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Monte Carlo simulation of block copolymer brushes

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Abstract

We studied a simplified model of a polymer brush formed by linear chains, which were restricted to a simple cubic lattice. The chain macromolecules consisted of a sequence of two kinds of segment, arranged in a specific sequence. The chains were grafted to an impenetrable surface, i.e. they were terminally attached to the surface at one end. The number of chains was varied from low to high grafting density. The model system was studied under different solvent quality, from good to poor solvent. The properties of this model system were studied by means of Monte Carlo simulations. The sampling algorithm was based on local changes of the chain's conformations.

1. Introduction

The properties of heteropolymers and polypeptides in the bulk and at interfaces have recently been the subject of experimental and theoretical efforts. Such systems are of great interest because of the importance of their industrial and biomedical applications, such as lubrication, adhesion and stabilization of colloids [1, 2]. Polymer brushes have also been the subjects of experiments, and the experimental techniques of synthesizing and studying such systems have recently been reviewed [3]. Polymer brushes consisting of grafted linear chains have also been extensively studied theoretically by means of computer simulations [4]. A series of theoretical works on grafted block copolymers has been presented by the group of Balazs [5–7]. Investigations of the off-lattice model of amphiphilic chains on surfaces and amphiphilic monolayer chains on nanorough surfaces have also been performed by means of computer simulations [8, 9]. Simplified lattice models of brushes formed from polypeptide chains have been studied by means of Monte Carlo simulations [10–12].

In this paper we present the dynamic properties of polymer brushes built of block copolymers. These polymer chains at interfaces were represented by a reduced lattice model consisting of a chain of statistical segments. We built a model of a brush consisting of linear chains embedded to a simple cubic lattice and grafted to an impenetrable surface. The model chains were constructed of two types of monomer immersed in selective solvents. The solvent–monomer interactions were different for both kinds of monomer. The properties of the model system were determined by means of Monte Carlo simulations with a sampling algorithm of a Verdier–Stockmayer type.

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2. Model and simulation algorithm

The polymer brush was formed by a certain number of linear chains that were terminally attached (grafted) onto an impenetrable surface. In our simulations we attached the chains to a square surface of a size 100×100 lattice units with periodic boundary conditions; therefore, we could treat the model as infinite. A pair of non-bonded segments interacted via a contact potential which was defined as follows:

$$V_{ij} = \begin{cases} \infty & \text{for } d < l \\ \varepsilon & \text{for } d = l \\ 0 & \text{for } d > l \end{cases} \tag{1}$$

where d is a distance between a pair of residues, and l is the length of a lattice unit.

The model chains were built of segments of two kinds (A and B). We assumed that all interaction parameters present in the system were equal to zero except the attractive interactions between the monomers of the poorly soluble fragment of the chain (hereafter denoted as A). Thus we could assume that $\varepsilon_{AA}/k = -1$, where $k = 1$ is the Boltzmann constant, and the solvent quality was characterized by the reduced temperature T. Each macromolecule consisted of a total number of N segments, of which half were A type and half were B type, arranged in block sequences along the chain length. We simulated chains of two different sequences: with $N/2$ A-type segments attached to the surface and $N/2$ B-type segments on the top part of the chain. In the second case the chains consisted of reversed sequences (with B-type segments attached to the surface). Model polymers were built on a simple cubic lattice, i.e. the positions of polymer segments were restricted to vectors of the type $[\pm 1, 0, 0]$. Interactions between polymer segments and solvent molecules were assumed arbitrarily according to the properties of the segments. The double occupancy of lattice sites by polymer segments was forbidden, which meant that the excluded volume was effective in the model.

During the simulation the grafted end remained at the surface, although it could slide along it. In our simulations the number of grafted chains varied, which enabled us to study the effect of the density on some properties of the system. The polymer brush formed by the grafted chains was put into the Monte Carlo (MC) box. A surface was placed at the plane $z = 0$. In order to avoid the finite-size effect, periodic boundary conditions were imposed in the x and y directions; in the z direction the MC box was 100 lattice units long. The polymer brush was then simulated by the Monte Carlo method in order to obtain the mean properties of the system. The algorithm used was based on the classical asymmetric Metropolis scheme, where all chains underwent a series of random local changes of conformations. We used a set of conformation micromodifications which was constructed for linear chain models on a simple cubic lattice: 2-bond move, 3-bond move, 3-bond crankshaft move, and 1-bond and 2-bond end reorientations [12]. One attempt of every micromodification per polymer segment was defined as a time unit. A new conformation of a chain was accepted according to a criterion provided by the Metropolis sampling algorithm which worked as follows. The total energy of the system was calculated as the sum of all long-range (non-bonded) interactions in the system. During the evolution in the simulation run the number of A–A contacts changed as the micromodifications of the chains were performed. The acceptance of each micromodification was possible, if the following three circumstances were present: (1) chain connectivity was maintained, (2) the excluded volume effect was satisfied, (3) the Metropolis sampling algorithm enabled the change of the conformation with the probability

$$P_{\text{old}\Rightarrow\text{new}} = \min[1, \exp(-\Delta E/kT)] \tag{2}$$

where ΔE is the difference between the energy of the new and the old conformations.

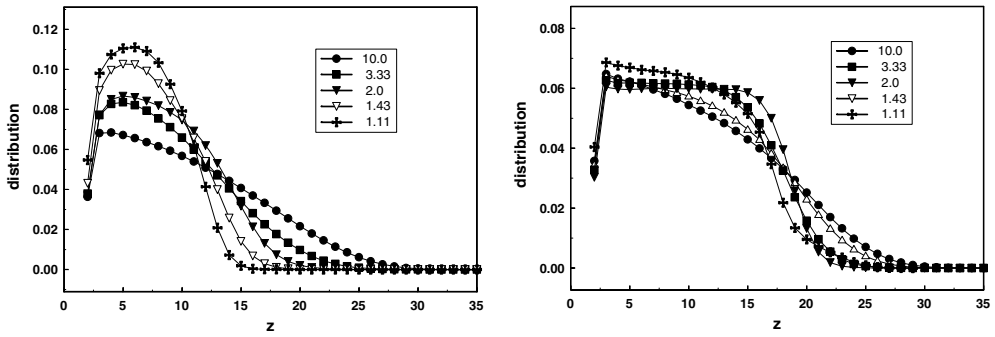

Figure 1. Distribution of segments in stems for AB (left) and BA (right) architectures for grafting density $\sigma = 0.125$. The values of temperature are given in the insets.

The Monte Carlo simulation runs consisted of 10^6–10^7 time units and were performed 20 times, starting from quite different conformations, in order to preserve the proper sampling of the conformational space. The initial configuration of a brush was prepared in the following way. M points were selected at random on the grafting surface. Then, self-avoiding (non-intersecting) random walks originating from these points were constructed. The construction of the walks was continued until the length of each chain reached the required N segments. During the entire procedure of chain propagation the system was equilibrated, i.e. it underwent a series of local micromodifications. After the system was built, the simulation run started. The annealing of the brush took place and the system was equilibrated before the data for each temperature point were collected. During the simulation runs, the trajectory of the system containing the coordinates of all segments was recorded for further analysis.

3. Results and discussion

The total number of segments in one chain was $N = 100$. We investigated the structure of the brush layers formed for different grafting density, various temperatures and different architectures. The simulations were carried out for two cases: in the first the chains were attached to the surface with the block consisting of B type (athermal); in the second case the chains were attached with an A-type block to the surface. For further investigations we treated the polymer chain as being composed of two parts of equal length: the 'stem', which was grafted to the surface and the second, upper part of the chain, called a 'branch' hereafter. For each case we simulated the system at a certain temperature, which varied the interactions of A-type segments from good to poor solvent conditions. The grafting density σ was calculated as the number of chains per lattice site of the grafting surface. This parameter was changed between 0.0125 and 0.25. The simulation parameters (temperature, densities) were in the range which located the system below the coexistence curve [13].

In order to characterize the structure of the brush we calculated the distribution of the polymer segments (a volume fraction) along the direction perpendicular to the grafting surface. The distributions were given for stems and for branches separately at the grafting density $\sigma = 0.125$. The distributions of segments in stems are shown in figure 1 for the cases AB and BA respectively. The corresponding distributions of segments in branches for the same systems are presented in figure 2. One can see that in the AB case the distribution of stems depends strongly on the temperature. At temperatures below $T = 2$ the layer formed by stems is dense in the vicinity of the wall (for z up to 10) whilst for the higher temperature one observes

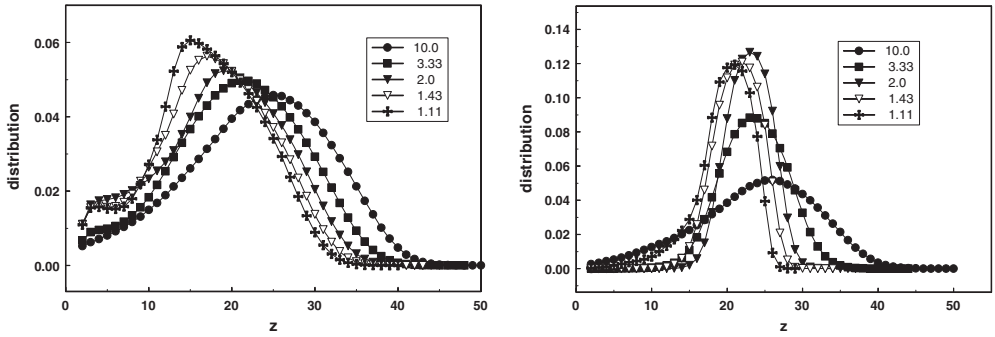

Figure 2. Distribution segments in branches for AB (left) and BA (right) architectures for grafting density $\sigma = 0.125$. The values of temperature are given in insets.

a long tail. The corresponding distribution of the density of branches remained quasi-Gaussian, with the maximum moving towards the wall as the systems is cooled. This effect shows that the branches follow the contracting (at low temperatures) layer of stems and fill the adjacent region with B-type segments. For the BA architecture case the segment distributions are quite different from the latter case. The distribution of segments in stems remained almost constant with the changes of temperature, whilst the distribution of segments in branches was almost pure Gaussian, with the distribution narrowing as the system was cooled. The plots show us that, in the case of BA architecture, the structure of stems did not change as the system was cooled; the branches formed a well-defined layer whose depth depended on the temperature of the system.

In order to characterize the surface of the brush we determined the roughness parameter R_a, which was calculated as the mean deviation of the surface z_i coordinate from its mean value $\langle z_i \rangle$, which can be written as

$$R_a = \langle |z_i - \langle z_i \rangle| \rangle, \tag{3}$$

where averaging was made over all segments that formed the outer surface of the brush. The outer surface was defined as a set of maximum values of the z-coordinate occupied by polymer beads for a given (x, y) point on the grafting surface. This parameter is commonly used in the description of the quality of surfaces. Figure 3 presents the values of the roughness parameter for different architectures as a function of the temperature. One can observe that for the case of AB architecture the surface of the brush remains almost constant at different temperatures; however, some decrease of the roughness apparently induced by the collapse of the stems is observed. This effect corresponds well with the distribution shown in figure 2, where the distribution of density of branches was broad over the whole range of temperature. For the case of BA architecture the roughness of the brush decreases significantly with the decrease of temperature. This shows that we observed the effect of the collapse of the chains forming the branches of the brush. The increase of the number of energetic contacts in the branch consisting of A-type segments contracted the outer surface of branches, and thus the roughness decreased at low temperatures.

The dependence of the roughness parameter on the grafting density σ is shown in figure 4. The plot was done for the two architectures over a wide range of grafting density. One sees that the roughness parameter for small grafting density (a mushroom regime) is similar in all cases. One can observe that the increase of the number of chains in the system gives the reduction of the roughness of the surface. This effect is especially intense in the case of a BA architecture in which the most distant segments collapsed and formed a relatively smooth surface at high

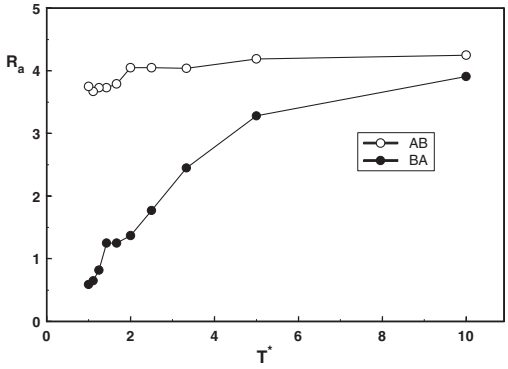

Figure 3. Plot of the roughness parameter of the brush as a function of temperature for grafting density $\sigma = 0.125$.

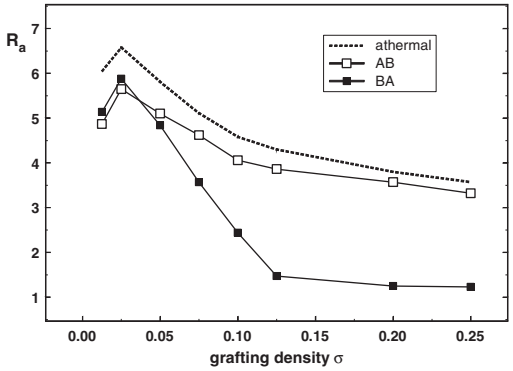

Figure 4. Plot of the roughness parameter of the brush as a function of the grafting density for AB and BA architectures at temperature $T = 2$. The values for an athermal brush are also given for the comparison.

grafting density (a brush regime). The AB architecture behaves similarly to the athermal system. Thus, we can conclude that the smoothing of the surface along with the increase of the grafting density is caused by both a local crowding effect and the interactions between the monomers. The overlap grafting density can be found from the greatest slope region of the R_a versus σ curves. In this case the overlap density can be estimated as $\sigma = 0.08 \pm 0.02$.

4. Conclusions

In this work we analysed the structure of two different types of polymer brushes immersed in a solvent. The chains were constructed as the block copolymers of type $AAA \ldots BBB$ or $BBB \ldots AAA$ grafted to the surface. The spatial distribution along the z-axis of segments in the brush depended on the temperature of the system. The A-type stems formed a dense layer close to the surface during the cooling of the system, while for B-type stems the temperature almost did not change the distribution of segments, which caused the position of the A-type brushes to be unaffected by the temperature changes. The results show that the roughness of the system depends mainly on the grafting density of the system; however, the influence of the temperature is noticeable in the case of brushes formed of the branches that interact with the solvent.

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