local moves) and, therefore, should be confirmed by other calculations. For the chain with obstacles the diffusion constant becomes almost constant at low temperatures. This can be explained by the fact that obstacles have major impact on the chain motion and the influence of the attractive surface becomes less important.

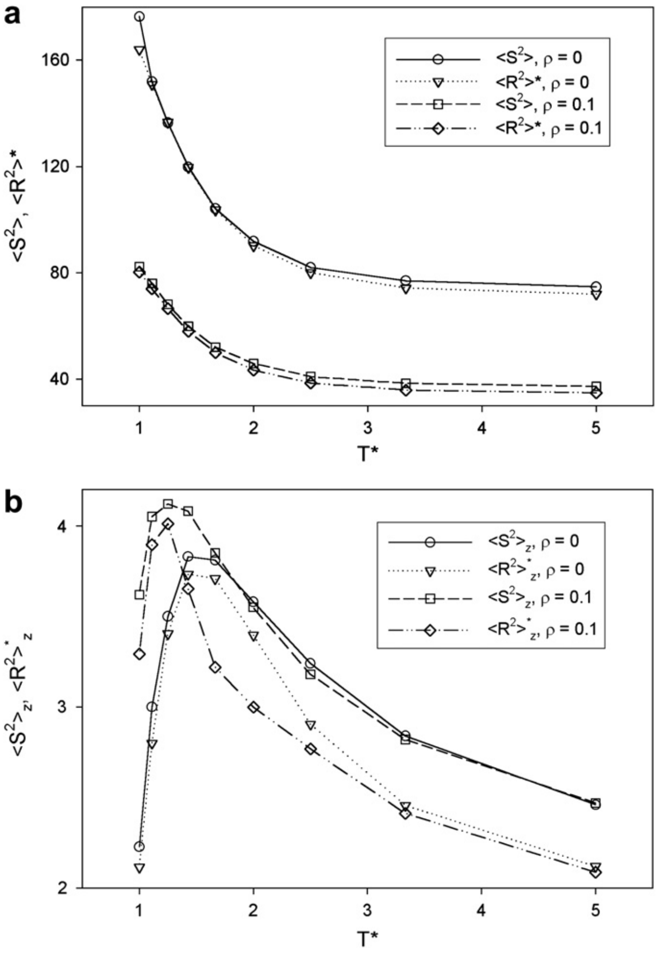


Fig. 2. The mean-squared radius of gyration $<S^2>$ and the reduced mean-squared center-to-end distance $<R^2>^*$ as a function of the temperature T^* (a). The z-contribution to $<R^2>^*_z$ as a function of T^* (b). The densities of obstacles are given in the inset.

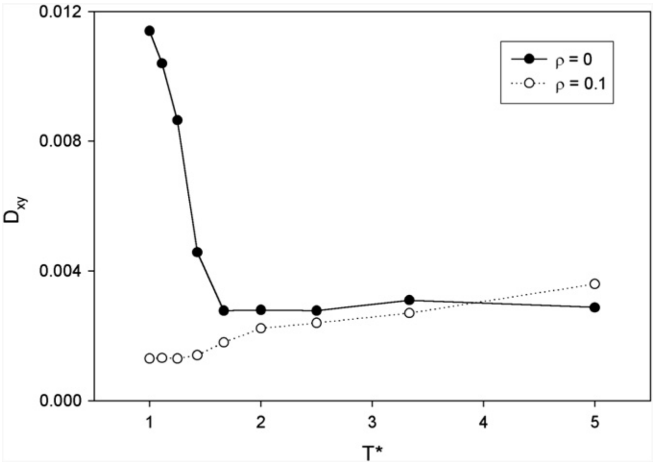


Fig. 3. The self-diffusion coefficient D_{xy} as a function of the temperature T^*. The densities of obstacles are given in the inset. The values of D_{xy} for $\rho = 0.1$ are multiplied by the factor 10^3.

In Fig. 4a we present the size parameters $<S^2>$ and $<R^2>^*$ as functions of the obstacles density ρ for two temperatures: $T^* = 1$ (strong adsorption regime) and $T^* = 2$ (the crossover from the weak to the strong adsorption regime [8]). One can observe that the size of a strongly adsorbed chain is larger as its expansion goes in two dimensions (along the surface) only. The increase of the obstacle density led to the decrease of the chain's size which is considerably more rapid for strongly adsorbed chains. For higher density of obstacles $\rho \geq 0.2$ the changes of chains dimensions become less pronounced and the differences between both adsorption regimes are smaller. This implies that in this region the density of obstacles replaces the temperature as the main factor governing the chain's size. Similar behavior was found for the unconfined polymer chain with obstacles [15]. The contribution to $<S^2>$ and $<R^2>^*$ in the direction perpendicular to the surface vs. the obstacle density is presented in Fig. 4b. The size of the chain along the z-axis increases slightly with the increase of the obstacle density if the temperature is higher ($T^* = 2$). For the chain at lower temperature ($T^* = 1$) its $<S^2>_z$ and $<R^2>^*_z$ behave in the opposite way and decrease significantly. The larger difference between $<S^2>_z$ and $<R^2>^*_z$ for the higher temperature is caused by the higher mobility of chain ends (tails) in the latter case. Fig. 5 presents the dependency of the diffusion coefficient on the density of obstacles for temperatures $T^* = 1$ and 2. The mobility of chains in both cases rapidly decreases. This behavior is qualitatively the same as for chains in slit built of neutral impenetrable surfaces although the mobility is considerably higher in the latter case [10]. The diffusion coefficient for chains at temperature $T^* = 2$ became higher that than for $T^* = 1$ after adding even a small amount (1%) of obstacles into the system.

The introduction of obstacles into a slit excluded some parts of the space for the polymer segments since the obstacles were distributed at random and some small 'cavities' could have been formed. In Fig. 6 we present a map describing the normalized number of visitations of the polymer segments in all lattice points in the slit as projected on the xy plane. The shades of gray corresponded to a number of segment visitations at the given point of the lattice. The presented case corresponds to intermediate obstacle densities ($\rho = 0.1$). In contrast, in the case of the system without obstacles one can observe well established areas in which the chain was present for a considerably longer period of time. These areas called 'cavities' were actually almost lonely islands separated from one another by the area of relatively high obstacle density [6]. The regions with intermediate density of obstacles

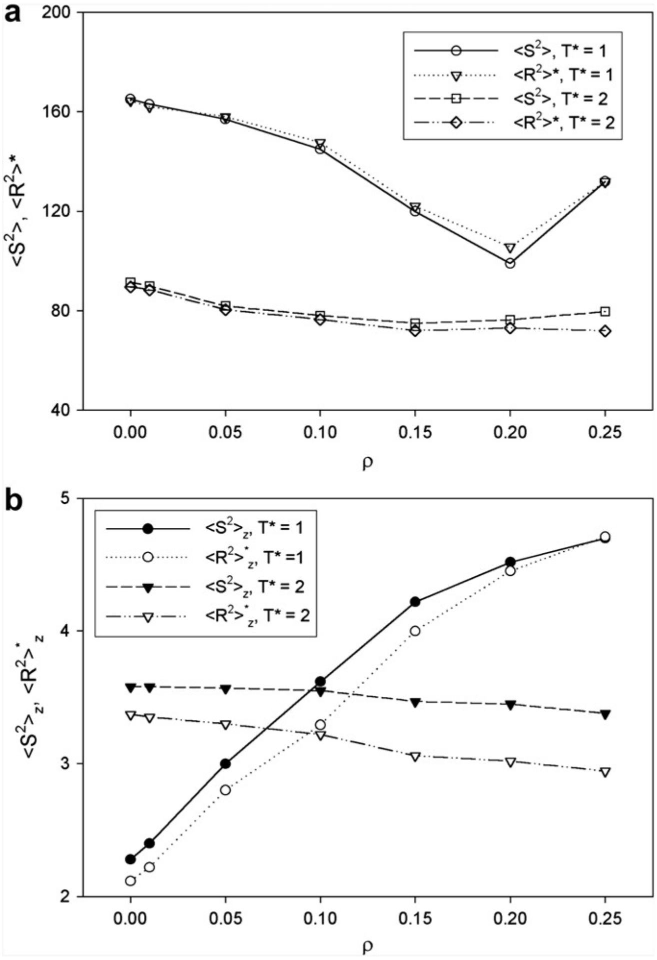


Fig. 4. The mean-squared radius of gyration $<S^2>$ and the reduced mean-squared center-to-end distance $<R^2>^*$ as a function of the density of obstacles ρ (a). The z-contribution to $<R^2>^*_z$ as a function of ρ (b). The temperatures are given in the inset.

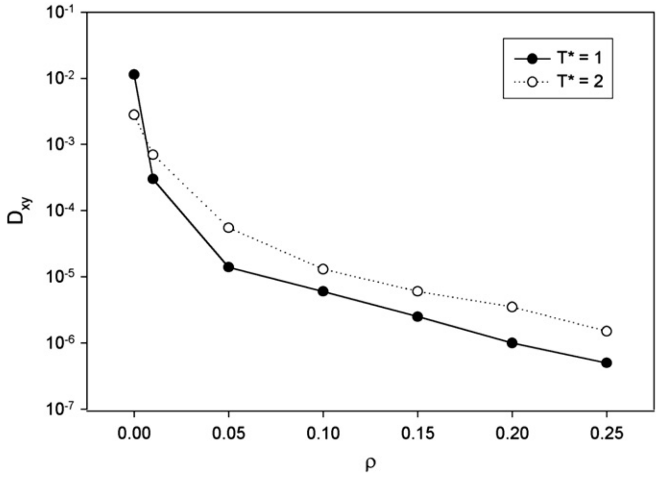


Fig. 5. The self-diffusion coefficient D_{xy} as a function of the density of obstacles ρ. The temperatures are given in the inset.

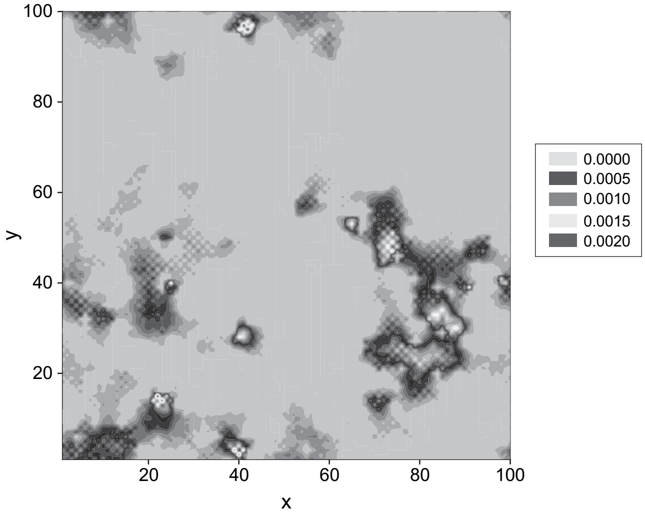


Fig. 6. The map showing the trail of polymer motion in the slit. The case the density of obstacles $\rho = 0.1$ and the temperature $T^* = 2$. See text for details.

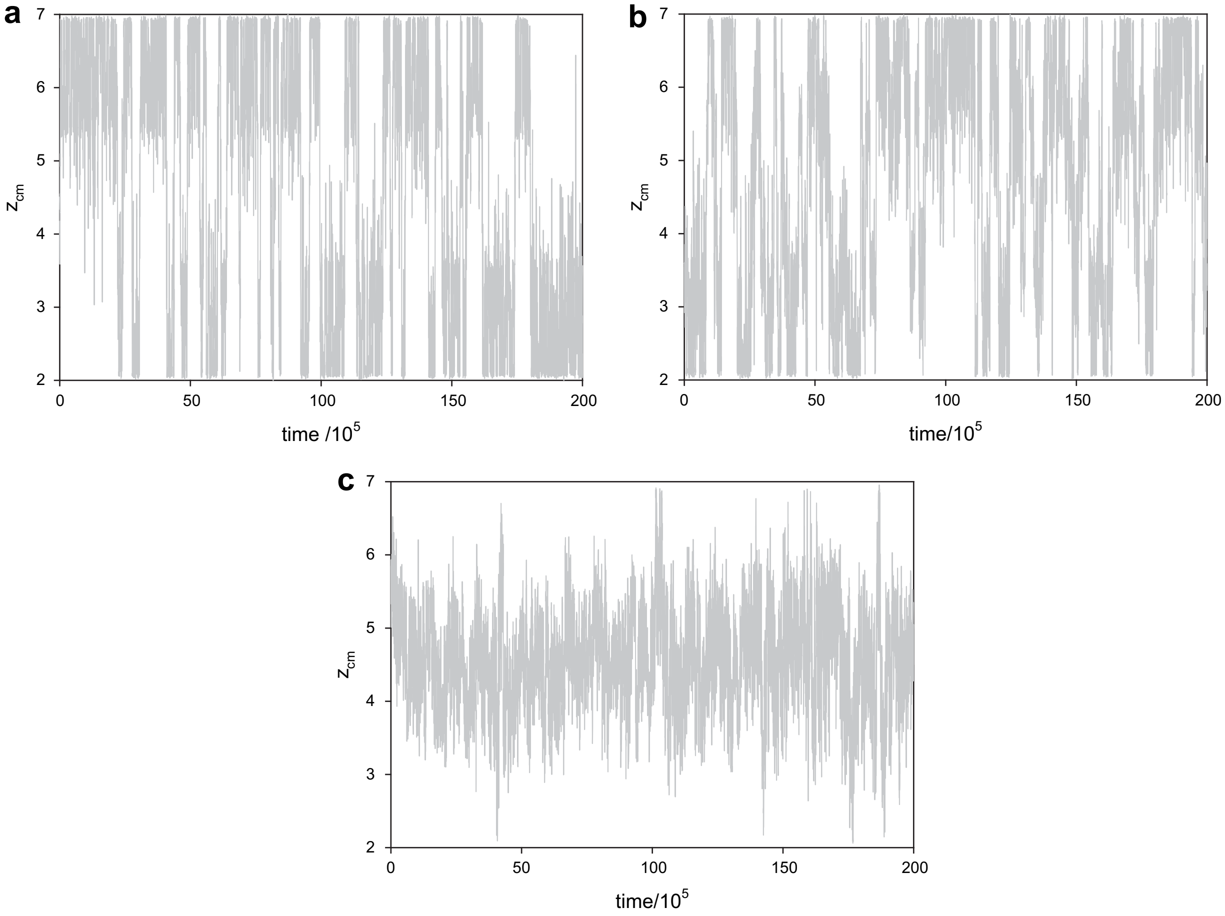


Fig. 7. Flow-chart of chain center-of-mass position across the slit z_{cm} for the density of obstacles $\rho = 0$ (a), $\rho = 0.1$ (b) and $\rho = 0.25$ (c). The case of the temperature $T^* = 1.25$.

played the role of the channels that the polymer chains used in order to move from one ‘cavity’ to another one.

The recent simulation results concerning star-branched chains in the adsorbing slit showed that at low temperatures strongly adsorbed chains were usually located at one of the confining surfaces only [10]. After a certain time the chain jumped to another surface. A jump started by the detaching of one arm end and subsequently the entire arm. Then, the second arm is being transported in the same manner. The third arm moves in a different mode because it starts from the branching point and then the remaining parts are transferred. In general, within the frame of the present model the jumps of star-branched chains can be performed for slits $5 \leq d \leq 8$ and at temperatures $T^* \leq 1.25$ [10]. In Fig. 7a–c we present the flow-charts of the z-coordinate of chain's center-of-mass taken from the simulation trajectories. One can see that the introduction of the small number of obstacles ($\rho < 0.15$) decreased the frequency of jumps but not significantly. For the system with a high density of obstacles (see Fig. 7c for $\rho = 0.25$) one can observe quite a different behavior. The chains are not adsorbed to one surface only and their center-of-mass is usually located near the middle of the slit. The adsorbing energy is still low (-155 kT what is ca. 15% higher than -175 kT for the system without obstacles) because the chain's structure is different for the system with a higher density of obstacles: the chain is now adsorbed simultaneously at both surfaces; one arm at one surface and the other two arms on the second surface. The flow-chart of the center-of-mass presented in this case is similar for those for high temperatures or a wide slit [10].

4. Conclusions

In this work we studied properties of star-branched polymer chains in porous media by means of Monte Carlo simulations. Chains were built without atomic details as sequences of identical segments which positions were restricted to vertices of a simple cubic lattice. The chains were put into a slit formed by two parallel impenetrable walls. The confining surfaces were attractive for polymer segments and impenetrable obstacles were randomly distributed in the slit. It was found that the size of the chain was controlled by the temperature for low obstacle densities only. The chains in the environment of obstacles frequently occupied the areas in which the local concentration of obstacles was relatively low (‘cavities’) and after a certain period of time it moved to another place through the path in which the density of obstacles was also low. The mean dimensions of the chains depended strongly on the concentration of obstacles and it diminished with the obstacle density.

The mobility of chains decreased strongly with the number of obstacles but at low temperatures it increased because of a different mechanism of motion. It was also shown that the introduction of the attractive potential of the confining surfaces changed significantly the structure of chains in the slit at lower temperatures. An adsorbed polymer can detach from a surface on which it is adsorbed and jump to another surface and this process was observed at lower temperatures and for considerably narrow slits only. The introduction of the larger amount of obstacles suppressed this mechanism of motion.

Acknowledgment

The computational part of this work was done using the computer cluster at the Computing Center of the Department of Chemistry, University of Warsaw.

References

[1] Baumgärtner A, Muthukumar M. Adv Chem Phys 1996;94:625.
[2] Ediger M. Annu Rev Phys Chem 2000;51:99.
[3] Eisenriegler E. Polymers near surfaces. Singapore: World Scientific; 1993.
[4] Teraoka I. Prog Polym Sci 1996;21:89.
[5] Binder K, Milchev A. J Comput Aided Mater Des 2002;9:33.
[6] Sikorski A. Solid State Phenom 2008;138:451.
[7] Sikorski A, Romiszowski P. J Chem Phys 2002;116:1731.
[8] Sikorski A, Romiszowski P. J Chem Phys 2004;120:7206.
[9] Romiszowski P, Sikorski A. Comput Mater Sci 2008;43:127.
[10] Sikorski A, Romiszowski P. J Chem Phys 2005;123:104905.
[11] Yethiraj A, Hall CK. J Chem Phys 1989;91:4827.
[12] Martinez-Haya B, Gordillo MC. Macromol Theory Simul 2005;14:421.
[13] Nixon GI, Wu SY. Phys Rev Lett 1995;75:164.
[14] Yamakov V, Stauffer D, Milchev A, Foo GM, Pandey RB. Phys Rev Lett 1997; 79:2356.
[15] Yamakov V, Milchev A. Phys Rev E 1997;55:1704.
[16] Nixon GI, Slater WG. Phys Rev E 1999;60:3170.
[17] Saville PM, Sevick EM. Macromolecules 1999;32:902.
[18] Chern SH, Coalson RD. J Chem Phys 1999;111:1778.
[19] Dua A, Cherayil BJ. J Chem Phys 2000;112:421.
[20] Nixon GI, Slater WG. J Chem Phys 2002;117:4042.
[21] Bhattacharya A. J Phys Condens Matter 2004;16:5203.
[22] Moreno AJ, Kob W. J Chem Phys 2004;212:380.
[23] Randall GC, Doyle PS. Macromolecules 2006;39:7734.
[24] Chang R, Yethiraj A. Phys Rev Lett 2006;96:107802.
[25] Hickey OA, Slater WG. Phys Lett A 2007;364:448.
[26] Balducci A, Doyle PS. Macromolecules 2008;41:5485.
[27] Kolinski A, Skolnick J, Yaris R. J Chem Phys 1987;86:7164.