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Monte Carlo Simulations of Random Copolymers near Solid Surfaces

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ABSTRACT: Monte Carlo simulations have been performed to examine the equilibrium structure of single chains of random AB copolymers confined between two solid surfaces. Monomers of type A are attracted to the surfaces with a strength ϵ, while monomers of type B are repelled from the surface with the same strength. The copolymer chains are not permanently attached to the surfaces, so they can undergo transitions from adsorbed states, localized near one of the two solid surfaces, to desorbed states, delocalized in the central region between the surfaces. For chains that are strongly adsorbed, the disparity between the surface affinities of A and B segments leads to microphase segregation, with narrow A-rich regions directly adjacent to the surfaces and wider B-rich regions farther away from the surfaces. As a function of the segment–surface interaction energy and the copolymer composition, we calculate monomer density profiles and order parameters which characterize the adsorption–desorption transition and the extent of microphase ordering in the adsorbed states. The simulation results are in excellent qualitative agreement with recent theoretical calculations for confined random copolymers. Our model system may also be considered as a crude representation of polyampholyte chains subject to strongly screened electrostatic interactions with a charged surface. The Monte Carlo simulations indicate, in accord with theoretical predictions and experimental findings, that a polyampholyte can adsorb to a charged surface even when the polymer chain and the surface carry net charges of the same sign.

1. Introduction

Interest in the behavior of random copolymers at surfaces originates from several sources, including the use of random copolymers as adhesion promoters at polymer interfaces. The addition of random AB copolymers to the interface between immiscible A and B homopolymers, for example, can improve adhesion between the two polymer phases.[1–3] Improved adhesion can also be achieved through the addition of diblock copolymers[4–6] or graft copolymers,[7] but random copolymers can be synthesized more readily and thus offer an advantage over other chain architectures in commercial applications. It has also been suggested on the basis of theoretical considerations that random copolymers may be used as adhesion promoters at interfaces between polymers and other nonpolymeric solid materials like metals and ceramics.[8]

Tailoring the composition of a random copolymer for optimal adhesive properties in a specific material system will require detailed knowledge of the interfacial structure. In the case of random AB copolymers at an A/B polymer–polymer interface, the random copolymers adsorb to a penetrable surface, since segments of the copolymer can reside in the homopolymer phases. Metal or ceramic surfaces, in contrast, are impenetrable to random copolymers. The adsorption of AB random copolymers at penetrable surfaces has been studied in recent years through analytical theory,[9] computer simulations,[10] and neutron reflection experiments.[11] Several theoretical studies of random copolymer adsorption at impenetrable, solid surfaces have also been reported; these have included analytical treatments[9,12] and computer simulations.[13–15]

Gutman and Chakraborty[8] have recently developed a new theoretical description of random copolymers confined between solid surfaces. Averages over all possible monomer sequences are calculated using the replica method of spin glass theory,[16] and nonlocal couplings in the free energy functional are decoupled by introducing a set of random fields. When one copolymer constituent is attracted to the surfaces while the other is repelled, an adsorption–desorption transition is predicted to occur as a function of the fraction of attracted monomers and the strength of their interaction. When adsorption occurs, it induces microphase ordering of the copolymer segments into A-rich and B-rich regions. This microphase segregation is expected to have a strong influence on the thermodynamic work of adhesion and the energy dissipated during adhesive failure.

Random copolymers with both attractive and repulsive segment–surface interactions can also be viewed as models of polyampholytes interacting with charged surfaces. Joanny[17] has recently analyzed the adsorption of polyampholytes onto charged solid surfaces in the limits of strong and weak screening of electrostatic interactions. In accord with recent experiments,[18] the theoretical analysis in ref 17 predicts that polyampholyte chains can adsorb onto a charged surface even when the polymer chain and the surface carry net charges of the same sign. The short-ranged segment–suface interactions used in the present study can model the limit of strong electrostatic screening, so we can interpret our Monte Carlo simulations in the context of polyampholyte adsorption in the presence of high salt concentrations.[17]

In this report, we present results from Monte Carlo simulations of confined random copolymers; the simulations are designed to complement the theoretical calculations of Gutman and Chakraborty[8] and of Joanny.[17] To this end, we focus on aspects of random copolymer adsorption that have not been extensively studied in previous computer simulations,[13–15] specifically the transition between adsorbed and desorbed states and the significant microphase ordering in AB random copolymers near solid surfaces. Although we cannot make direct quantitative comparisons (for reasons to be

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discussed below), there is excellent qualitative agreement between the simulations reported here and the theoretical predictions.[8,17]

2. Computational Method

The computer simulations reported here have examined the interactions of random copolymers with solid surfaces. Each simulation has been conducted with a single AB random copolymer of N repeat units confined between two surfaces, so the simulations represent the adsorption of random copolymers from very dilute solution. The distance separating the two surfaces, H, is large enough so that the single copolymer chain cannot simultaneously interact with both surfaces; the central region of the confined space should therefore contain chain configurations that are representative of those in free solution.

Lattice Model. In this simulation study, we employ a one-site fluctuating bond model[19] to represent the configurations of the random copolymer chains. This coarse-grained lattice model, which is described in detail in ref 19, was derived from the original bond fluctuation models of Carmesin and Kremer[20] and Deutsch and Binder.[21] In the model that is used here, each of the N repeat units of the random copolymer is represented by a segment or "bead" which occupies one site on a cubic lattice. Two solid surfaces are introduced at lattice layers $z = 0$ and $z = H + 1$ so that the polymer segments are confined to the region $1 \leq z \leq H$. Periodic boundary conditions are applied in the x and y directions. The size of the simulation box is $L \times L \times H$, with $L = 100$ and $H = 50$. The length L is much larger than the end-to-end distance of the random copolymer chains, so there are no interactions between periodic images of the chains.

Chain configurations evolve during the course of the Monte Carlo simulation by attempting random displacements of single beads to nearest-neighbor sites on the cubic lattice. These attempted moves change the lengths of the bonds within the chain; chain connectivity is maintained by restricting the bond lengths to the values of 1, $2^{1/2}$, and $3^{1/2}$. Excluded volume interactions are enforced by allowing at most one bead at each lattice site. Appropriate energetic acceptance criteria (described below) are applied to attempted moves which bring beads into or out of the lattice layers that are directly adjacent to the surfaces.

If no further restrictions on the Monte Carlo moves are applied, the simulation rules just described will allow chains to pass through each other.[19] Polymer chains simulated under these conditions were referred to as "crossing" chains in ref 19; they possess a phantom topology and behave dynamically as Rouse chains for all chain lengths and densities. With proper restrictions on the Monte Carlo moves, however, the physically correct "noncrossing" topology can be preserved. Noncrossing chains at melt densities show all characteristic signs of topological constraints, including the crossover from unentangled to entangled (Rouse-like to reptation-like) chain dynamics with increasing chain length.[19,22] In the simulations reported here, we have deliberately chosen to use the phantom chain topology, since we are interested here only in *static*, *structural* quantities at equilibrium. The simulations in ref 19 demonstrate that the chain crossing condition has only insignificant effects on static, structural properties. This perhaps surprising result can be understood by emphasizing that the phantom topology still preserves excluded volume interactions and chain connectivity; these two conditions govern the structural characteristics of polymer chains. The choice of crossing versus noncrossing chains for simulations of static, structural properties can therefore be made simply on the basis of computational efficiency. Isolated crossing chains have relaxation times that are lower by a factor of about 2 than those for noncrossing chains of the same length. Equilibration and data collection for isolated crossing chains can therefore be achieved in about one-half of the time required for noncrossing chains. An additional benefit is present for simulations that involve adsorption. Earlier simulations of the *dynamics* of random copolymer adsorption[23] employed an eight-site bond fluctuation model that forbids chain crossings.[21] In that previous work, we observed long-lived nonequilibrium chain configurations that were the direct result of the noncrossing chain topology and the restrictions imposed by the lattice model.[23] In the present study, we have avoided this complication by using the one-site bond fluctuation model with the phantom, crossing chain topology.

Monomer Sequences. The chemical composition of a random copolymer is specified by a sequence of labels, A and B, which denote the chemical identity of each repeat unit. The chemical constitution of a given copolymer is generated simply by assigning a label of A or B to each bead with probability f_A that label A is chosen (and probability $1 - f_A$ that label B is chosen). Since the assignment of each bead's label is statistically independent of the labels given to all other beads, the labeling procedure generates "ideal" random copolymers with no compositional correlations along the chain. Using the nomenclature of Fredrickson and Milner,[24] the parameter λ, quantifying the nature and strength of compositional correlations, has a value of zero.

We will refer to f_A as the fraction of type A segments, although in an individual copolymer of N repeat units the number of type A segments may differ from f_AN; the number of type A segments is only f_AN when averaged over the entire sequence distribution. At a fixed value of N and f_A, structural quantities obtained from simulations must reflect averages with respect to the distribution of compositional sequences. To obtain the proper averages, we have performed a large number of separate simulations with different realizations of the random copolymer composition (for each value of N, f_A, and the strength of the segment–surface interactions, ϵ). The profiles of segment density and order parameter that will be reported below are arithmetic averages of the profiles of 250 individual simulations.

Surface Interactions. In our simulations and in the theoretical calculations of Gutman and Chakraborty[8] and Joanny,[17] the labels A and B serve only to differentiate the polymer segments with respect to their interactions with the solid surfaces. Apart from the interactions of the polymer segments with the surfaces and a hard-core excluded volume interaction, there are no other enthalpic interactions in our model system. As a result, there is no incompatibility between type A and type B segments in the bulk phase or in solution. (The interesting phase behavior of random copolymers[24,25] and polyampholytes[26,27] in bulk phases or solutions would not be captured under these conditions.) We have made this simplification so that any microphase segregation of A and B segments will be driven exclusively by the following disparity in the surface affinities of the two segments: Segments of type A are attracted to the solid surfaces, with an adsorption energy per segment given by $-\epsilon$. In contrast, segments of type B are repelled from the surfaces, with an adsorption energy of $+\epsilon$. We have conducted simulations for values of $\epsilon/k_BT = 1$, 2, and 4.

Monte Carlo Procedure. The chain configurations evolve through the following Monte Carlo process: One bead is chosen at random, and an attempt is made to displace this bead to one of the six nearest-neighbor sites on the lattice. If the attempted move violates the excluded volume condition or the restrictions on bond lengths, then the move is rejected. Attempted moves that satisfy the excluded volume condition and bond length restrictions are accepted with probability $p = \exp(-\Delta E/k_BT)$, where ΔE is the change in energy that accompanies the attempted move. We take the range of the surface interactions to be limited to one lattice layer, so $\Delta E = 0$ for any attempted moves that do not involve entering or leaving lattice layers $z = 1$ or $z = H$. Attempted moves of type A segments that correspond to desorption (moves from $z = 1$ to $z = 2$ or from $z = H$ to $z = H - 1$) are subject to an activation energy equal to the strength of the attractive interaction, so $\Delta E = \epsilon$. Since segments of type B are repelled from the surface due to an unfavorable adsorption energy ϵ, attempted moves of type B segments that correspond to *adsorption* (moves from $z = 2$ to $z = 1$ or from $z = H - 1$ to $z = H$) are subject to an activation barrier with $\Delta E = \epsilon$.

Below we present results for the density profiles of type A and type B segments and an order parameter which quantifies the degree of microphase segregation induced by the solid surfaces. Those quantities are obtained as follows: A single polymer chain is grown as a self-avoiding random walk, starting from a lattice site chosen at random between the two solid surfaces. The random A/B monomer sequence is then assigned as discussed above. An equilibration period then begins, in which the Monte Carlo simulation is executed for a number of time steps equal to 50 times the longest relaxation time of the polymer chain. Following the equilibration period, the simulation continues for at least 100 relaxation times, and data for the profiles of segment density and order parameter are accumulated. During this period of data accumulation, the copolymer chains are able to sample many representative configurations. The data reported for fixed values of N, f_A, and ϵ reflect averages over 250 separate realizations of the random copolymer composition (monomer sequences).

3. Results and Discussion

To begin characterizing the adsorption–desorption transition, we present in Figure 1 the total segment density profiles, $\rho(z)$, for AB random copolymers confined between two solid surfaces. (Note that $\rho(z)$ contains contributions from both A and B segments.) The curves in Figure 1 correspond to chains of length $N = 50$ at three different values of f_A, the average fraction of type A segments. In this figure, the segment–surface interactions have a magnitude given by $\epsilon/k_BT = 2$; recall that segments of type A are attracted to the surface with this strength while segments of type B are repelled from the surface with the same strength. The distance separating the surfaces, H, is 50 lattice units.

An adsorption–desorption transition is apparent from the segment density profiles plotted in Figure 1. For random copolymers with a low A content ($f_A = 0.10$), the polymer–solid interactions are predominantly repulsive, and the polymer chains are almost entirely excluded from the surfaces. The depletion of segment density in this case extends over a length scale of roughly 10 lattice units, several times the magnitude of the radius of gyration of the isolated random copolymers. It is well known that the depletion is caused by the reduction in entropy associated with confining chain molecules near surfaces.[28,29] The random copolymers adsorb readily, in contrast, when the chains contain a large fraction of type A segments. For $f_A = 0.50$, the monomer density is greatly increased near the solid surfaces, and the region of enhanced segment density extends over a length scale that is comparable to the depletion region that is observed when $f_A = 0.10$.

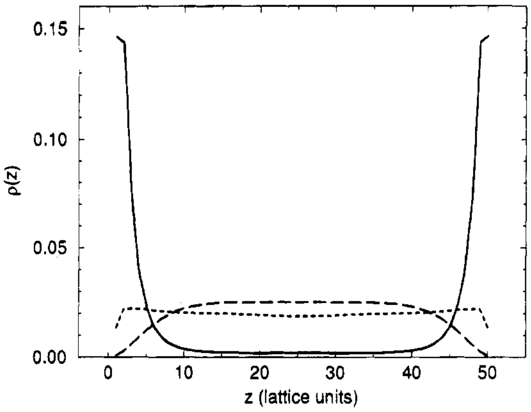

Figure 1. Total segment density profiles, $\rho(z)$, for random AB copolymers of chain length $N = 50$ confined between solid surfaces located at $z = 0$ and $z = 51$. The segment–surface interactions have a strength given by $\epsilon/k_BT = 2$. As described in the text, segments of type A are attracted to the solid surface with this strength, while segments of type B are repelled with the same strength. Density profiles are given for three copolymer compositions, specified by the fraction of type A segments, f_A. The long-dashed line corresponds to $f_A = 0.10$, the dotted line corresponds to $f_A = 0.25$, and the solid line corresponds to $f_A = 0.50$. In each case, the density profiles have been obtained by averaging over 250 separate monomer sequences.

A transition from primarily desorbed states to adsorbed states occurs at a composition between $f_A = 0.10$ and $f_A = 0.50$. When $f_A = 0.25$, for example, the random copolymers contain enough attractive segments so that the enthalpic gains of adsorption roughly balance the entropic penalties. The monomer density profile in this case is approximately uniform throughout the confining region, as shown in Figure 1. Explicit examination of Monte Carlo trajectories illustrate that the chains can pass easily between adsorbed and desorbed configurations. Figure 2a presents a representative trajectory of the center of mass of one random copolymer chain with $N = 50$, $f_A = 0.25$, and $\epsilon/k_BT = 2$. The copolymer begins the simulation in a desorbed state. In a short time, it diffuses to the upper surface and adsorbs; later, it desorbs and diffuses to the lower surface. Subsequent transitions between adsorbed and desorbed states, followed by diffusion across the "free solution" region are also observed. Transitions between adsorbed and desorbed states are shown clearly in Figure 2b, where the instantaneous number of adsorbed segments is given for the simulation run that yielded the center-of-mass trajectory in Figure 2a.

More information about the copolymer structure can be obtained by examining the individual density profiles of type A and type B segments, $\rho_A(z)$ and $\rho_B(z)$; these quantities are presented in Figure 3a for the strongly adsorbed copolymers whose total segment density pro-

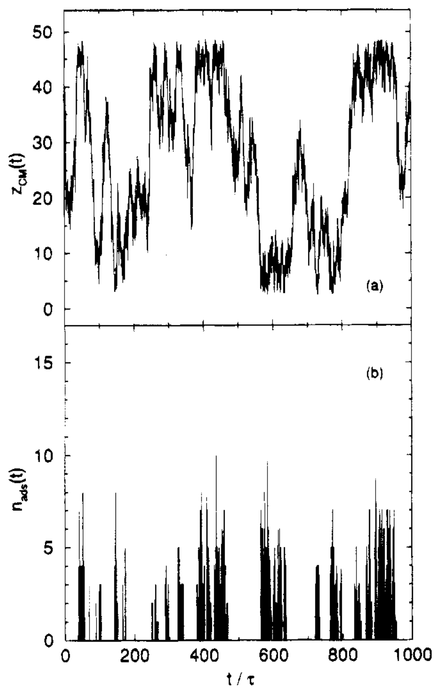

Figure 2. Monte Carlo trajectories for a single random copolymer chain near the adsorption–desorption transition: $N = 50$, $\epsilon/k_BT = 2$, and $f_A = 0.25$. The distance between the surfaces, H, is 50 lattice units. In the upper figure (a), the z-coordinate of the copolymer center of mas is given as a function of the number of Monte Carlo steps, t. The time variable t is normalized by the relaxation time of the end-to-end vector autocorrelation function, τ. In the lower figure (b), the number of adsorbed segments is plotted as a function of the number of Monte Carlo steps. Segments are counted as adsorbed if they lie in lattice layers $z = 1$ or $z = 50$.

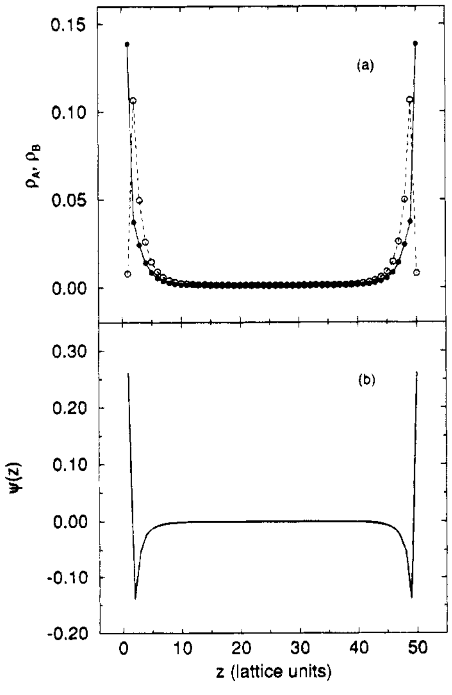

Figure 3. (a) Individual segment density profiles, $\rho_A(z)$ and $\rho_B(z)$, for segments of type A and B in random AB copolymer chains with $N = 50$, $\epsilon/k_BT = 2$, $f_A = 0.50$, and $H = 50$. Filled circles are data for type A segments, open circles for type B segments. (b) Order parameter, $\psi(z)$, defined by eq 1 for the segment densities given in the upper figure.

file was given in Figure 1: $N = 50$, $f_A = 0.50$, and $\epsilon/k_BT = 2$. The density of type A segments is peaked in the layers directly adjacent to the solid surfaces, $z = 1$ and $z = H$, due to the strongly attractive interactions with the surface. The segments of type B, in contrast, are strongly repelled from the surface, and their density in the surface layers is very small. Nevertheless, the chain connectivity constraint forces B segments to accompany A segments into the near-surface region. As a result, the density of B segments is sharply peaked in the layers that are second-nearest to the solid surfaces, $z = 2$ and $z = H - 1$. In lattice layers farther away from the surfaces, the densities of both A and B decay to their bulk values.

The local differences between the densities of A and B segments can be quantified through an order parameter, $\psi(z)$, defined as follows:

$$\psi(z) = \frac{\rho_A(z)}{f_A} - \frac{\rho_B(z)}{1 - f_A} \tag{1}$$

In a homogeneous phase, the segment densities are constant and proportional to the corresponding segment fractions, $\rho_A/f_A = \rho_B/(1 - f_A)$; the order parameter is then identically equal to zero. When the segment densities are inhomogeneous, $\psi(z)$ is positive in regions that are locally rich in segments of type A, while the order parameter is negative in regions rich in B. Note that the order parameter, $\psi(z)$, defined in eq 1 differs from the order parameter, $m(z)$, used by Gutman and Chakraborty:[8]

$$m(z) = (1 - f_A)\rho_A(z) - f_A\rho_B(z) \tag{2}$$

These two order parameters are simply related by

$$\psi(z) = \frac{m(z)}{f_A(1 - f_A)} \tag{3}$$

The form given by eq 1 is more convenient for later comparisons of the magnitudes of the order parameters at different values of f_A.

Figure 3b shows the order parameter corresponding to the A and B density profiles given in Figure 3a. The large positive values of $\psi(z)$ in the surface layers ($z = 1$ and $z = H$) indicate a strong preferential adsorption of type A segments. Although segments of type B are repelled from the surface, the constraint of chain connectivity requires the presence of B segments in the interfacial region; these segments reside preferentially in the layers near, but not directly adjacent to, the solid surfaces. As a result, $\psi(z)$ becomes negative in the layers that are next nearest to the surface ($z = 2$ and $z = H - 1$); the order parameter decays toward zero over a distance comparable to the width of the region where the total segment density is enhanced due to adsorption (Figure 1).

The order parameters can also be used to identify the adsorption–desorption transition as a function of f_A at fixed values of ϵ and N. In Figure 4, we present the order parameters, $\psi(z)$, for two of the random copolymers whose total density profiles are given in Figure 1: $N = 50$ and $\epsilon/k_BT = 2$. The vertical scale matches with that of Figure 3b for comparison of the magnitudes of $\psi(z)$ at different values of f_A. Referring to Figure 4a, the chains with a small fraction of attractive segments ($f_A = 0.10$) are below the adsorption threshold and reside primarily in the free space between the surfaces. The order parameter is very close to zero at all locations between the surfaces, as expected for a homogeneous distribution of A and B segments according to their

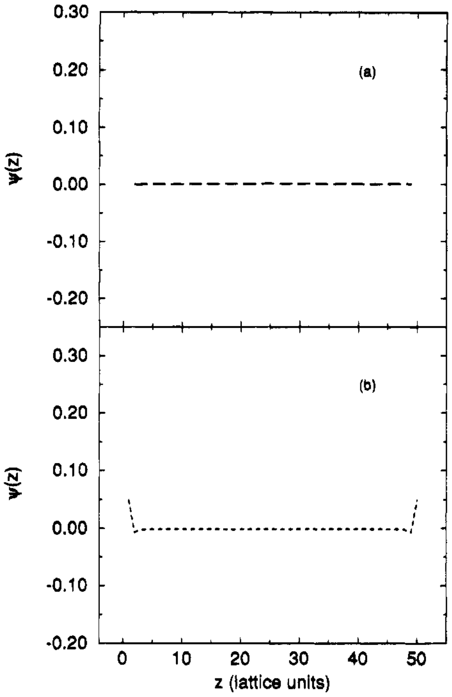

Figure 4. Order parameter profiles, $\psi(z)$, for random AB copolymers with $N = 50$, $\epsilon/k_BT = 2$, and $H = 50$. The long-dashed line corresponds to $f_A = 0.10$, the dotted line to $f_A = 0.25$.

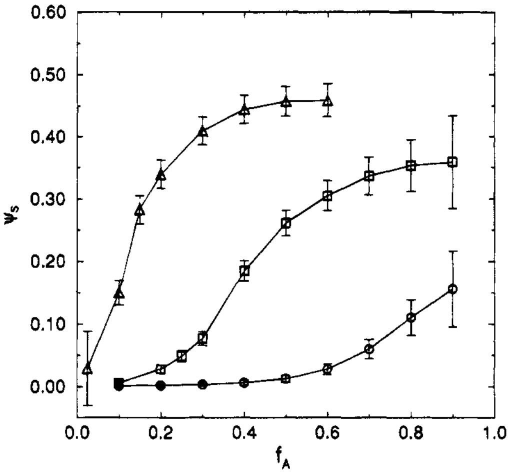

Figure 5. Order parameter evaluated at the surface, ψ_S, for chains of length $N = 50$, as a function of the fraction of type A segments, f_A. Three values of the segment–surface interaction energy, ϵ, are represented. The circles correspond to $\epsilon/k_BT = 1$, the squares to $\epsilon/k_BT = 2$, and the triangles to $\epsilon/k_BT = 4$.

overall mole fractions. When f_A is increased to 0.25, the order parameter grows to about 0.05 at the solid surfaces and decreases to slightly negative values in the adjacent layers, indicating that a moderate fraction of copolymer configurations are in adsorbed states (with preferential adsorption of type A segments). The order parameter for $f_A = 0.50$ from Figure 3b can be used to compare the magnitudes of $\psi(z)$ as a function of f_A; the greater magnitude of $\psi(z)$ for $f_A = 0.50$ indicates that these random copolymer chains are much more strongly adsorbed than those with $f_A = 0.25$.

Given that the magnitude of $\psi(z)$ can be used to judge the strength of adsorption, Figure 5 presents the quantity ψ_S, the value of the order parameter evaluated at the surface (in the layer $z = 1$); ψ_S is presented as a function of the fraction of adsorbing segments, f_A, for several values of the adsorption energy per segment, ϵ. When $\epsilon/k_BT = 1$, f_A can be increased to 0.50 without significant adsorption of the random copolymers; ψ_S remains below 0.015 for $f_A \leq 0.5$. Further increases in f_A result in small increases in ψ_S, but the adsorption remains relatively weak even for $f_A = 0.90$. For stronger segment–surface interactions, with $\epsilon/k_BT = 2$, the adsorption–desorption transition is shifted to lower values of f_A, and the value of ψ_S approaches a plateau at the highest fractions of type A monomers. Finally, the variation of ψ_S with f_A for the largest segment–surface interaction energies, $\epsilon/k_BT = 4$, naturally indicates the strongest adsorption. In this case, the random copolymers with a fractional A content of only 0.10 show significant adsorption. The degrees of adsorption and microphase segregation, as indicated by the values of ψ_S, increase with increasing content of A segments until $f_A = 0.50$, where ψ_S reaches a plateau. This behavior is qualitatively similar to the increase in the number of homopolymer segments adsorbed to a surface as a function of the adsorption energy per monomer.[30-32] (The adsorption–desorption transition in the present simulations is rounded and continuous, rather than sharp and discontinuous as in refs 30–32, due to the finite chain length employed in the simulations.)

We can now compare our simulation results to the theoretical predictions of Gutman and Chakraborty.[8] Figures 5 and 6 in ref 8 show the variation of the total segment density, $\rho(z)$, and the order parameter, $m(z)$, defined by eq 2, with the fraction of type A segments. A direct quantitative comparison of simulation and theory is not possible, since the energetic parameters and chain lengths are not exactly equal.[33] Nevertheless, there is very close qualitative agreement between the present Monte Carlo simulations and the field-theoretic predictions.[8] The segment density profiles given in Figure 5 of ref 8 exhibit the same general features that are present in the density profiles plotted here in Figure 1: A depletion region develops near the surface when the content of type A segments is low. Upon increasing the fraction of A segments, a value of f_A is reached where the segment density is roughly constant throughout the region between the solid surfaces; this marks the point of the adsorption–desorption transition. Finally, copolymers with the highest A content adsorb strongly to the surface, and the total density is greatly enhanced in the near-surface region.

The order parameter profiles shown in Figure 6 of ref 8 also share the same qualitative features as those which were obtained in the present study and which are plotted here in Figure 4. At compositions below the adsorption threshold, the order parameter ($m(z)$ defined according to eq 2) is essentially zero. For adsorbed copolymers, the order parameter is large and positive at locations directly adjacent to the solid surfaces; it then becomes negative and decays slowly to zero as one moves farther out away from the surfaces. As discussed above, the spatial variation of $m(z)$ indicates that the disparity in the segment–surface interactions induces microphase ordering into A-rich and B-rich regions when the copolymers adsorb. An A-rich domain resides in a narrow region directly adjacent to the surfaces, while a B-rich region extends farther out toward the bulk solution phase.

The simulation results presented here may also be used to complement a recent theoretical analysis of the adsorption of polyampholyte chains onto charged surfaces. Joanny has examined the adsorption of polyampholytes under conditions of strong and weak screening of electrostatic interactions.[17] His model of strong screening is very similar to the random copolymer model considered here. In ref 17, a fraction f of the monomers in the polyampholyte chain carry the same charge as the solid surface, a fraction g carry the opposite charge, and the remaining fraction $1 - (f + g)$ of monomers are electrically neutral. In the model of strong screening, the polyampholyte chains are placed on a lattice, and the screened electrostatic interactions extend only to the lattice layer that is directly adjacent to the surface. The monomers carrying the same charge as the surface are repelled with a strength k_BTV when they lie in the first lattice layer, while the monomers with the opposite charge feel an attractive interaction of strength k_BTV at that location. Thus, the present model of random copolymers can be mapped onto the model of Joanny by taking $V \equiv \epsilon/k_BT$, $g \equiv f_A$, and $f \equiv (1 - f_A)$. In our nomenclature, the magnitude of the net charge per chain is therefore $|(2f_A - 1)q|N$, where q is the magnitude of the charge per monomer.

One weakness in the theoretical analysis and the present computer simulations is the neglect of electrostatic interactions among the monomer units. The absence of segment–segment electrostatic interactions should cause quantitative inaccuracies, but we expect the qualitative behavior to be captured by the simplified model, especially since the calculations and simulations are performed in the limit of strong screening. The greatest effect of the intrachain electrostatic interactions should be to disfavor the microphase ordering that is indicated by the order parameter profiles in Figure 4. The electrostatic interactions will be unfavorable on average if the overall segment density in the A-rich and B-rich regions is large. For the dilute single-chain limit considered here, incorporation of intrachain electrostatic interactions should cause the trains of adsorbed A segments and the loops of nonadsorbed B segments to expand so that the average distance between like segments is greater than the screening length of the electrostatic repulsion (one lattice unit in the present model).

A primary goal of theoretical analysis presented in ref 17 was to understand the surprising experimental result that polyampholyte chains can adsorb onto charged surfaces even when the polymer chain and the surface have net charges of the same sign.[18] To this end, Joanny derived an expression for an adsorption threshold in terms of the critical interaction energy, V_c, as a function of the polyampholyte composition (eq 11 in ref 17). That equation can be rearranged to give a prediction for the critical fraction of type A segments (those carrying a charge opposite from the surface) required for adsorption, $f_A^{(*)}$ in our nomenclature, as a function of the strength of the screened electrostatic interaction, ϵ:

$$f_A^{(*)} = \frac{1}{1 + \exp(\epsilon/k_BT)} \tag{4}$$

The above expression is based on a first-order perturbation expansion[17] that may not be applicable over the full range of our simulation conditions; it is of interest, nevertheless, to compare the qualitative predictions of eq 4 to the simulation results. Our random copolymers are predicted to favor adsorption at a fixed value of ϵ when $f_A > f_A^{(*)}$. The critical fraction of type A segments is a strongly decreasing function of ϵ according to eq 4. Referring to the surface order parameters, ψ_S, plotted here in Figure 5, our simulation results reproduce the qualitative behavior suggested by eq 4. To achieve the same degree of adsorption, as indicated by similar values of $\psi_S \approx 0.05$, f_A must be raised to roughly 0.7 when $\epsilon/k_BT = 1$, as opposed to 0.25 when $\epsilon/k_BT = 2$. For $\epsilon/k_BT = 4$, this value of ψ_S can be achieved for $f_A < 0.1$. In the context of polyampholyte adsorption, these results indicate that chains carrying a large net charge of the same sign as a charged surface can still adsorb onto the surface if the electrostatic interactions can be screened on a length scale commensurate with the statistical segment length. In this case, the polymer segments carrying the same charge as the surface can reside in loops and tails outside of the surface layer, where they are beyond the range of the repulsive electrostatic interactions.[17]

4. Conclusions

We have presented a Monte Carlo simulation of random AB copolymers confined between two solid surfaces. In the model of random copolymers considered here, segments of type A were attracted to the surface due to a favorable adsorption energy $-\epsilon$; segments of type B were repelled from the surface by an unfavorable adsorption energy $+\epsilon$. This model system is similar to the ones considered in theoretical analyses of the adsorption of random copolymers[8] and polyampholytes.[17] The Monte Carlo simulations are in qualitative agreement with the theoretical predictions given in refs 8 and 17. At a fixed value of ϵ/k_BT, we observe an adsorption–desorption transition as the fraction of attractive segments, f_A, is increased. The critical content of attractive segments required for adsorption, $f_A^{(*)}$, is a strongly decreasing function of ϵ/k_BT. Adsorption of the random copolymers induces microphase ordering of the A and B segments, as indicated by the order parameter, $\psi(z)$, defined in eq 1. A narrow region rich in type A segments develops near the surfaces, followed by a wider B-rich region farther away from the surfaces. The variation of the microscopic structure of adsorbed random copolymers with the parameters f_A and ϵ/k_BT is of interest in the molecular design of optimal copolymer architectures for adhesives.[8] Further simulations of multichain systems will be required to analyze the extent of interchain entanglements, which will greatly influence the mechanical strength of a polymer–solid interface that is reinforced with adsorbed random copolymers.

In the context of polyampholyte adsorption under conditions of strong screening, the Monte Carlo simulations reproduce the theoretical prediction that polyampholyte chains can adsorb onto a charged surface even when the net charge on the chain has the same sign as the surface charge.[17] A more complete model, including segment–segment electrostatic interactions and the relaxation of the assumption of strong screening, would be necessary to generate quantitative agreement between the simulations and experimental results.[18]

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