MONTE CARLO SIMULATION OF ADSORPTION OF DI-BLOCK COPOLYMERS

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Introduction

In this paper we are concerned with the morphology of the polymers adsorbed on surfaces, in particular di-block copolymers. Our work is motivated by the experimental findings of Hadziioannou et al. [1] on the steric forces between two adsorbed layers of di-block poly(vinyl-2-pyridine)/polystyrene (PV2P/PS) copolymer on mica surfaces. The PV2P block binds strongly on the mica surfaces and the PS block extends into the solvent toluene (good solvent for PS). Hadziiouannou et al. found that the repulsive forces between the two surfaces start at a distance D larger than 10 times the radius of gyration R_G of a free PS in toluene. Furthermore, the starting distance D increases with increasing degree of polymerization N of PS in a fashion $D \sim N^a$ with a close to 1. We study the adsorption of di-block copolymer with Monte Carlo simulations. The Monte Carlo simulations are especially powerful in dealing with kinetics which is important in systems where hysteresis is observed [1] and cannot be appropriately taken into account by analytical (or numerical) calculations based on equilibrium assumptions.

Model

We consider a cubic lattice in which there are M copolymer chains, each of which has N_2 anchoring segments and N_1 non-sticking segments (or monomers). Volume exclusion is taken into account by allowing no more than one monomer to occupy one lattice site. In general, we consider the monomer-monomer interaction up to the next-nearest-neighbor distance. The nearest-neighbor interaction E_1 and the next-nearest-neighbor interaction E_2 can be positive, zero, or negative, depending on solvent conditions. For instance, $E_1 = E_2 = 0$ represents an athermal polymer solution, which is the case we study in the present paper. Besides monomer-monomer interactions, a monomer also interacts with walls on the top and bottom of the lattice. When a monomer is right next to the wall, it gains energy E_b, where E_b can be either positive or negative. In the present study, E_{b1} is positive and E_{b2} is negative, 1 indicates a non-sticking polymer and 2 indicates an anchor polymer. We use the periodic boundary conditions in the xy directions.

In the simulations, the polymers are generated according to energy parameters using the Monte Carlo method, which means that whether or not a new monomer is added to a chain at a certain site in the process of polymerization is determined by the Boltzmann factor $e^{-\Delta E/T}$, where ΔE is the energy cost of the process and T is the absolute temperature. During the process of polymerization, as well as during other processes we will describe, the interaction between two adjacent monomers along a chain is not counted since they are chemically bonded to each other. When $E_1 = E_2 = 0$, the polymers we generated would be equivalent to self-avoiding random walks.

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We allow three types of movements of the polymer chains. The first type is the Brownian motion, i.e., the polymer chains can move as a whole in a random fashion, illustrated in Fig. 1a. The second type is that of polymer wiggling; specifically, a monomer in a chain can flip, as illustrated in Fig. 1b. The third type is reptation, in which either end of a chain moves randomly to an adjacent unoccupied site and drags the rest of the chain along a "tube" that is shaped by its body, as illustrated in Fig. 1c. Reptation is especially important when the density is so high that the first two types of motion cannot effectively move the polymers. As the polymeric density increases, the motion of a polymer chain should be modified by the presence of other polymers and by itself (that is, the motion of one part of a polymer chain can be hindered by another part of the chain). The hindrance of motion is governed by the Boltzmann factor $e^{-\Delta E'/T}$, where $\Delta E'$ is the energy change due to the motion. Again, this process is simulated using the Monte Carlo method.

In order to compare with Ref. 1, we simulate polymers in a good solvent. For simplicity, we choose $E_1 = E_2 = 0$ for both the non-sticking polymers and the anchor polymers. The anchor polymers are of the strongly affinitive type whose $E_{b2} = -5T$, which means the adsorbed anchor polymers lay flat on the walls. For the non-sticking polymers, the walls are repulsive, i.e., $E_{b1} = 1T$. In the following, we fix the length of the anchor polymers, i.e., $N_2 = 10$ and change the length of the non-sticking polymers, i.e., N_1. For different values of N_1, we adjust the size of the simulation cell so that each dimension of the cell is more than 10 times the radius of gyration of the non-sticking polymers. For example, for $N_1 = 55$, the simulation cell is 42x42x60. The number of chains M in each run can be up to several hundred depending on the concentration.

Results and Discussion

Because of the strong affinitive nature of the anchor polymers, the walls prefer to be covered as much as possible by anchor polymers. At low initial segment density (defined as the average occupancy of a lattice site), the added di-block copolymers will all adsorb on the walls. As the initial segment density is increased, full surface coverage is reached quickly with shorter chains while the adsorption of longer chains begins to be limited by kinetics where surface coverage denoted as α is defined as the fraction of the surface sites that are occupied. To illustrate, we show the adsorption amount Γ, which is defined as the total number of segments of the adsorbed polymers, i.e., segments that are connected to the wall, per site, as a function of time for different chain lengths in Figs. 2-3. For $N_1 = 30$, 55% surface coverage is reached at about 6,000 Monte Carlo steps, as shown in Fig. 2. For longer chains ($N_1 = 45$), 45,000 Monte Carlo steps when we stop the simulation (see Fig. 3) the surface coverage is only about 52%. In the special case of di-block copolymers with non-sticking blocks and strongly affinitive anchors, the adsorption amount Γ is proportional to surface coverage α and can be expressed as $\Gamma = \alpha(N_1 + N_2)/N_2$. However, in general Γ is related to α but not necessarily proportional to α; for example, in the homopolymer case, one can have the same surface coverage but higher adsorption amount at higher bulk densities where the number of chains on the surface is higher but the fraction of a chain that is on the surface is smaller. The slow adsorption of long chains is the manifestation of the slow kinetics typical of long chains. Thus, the slow adsorption we observed is also indicative of the hysteresis behavior in the mechanical properties observed in experiments [1].

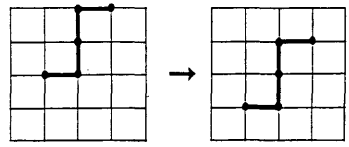

Fig. 1a. A polymer can diffuse as a whole (Brownian motion).

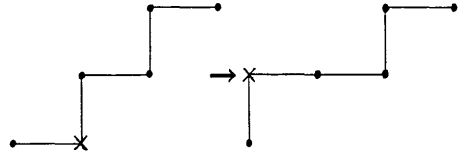

Fig. 1b. A monomer can wiggle within a chain (segment flipping).

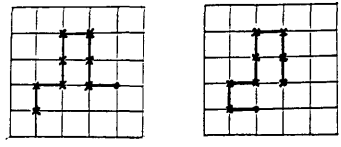

Fig. 1c. Reptation

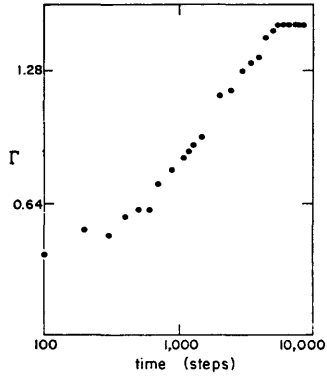

Fig. 2. The adsorption amount Γ vs. time for $N_I = 30$.

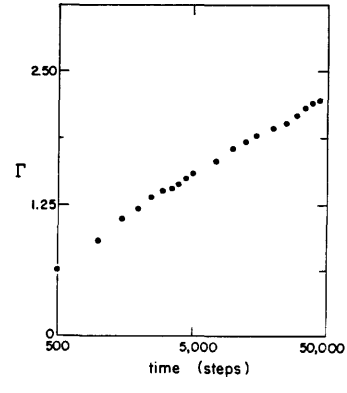

Fig. 3. The adsorption amount Γ vs. time for $N_I = 45$.

Typical adsorption segment density profiles of both di-block copolymers and homopolymers are shown in Figs. 4 and 5. Figure 4 shows that the segment density of the adsorbed homopolymers decreases monotonically away from the surface and reaches the bulk value at a distance about 2 to 3 times the radius of gyration, R_G (for $N=45$, $R_G=3.9$). A more detailed study of the adsorption of homopolymers will be published elsewhere. The segment density profiles of the di-block copolymers adsorbed on the wall of various N_1 values are shown in Fig. 5. Since the anchor polymers are strongly affinitive, the segment density at $z=1$ is mainly due to the anchor polymers. At $z \geq 2$, the segment density is attributed to the non-sticking polymers. The depletion of segments at $z=2$ is due to the repulsive interaction of the non-sticking polymers with the surfaces, i.e., $E_{b1}=1T$. The width of the depletion layer is roughly the radius of gyration R_{G_1} of the non-sticking polymers. This is why the width of the depletion layer increases with increasing values of N_1. Also note that for $N_1=10$, the surfaces are completely covered with anchor polymers, hence the depletion of segments at $z=1$ does not occur in this case. Overall, one can see that the adsorbed di-block copolymers have a more uniform density profile than the homopolymers. Furthermore, the adsorbed di-block copolymers can extend out much farther (about 5 R_{G_1}) than the homopolymers. Note that the extension of an adsorbed di-block-copolymer layer is already very large at low surface coverage ($N_1=45$ in Fig. 5 is an example) which is very different from that of an adsorbed homopolymer layer which is small at low surface coverage. The difference lies in that all the segments of a homopolymer are affinitive to the walls and therefore would prefer to lie on the walls when the surface coverage is low, resulting in very small layer thickness, whereas the non-adsorbing segments of a di-block copolymer do not stick.

In Fig. 6, we show the extension of the adsorbed di-block copolymer layers at high surface coverage with respect to N_1. In principle, the comparison should be made at the same surface coverage, since the layer thickness which may be characterized by the root-mean-square thickness H_1 or the outmost distance of the layer from the wall surface H_m increases with the increasing adsorption even though slowly. For $N_1 \leq 20$, we can have the wall surfaces completely covered with anchor polymers, namely, 100% surface coverage in a short time (4000 steps for $N_1=10$). With increasing chain length, the adsorption kinetics are slower, as we have discussed above, and it is difficult to achieve complete surface coverage. However, for the longer chains the adsorbed layer can extend to a distance ≥ 5 R_{G_1} even at about 55% surface coverage; for instance, for $N_1=45$ ($R_{G_1}=3.9$), $H_m=19$ and for $N_1=55$ ($R_{G_1}=4.2$), $H_m=24$. We plot H_m, H_1 of the adsorbed layers as a function of N_1 in Fig. 6. For $N_1=10$, the values of H_m and H_1 are taken at about complete surface coverage, for $N_1=20$ at about 76% coverage and for $N_1 \geq 30$ at about 55% coverage. The radius of gyration R_{G_1} of free polymers of equivalent length is also plotted for comparison in Fig. 6. It can be readily seen that the values of H_m are larger than 5 R_{G_1} (of free polymers in the solution) as we have discussed above. This agrees very well with Ref. 1 that the onset distance of repulsion between two layers is about 2 H_m, which is larger than 10 R_{G_1}.

Notice that in Fig. 6, H_m first increases with N_1 with power 0.6 for $N_1 \leq 30$ and with power 1.0 for larger N_1. The power 0.6 is in good agreement with the Flory's exponent [2] (see the exponent of R_{G_1} vs. N_1 in Fig. 6) and indicates that the non-sticking polymer behaves as in the bulk. The reason for a larger power at larger N_1 is that squeezing in the lateral direction occurs when N_1 is substantially larger than N_2 and the lateral squeezing forces the polymers to extend out in the normal direction. To clarify this point further, we compare the

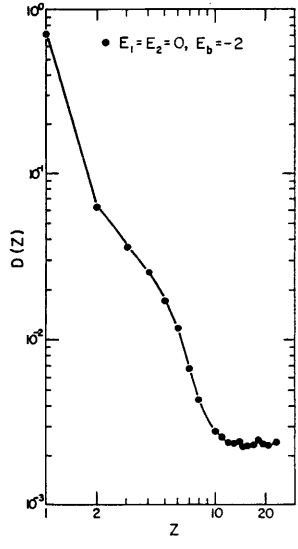

Fig. 4. The adsorption density profile of homopolymers of N = 45.

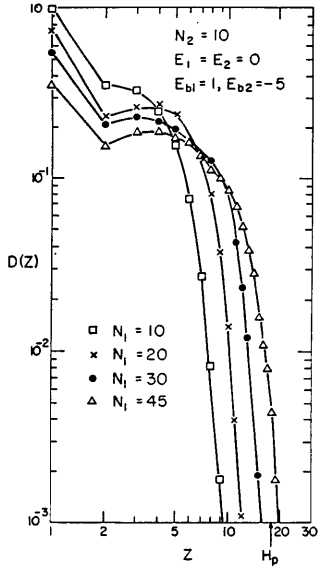

Fig. 5. The density profiles of adsorbed di-block copolymers.

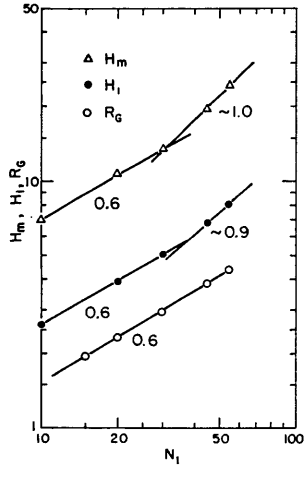

Fig. 6. The root-mean-square thickness H_1, the outmost distance of the adsorbed layer H_m, the radius of gyration R_G (of free polymers) vs. N_1.

projection of the radius of gyration of the non-sticking polymers on the surface (the *xy* plane), $R_{G_{1,xy}}$ to the radius of gyration of the anchor polymers R_{G_2} on the surface.

(a) If $R_{G_{1,xy}} \leq R_{G_2}/\sqrt{\alpha}$, the non-sticking polymers are hardly squeezed and should retain their free-polymer-like conformation. In this regime, H_1 and H_m should scale with N_1 with power 0.6.

(b) When $R_{G_{1,xy}} > R_{G_2}/\sqrt{\alpha}$, the non-sticking polymers are then squeezed in the lateral direction and hence would extend out in the perpendicular direction. H_1 and H_m in this case would scale with N_1 with a power close to 1 as predicted by the scaling theory of Alexander and de Gennes [3]. For all our cases, $R_{G_2} = 1.75$ while $R_{G_{1,xy}} = 1.19$ for $N_1 = 10$ at $\alpha = 100\%$; $R_{G_{1,xy}} = 1.75$ for $N_1 = 20$ at $\alpha = 76\%$; and for $\alpha \approx 55\%$, $R_{G_{1,xy}} = 2.24$ for $N_1 = 30$; $R_{G_{1,xy}} = 2.9$ for $N_1 = 45$; and $R_{G_{1,xy}} = 3.13$ for $N_1 = 55$. One can see that for small N_1, it falls into category (a) and for large N_1, it falls into category (b). The crossover occurs at about $N_1 = 30$ where $R_{G_{1,xy}} \cong R_{G_2}/\sqrt{\alpha}$. The behavior of $H_m \sim N_1^{1.0}$ at large N_1 is in agreement with Ref. 1.

Conclusions

We have simulated the adsorption behavior of di-block copolymers in a good solvent with the Monte Carlo method. We have shown that the segment density profiles of the adsorbed di-block copolymers are more uniform and the adsorbed di-block copolymer layers can extend much farther (at $H_m \geq 5R_{G_1}$), as compared to those of adsorbed homopolymers. We have also shown that at high surface coverage, H_m increases with increasing N_1; for small N_1, $H_m \sim N_1^{0.6}$ while for large N_1, $H_m \sim N_1^{1.0}$. The crossover occurs at $N_1 = 30$ for the cases we studied, i.e., $N_2 = 10$. The large N_1 behavior agrees with the experiment in Ref. 1. In addition, we have also shown that the adsorption of longer chains is very slow, which is the manifestation of the slow kinetics typical of long chains and is indicative of the hysteresis observed in the mechanical properties.

Acknowledgments

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