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Properties of branched polymer chains adsorbed on a patterned surface

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The aim of this study was to investigate the properties of polymer chains strongly adsorbed on a planar surface. Model macromolecules were constructed of identical segments, the positions of which were restricted to nodes of a simple cubic lattice. The chains were in good solvent conditions, thus, the excluded volume was the only interaction between the polymer segments. The polymer model chain interacted via a simple contact potential with an impenetrable flat surface with two kinds of points: attractive and repulsive (the latter being arranged into narrow strips). The properties of the macromolecular system were determined by means of Monte Carlo simulations with a sampling algorithm based on the local conformational changes of the chain. The structure of adsorbed chains was found to be strongly dependent on the distance between the repulsive strips, whenever this distance was very short. The mobility of the chains was also studied and it was found that diffusion across repulsive strips was suppressed for large distances between the strips.

1. Introduction

Systems containing adsorbed polymer chains have recently become the subject of many experimental and theoretical works, owing to their practical importance, e.g. lubrication, colloidal stabilization, chromatography etc. [1]. Adsorption of macromolecules is also interesting from a theoretical point of view, as the presence of the attractive surface changes the properties of the adsorbed chain, compared with a non-adsorbed chain in solution. Most of the theoretical works were devoted to adsorbed linear polymer chains, while mean field theories are most commonly applied to describe adsorbed macromolecules [2–5]. Several dynamic properties of adsorbed linear polymer chains were determined by Binder et al. from off-lattice Monte Carlo simulations [6–8]. Studies of DNA molecules adsorbed on a lipid bilayer, performed by means of fluorescence microscopy showed that the diffusion coefficient scales with the length of the molecule (number of base pairs) as N^{-1}, which corresponds to the scaling for a two-dimensional chain model [9]. On the other hand, Granick et al. found much stronger scaling, namely $N^{-3/2}$ for adsorbed polyethylene glycol [10,11].

The properties of branched polymer chains differ from the properties of their linear counterparts and this effect is particularly visible at interfaces [12]. The simplest model of a non-linear macromolecule is a regular star-branched polymer consisting of three equal length branches originating from a common point – the branching point. These star-branched polymer chains can be synthesized, their properties can be studied experimentally, and they are particularly useful for theoretical considerations [12,13]. Recently, Kosmas showed that the differences in adsorption of star-branched polymers with several arms, and of linear polymers, are almost negligible: for stars with a small number of arms, the adsorption is slightly (6%) higher than for linear chains [14]. As the number of arms increases, so does the degree of adsorption of the polymer chain due to compactness of star polymers, as compared to linear ones. Scaling analysis of adsorbed star-branched polymers was performed by Ohno and Binder [15,16]. They showed that the density profile exponents depend on the number of arms. It was also found that in the case of strong attraction, the chain becomes almost two-dimensional. The distribution of polymer segments near the adsorbing surface, as well as its dependence on the strength of adsorption were studied; the competition between this interaction and the intra-chain attraction was investigated; and certain dynamic properties of such polymers were also determined. Coarse-grained models of adsorbed star-branched polymer chains on homogenous planar surfaces have recently been developed and studied by means of Monte Carlo simulations [17–19]. The size and structure of adsorbed star-branched polymer chains, as compared to linear polymers, were studied and the simulations revealed that the degree of adsorption was similar for star-branched and linear chains, and was ca. 40% larger for ring polymers. The above-mentioned model was also extended by introducing a second

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adsorbing surface, which served to confine the chains in the slit [20]. The structure of star-branched chains in confinement was determined and discussed there. At low temperatures and for sufficiently narrow slits, the chains were fully adsorbed on one surface, but it was found that they could jump from one surface to another [20]. Star copolymers were also studied employing a mean field theory [21,22].

The development of nanotechnology enables one to design systems consisted of a surface with adsorbed polymers. Macromolecules adsorbed on patterned surfaces found numerous applications as antireflectors, biosensors, or in microelectronic etc. The influence of nanopatterns on the conformation and other properties of polymer chains are also of theoretical interest. Recently, the adsorption of polymer and protein chains on patterned surfaces has also become the subject of studies. Such systems were studied experimentally [23–29], theoretically [30–33] and by means of computer simulation [34–44]. Homopolymers, copolymers, copolymer blends, polyelectrolytes and polymer brushes constituted the objects of these studies. The process of adsorption on the patterned surface can be considered as consisted of two-stages: binding and rearrangement. Both these processes are well known but the dynamics of the chains in such conditions are still not described and understood. Star-branched polymers on patterned surfaces are scarcely investigated and they seemed to be an interesting object of computational studies. Moreover, the structure and certain dynamic properties of these macromolecules can be compared with the findings for homogenous attractive surfaces reported in Refs. [17,18].

In this work we examine regular star-branched homopolymers adsorbed on a strip-patterned surface. The model macromolecules were adsorbed on a patterned surface containing attractive and repulsive points, arranged into strips. The chains consisted of $f = 3$ arms (branches) and were embedded in a simple cubic lattice. The model chains were studied in good solvent conditions – the excluded volume was the only intra-chain potential and no attractive polymer segment nor polymer segment interactions were introduced. This choice was made in order to avoid competition between adsorption and chain collapse, which is the subject of forthcoming studies. The Monte Carlo algorithm used employed local micromodifications of chains of a Verdier-Stockmayer type [45,46]. The paper is organized as follows: *The model and the calculation method* outlines the assumptions of the model and the details of the simulation technique. *Results and discussion* presents the results concerning mostly the size and structure of chains, as well as their long-time dynamic properties. *Conclusions* section contains the most important concluding remarks.

1.1. The model and the calculation method

The star-branched chains under consideration consisted of $f = 3$ linear chains of equal length (‘arms’). These arms were built of sequences of identical segments originating from the branching point. Each polymer segment can be treated as a united atom representing several monomers of a real polymer. In order to make the calculations more efficient, the spatial positions of polymer segments were restricted to the vertices of a simple cubic lattice. The exclusion of the double occupancy of the same lattice site by polymer segments was introduced into the model, which was equivalent to the effect of the excluded volume in the system. This resembled good solvent conditions, where the excluded volume was not compensated by the attraction between non-bonded polymer segments. The simulations were carried out for single chains, i.e. for the case of an infinitely dilute polymer solution.

A single chain of a given length was located near the planar surface, parallel to the *xy* plane and set at $z = 0$. The surface was impenetrable to polymer segments and a simple square-well contact potential V was assumed between it and the polymer segment:

$$V(x_i, z_i = 1) = \begin{cases} \varepsilon_r & \text{for} \quad \mathrm{mod}(x_i, d_v) = 0 \\ \varepsilon_a & \text{for} \quad \mathrm{mod}(x_i, d_v) \neq 0 \end{cases} \tag{1}$$

where x_i and z_i are the coordinates of the ith polymer bead along the x and z axes, respectively. The interaction takes place when a polymer bead is located in the layer adjacent to the surface ($z = 1$). ε_a is the value of the attractive contact potential, while ε_r is the repulsive contact potential. The repulsive points on the surface are arranged in strips and d_v is the distance between the strips parallel to the y-axis. The strips are infinitely long and the width of each strip is one lattice unit. This kind of surface patterning is rather common in real experiments, where the surface is covered periodically by polar (silicon oxide, ethylene oxide) and non-polar (alkylsilan, polystyrene) compounds [23–29]. This periodic patterning of the substrate can be a factor governing the self-assembly of polymers and proteins. The schematic of a polymer chain at the adsorbing surface with the repulsive strips is shown in Fig. 1a. Periodic boundary conditions were imposed along the x and y directions only. The length L of the Monte Carlo box was chosen large enough to void the influence of its size on the results, i.e. the chain did not interacted with itself.

The Monte Carlo simulations of the model system were carried out using a sampling algorithm in which the conformation of the chain was locally changed by the following set of micromodifications [46]: (a) 2-segment motion, (b) 2-segment end reorientations, (c) 3-segment motion, (d) 3-segment crankshaft motion, and (e) the collective motion of the branching point. All these local moves involving one or two polymer beads are schematically presented on Fig. 1b. A fragment of the chain to be modified was selected at random during the simulation, while one average attempt of every micromodification per one polymer segment defined the time unit. It was shown that the choice of this set of local motions can reproduce the dynamics of real macromolecules, i.e. the Rouse-like behavior. The use of equal frequency of all motions is justified by the efficiency of the algorithm [45,47]. The conformation of a new chain was accepted according to chain connectivity and the excluded volume, with the probability proportional to its Boltzmann factor, as found from the Metropolis scheme with respect to changes of the adsorption energy of the system:

$$P_{\mathrm{old}\to\mathrm{new}} = \min[1, \exp(-\Delta E_a/kT)] \tag{2}$$

where $P_{\mathrm{old}\to\mathrm{new}}$ is the probability of the transition from the old to the new configuration, ΔE_a is the energy difference between the old and the new conformation, k is the Boltzmann constant and T is the temperature. Each simulation run consisted of 10^9–10^{10} time units and was preceded by an equilibration run, which consisted of 10^7–10^8 time units. This procedure was repeated 10–15 times, starting from different conformations of the chain. The use of the dynamic Monte Carlo method and of the lattice model can be justified by the fact that simulations of atomistic models with Brownian/Molecular Dynamics on such a large time scale are still beyond current computing capabilities. Since we studied the structure of entire chains and the dynamic behavior for time scales considerably longer than those on which conformational changes take place, the method is quite reliable.

2. Results and discussion

Most of the simulations were carried out for star-branched chains consisting of $n = 67$ segments in any arm, which implies