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# Monte Carlo study of block copolymer adsorption from dilute solutions

Wei Wang, Z.-Z. Lin,* and C. Ebner
*Department of Physics, The Ohio State University, Columbus, Ohio 43210*

Yvonne Nikas
*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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We present results from Monte Carlo simulations of a lattice model for block copolymers in dilute solution; we emphasize adsorption on a substrate. The model includes pairwise short-ranged interactions between monomers as well as interactions between monomers and the substrate. By varying the relative values of different interactions, the lengths of the different blocks in the copolymer, and the temperature, we are able to study systematically a variety of thermodynamic properties, including especially the adsorption temperature and the density distributions for the various blocks in the polymer. Special attention is paid to the case in which the $A$ monomers attract each other and are attracted to the substrate while the $B$ monomers experience no attractive forces from either themselves, the $A$ monomers, or the substrate. This case corresponds to having a selective solvent that is good for the $B$'s and poor for the $A$'s. Then the $A$ block becomes adsorbed at sufficiently low temperatures while a block of $B$'s does not, but rather extends some distance into the solvent. We also present for comparison simulations of the properties of a single block of monomers anchored at one end to the substrate. A general conclusion of this comparison is that when the $A$ block of the copolymer is firmly adsorbed to the substrate, the behavior of the $B$ block or blocks is qualitatively much the same as the behavior of a single block anchored at one end.

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## I. INTRODUCTION

Much research has been done on the properties of long chain molecules in dilute solution [1] and on the adsorption of such molecules on solid surfaces. In particular, polymer adsorption from solution on a solid substrate is reviewed extensively, with many references, by Kawaguchi and Takahashi [2]. The behavior of diblock ($AB$) and triblock ($BAB$) copolymers under conditions in which the solvent is good for one type of monomer and poor for the other is of particular interest because of the application to the stabilization of colloidal suspensions [3]. The central idea is that if the solvent is poor for, e.g., the $A$ monomers and good for the $B$'s, then under suitable conditions of temperature and concentration the $A$ block or blocks will tend to be adsorbed on a bounding surface of the solution (the colloidal particle) while the $B$ block or blocks will extend into the solution and form a repulsive buffer between particles, provided there is no effective attraction between a $B$ monomer and an $A$ monomer or between a pair of $B$ monomers that is sufficiently strong to cause a collapse of the $B$ blocks and/or attraction between the buffers on different particles. In this way the "brush" formed by the $B$ blocks prevents the colloidal particles from coagulating and producing flocculation of the suspension.

The adsorption of block copolymers has been addressed theoretically using several different approaches. Munch and Gast [4,5] first applied mean-field methods in the spirit of Scheutjens and Fleer's [6] (SF) theory to a study of $AB$ block copolymers. The adsorbed $A$ block is represented by a fixed anchor, with the $B$ block extending into the solution. One important result of their work is that for a dense system, meaning one with large surface coverage so that the mean distance between the anchors of individual polymers is smaller than the mean radius or Flory radius of a polymer, the brush extends into the solution a distance that scales as $N_B^{0.7}$ where $N_B$ is the number of monomers in the $B$ block. Numerous additional papers have dealt with further applications of mean-field theory to adsorption phenomena. A paper of particular relevance to the work we report here is one by Whitmore and Noolandi [7] in which the segment density profile of the brush in an $AB$ copolymer is determined for a variety of $N_B$'s and surface coverage.

Scaling arguments, largely pioneered by de Gennes [8], have also been employed to study block copolymer adsorption. For example, Marques, Joanny, and Leibler [9] applied this method to the adsorption of $AB$ block copolymers under conditions in which the solvent is poor for $B$'s and good for $A$'s, while Marques and Joanny [10] treated adsorption from a nonselective solvent. Johner and Joanny [11] examined the adsorption kinetics of diblock copolymers; they also briefly considered the copolymer adsorption problem in an extensive work dealing primarily with the adsorption of homopolymers [12].

Finally, there are several papers containing Monte Carlo simulations [13–17] of block copolymer (and random copolymer [18]) adsorption. The first of these, by Cosgrove *et al.*, contains SF theory for terminally attached chains and also describes simulations of attached chains of 50 monomers' length for comparison. Among the properties computed are the segment density as a function of distance from the substrate and the root-mean-square layer thickness. Effective interactions between monomers (the Flory-Huggins parameter) and between monomers and the substrate are included. A single chain is simulated with periodic boundary conditions applied in directions parallel to the bounding surface to approximate the presence of many chains. Chakrabarti and Toral [14] simulate systems of many chains of 50- and 100-monomer lengths, including the monomer anchored to the substrate, attached at random to a planar surface, but do not include additional interactions aside from the condition of the single occupancy of a lattice site. Ten Brinke and Hadziioannou [15] as well as Balazs and coworkers [16,17] simulate collections of chains such that both ends attach to the substrate.

In this paper we describe Monte Carlo simulations of the equilibrium properties of a three-dimensional lattice model for the adsorption of block copolymers on a substrate. The model, which includes interactions between different monomers on the polymer as well as between individual monomers and the substrate, is an extension of one that has been used previously by Szleifer, O'Toole, and Panagiotopoulos [19] to study the collapse transition of a homopolymer in bulk solution and by us [20] to investigate the phase diagram of dilute solutions of homopolymers including adsorption on a substrate. In this paper emphasis is placed on the adsorption of a single di- or triblock copolymer under conditions such that the solvent is good for $B$ monomers and poor for $A$ monomers. In particular, we examine, as a function of various effective interaction parameters and of the length of the $B$ blocks, the temperature at which adsorption takes place in the dilute limit where interactions among different polymers are not important. In the adsorbed state, we look also at the $B$ block segment density distribution and at the mean distance of a $B$ monomer from the substrate as functions of the lengths of the $B$ blocks and of various interactions. In this limit we compare our results with those from simulations of a single block of $B$ monomers anchored to the substrate.

The simulation technique is the same as in Ref. [20], which is to say, it is the scanning simulation method of Meirovitch [21], which was employed also by Szleifer, O'Toole, and Panagiotopoulos [19]. The model and numerical methods are described in more detail in Sec. II. Section III contains our results, and Sec. IV presents a discussion and summary.

## II. MODEL AND NUMERICAL METHODS

The molecule is modeled as two, in the case of a diblock copolymer, or three, for a triblock copolymer, connected chains, each of which comprises identical monomers. The total copolymer molecule is one linear chain of two or three blocks. A monomer occupies a site of a simple cubic lattice in three dimensions, with adjacent monomers in the chain constrained to occupy nearest-neighbor sites. A site may be occupied by at most one monomer. The lattice spacing is $a$. There is an effective interaction $U_{ij}$ between monomers on nearest-neighbor sites, except for a pair of monomers that are also adjacent constituents in the chain which are in any event constrained to occupy adjacent lattice sites. The subscripts $i, j$ refer to the type of monomer, $A$ or $B$. There are thus three monomer-monomer effective interactions $U_{AA}$, $U_{AB}$, and $U_{BB}$.

The lattice has $N$ layers in the $z$ direction so that it occupies the domain $Na \geq z \geq a$. In simulations reported here we use $N = 48$, 96, or 126. A monomer that is in either the first layer or the $N$th layer has an effective interaction energy $V_i$ with walls or substrates. There are two such interactions $V_A$ and $V_B$. Thus if we assign a site the indices $i, j, k$ such that $x = ia$, $y = ja$, and $z = ka$, then there is a $k$-dependent monomer-substrate potential that is not zero only for $k = 1$ or $k = N$. The system is invariant, and effectively infinite, in the $x$ and $y$ directions.

We proceed by generating an ensemble of self-avoiding walks (SAW's) and then evaluating means of various quantities over this ensemble. In the case of $BAB$ copolymers, we start from an $A$ monomer around the center of the $A$ block. It is located at $i{=}0{=}j$ with the $z$ position chosen according to the Boltzmann factor, $\exp[-V_A(\delta_{1k} + \delta_{Nk})/kT]$, where $T$ is the temperature, $k$ the Boltzmann constant, and $\delta_{ij}$ the Kronecker delta function. This procedure, which is used only to get started, does not give the correct distribution of polymers with respect to $z$; that is corrected in later steps as explained below. The random walk proceeds by adding monomers to the chain on either side of the original monomer. We do that either by alternately adding monomers on each of the two ends of the chain or by generating all monomers on one side of the starting monomer and then generating those on the other side. Given an $AB$ block copolymer, we start from the $A$ monomer at the end of the chain and generate the entire chain starting from that end. In all cases, it is important to start from an $A$ monomer, which is the kind preferentially attracted to the substrate.

Once a chain has been started, it is generated using the scanning simulation method of Meirovitch [21]. Before adding a particle to the chain one looks one or more steps ahead to determine the relative probabilities of the various possible choices. Once the choice is made, an appropriate weight is assigned to that move. For example, if one looks just one step ahead, it is necessary only to consider the consequences of placing the next monomer at each of the six neighboring positions to the previous one. Any occupied site is not allowed and so a step to those sites is assigned a zero probability. If the energy change that would result from adding a monomer at a particular site is $\delta E$, then that particular move is assigned a relative probability of $\exp(-\delta E/kT)$. One of the allowed moves is chosen on the basis of comparison with a computer-generated random number. If there are no allowed moves because all nearest-neighbor sites are occupied, the chain is rejected and a new one started. Finally, as the chain is generated, a weight for the chain is developed. At each step $i$ the weight is

$$w_i = \sum_{k=1}^{n(i)} e^{-\delta E_{ik}/kT}, \qquad (1)$$

where $\delta E_{ik}$ is the energy change that would accompany the particular move $k$, and there are $n(i)$ possible choices at this step. The total weight for the chain is the product of $w_i$'s over all moves,

$$W_l = \prod_i w_i. \qquad (2)$$

The subscript $l$ has been included in the total weight to indicate that it is the weight for the $l$th chain generated. Notice that for a chain of noninteracting segments or monomers, the factor $w_i$ is just the number of possible moves at step $i$ and all possible moves have the same probability of being selected.

In practice we have generated the chains, looking ahead by either one or two steps. Results from both methods have been compared and agree within statistical uncertainty. It is our experience that, although looking one step ahead is faster in that some seven or eight chains can be generated in the time it takes to generate just one when looking two steps ahead, the chains that are generated looking two steps ahead tend to be relatively the more likely ones, meaning they typically have large weights and lead to faster convergence of various computed mean quantities. However, when generating chains starting from the middle and adding monomers alternately on the two ends, errors are produced if one looks two steps ahead because a potential move of two successive steps identified at a given juncture at one end of the growing chain can be blocked by a monomer that is subsequently added at the other end, rendering invalid the weight assigned to the previous move. Consequently we have not used the combination of looking two steps ahead and generating chains by adding monomers alternately to the two ends.

The mean value of any quantity $Q$ over the ensemble of chains generated is

$$\langle Q\rangle = \frac{\sum_l W_l Q_l}{\sum_l W_l}, \qquad (3)$$

where $Q_l$ is the value of $Q$ for the $l$th chain in the ensemble and the temperature at which $\langle Q\rangle$ is to be obtained is the same as that at which the ensemble is generated. One may also use an ensemble generated at temperature $T$ to find $Q$ at $T'$ through the relation

$$\langle Q(T')\rangle = \frac{\sum_l W_l Q_l e^{-E_l(1/T'-1/T)}}{\sum_l W_l e^{-E_l(1/T'-1/T)}}, \qquad (4)$$

where $E_l$ is the energy of the $l$th member of the ensemble. This procedure will work well if $T'$ is not too different from $T$ and also if neither temperature is very small, or more to the point, if $\langle Q(T)\rangle$ is not very different from $\langle Q(T')\rangle$. This and related considerations are discussed in some detail by Szleifer, O'Toole, and Panagiotopoulos [19].

The final point concerning the generation of the ensemble is the value of $z$ or $k$ at which a chain is started. We generate a first set of 64 chains according to the prescription given above. Once this set is found, we use these chains to find a new distribution for starting a second set of 64. That is done by computing the distribution in $z$ of all $A$ monomers in the chains generated in the first set. The next set of polymers is generated by starting each $A$ block at a $z$ (or $k$) chosen according to this distribution. The third set of chains is generated using the distribution of $A$ monomers from the second set, and so on. The starting distribution rapidly—usually by the time 1000 chains have been generated—settles down and, aside from fluctuations, does not change as further sets are generated. Notice that both sides of the system in the $z$ direction present equivalent substrates to the polymer. In obtaining the segment density distributions shown in various figures, we take an appropriately normalized average of the distributions on the two substrates.

Our simulations can be divided into two distinct categories. First, we have determined the adsorption phase diagram of dilute polymer solutions as a function of $T$ and $N_B$ for various sets of interaction parameters. In this work we have generally employed an $A$ block of 20 or 40 monomers, $N_A = 20$ or 40. For $BAB$ copolymers, the lengths of both $B$ blocks are the same, with $5 \le N_B \le 30$. The second category involves the study of the distribution of $B$ blocks under conditions such that the $A$ block is firmly adsorbed to the substrate. For this work we have used $B$ block lengths up to $N_B = 240$, with $N_A$ typically equal to 20. For purposes of comparison, we have also done extensive simulations using only a $B$ block, with one end firmly anchored to the substrate.

The most thoroughly studied set of interaction parameters is $U_{AA} = -V = V_A$ and $U_{AB} = U_{BB} = U_B = 0$; $V$ is a positive energy. Under these conditions, at sufficiently low temperatures, meaning sufficiently large $V/kT$, the $A$ block will make a transition from an extended configuration to a collapsed one and will also become adsorbed to the substrate as described for homopolymers in Ref. [20]. The same effects are seen clearly in the current work. Several other sets of interaction parameters have also been employed for comparison.

Numerous thermodynamic properties of the copolymers have been accumulated and averaged. Among these are the energy and squared energy, from which the heat capacity may be obtained; the radius of gyration of each block as well as of the entire polymer; the distances between the centers of mass of the individual blocks; the angle formed by the displacement vectors from the center of mass of block $A$ to the centers of mass of blocks $B$ (in the case of $BAB$ triblock copolymers); the distance of the center of mass of each block from the substrate; the density of monomers in each block as a function of distance from the substrate; the density of monomers in each block as a function of the distance from the block's center of mass; and the density of monomers in the copolymer as a function of the distance from the copolymer's center of mass, assuming all monomers have the same mass. In addition, the components of the various displacements and radii of gyration in directions normal to and parallel to the substrate were determined. With this information we are in a position to give a fairly detailed picture of the behavior of the model. The quantities of most interest in this paper are the distances of the blocks' centers of mass from the substrate and the density distribution of the blocks, especially the $B$ blocks, as a function of $z$. Some of the other results will be reported elsewhere.

The number of copolymers generated for any given set of interaction parameters and temperature varied from 640 000 to several million. Typically, the longer the chain, meaning the longer the $B$ blocks, the larger the ensemble necessary to obtain good results.

## III. RESULTS

We first present results for the distribution of $B$ blocks when one end of the polymer, either an $A$ block or a fixed anchor, is adsorbed to the substrate. The simplest example is a single chain of $N_B$ monomers with one end anchored. Then the only interaction parameters of interest are $U_{BB}$ and $V_B$. Consider two cases, (i) $U_{BB} = 0 = V_B$ and (ii) $U_{BB}/kT = 2$, $V_B = 0$. The first corresponds to a simple self-avoiding walk while the second includes a strong, short-ranged, monomer-monomer repulsion. The principal noticeable consequence of the repulsion relative to the case with no repulsion is that the number of nearest-neighbor pairs, excluding pairs comprising adjacent monomers on the chain, is much reduced. For example, with a chain length of 240, we find that the mean value of the number of such pairs is around 48 for case (i) and about four for case (ii); the configuration of the chain is more open when repulsion is present. One consequence is that the polymer extends on average somewhat further from the substrate than when $U_{BB} = 0$.

Figures 1(a) and 1(b) show, respectively, the mean numbers of monomers per layer, $n(z)$, or segment density distribution, in case (i) and case (ii) for chain lengths $20 \leq N_B \leq 240$ in increments of 20. Close to the substrate there is a depletion region arising from decreased configurational entropy as a consequence of constraints imposed by the presence of the substrate. The density is largely independent of $N_B$ in this region. The maximum in the density and its position increase steadily with $N_B$, and there is a smooth decrease in the density to zero at large $z$. Overall, the position of the polymer is slightly further from the substrate in case (ii) than in case (i) because of the effective repulsion between monomers.

The mean distance $\langle z \rangle / a$ of a monomer from the substrate as a function of $N_B$, which is essentially the thickness of the brush formed by the anchored polymer, is presented in a log-log plot in Fig. 2. For large enough $N_B$ one expects [8,22] the curves to become straight lines reflecting power-law behavior, $\langle z \rangle \sim N_B^\nu$. Moreover, scaling analysis predicts [8,22] that $\nu = 0.6$ for a noninteracting SAW. Our results are consistent with this prediction, in that for the larger values of $N_B$ the points in Fig. 2 appear to be approaching linear behavior with slopes very close to 0.6. Notice that both cases appear to give almost the same behavior.

The density distributions shown in Fig. 1 and the results demonstrated by Fig. 2 suggest simple scaling behavior of $n(z, N_B)$. In Fig. 3 we display $(a/z) n(z, N_B)$ vs $[(z/a)/N_B^{0.6}]^{2.5}$ for $80 \leq N_B \leq 240$ in increments of 40. Aside from scatter at the larger values of the abscissa the points in both instances do lie very nearly on a single curve, supporting the scaling law

$$n(z, N_B) = z f(z/N_B^\nu), \tag{5}$$

with $\nu = 0.6$. We have selected the exponent 2.5 in making the plot because the scaling function in Eq. (5) is expected to decay at large values of the argument as $\exp[-A(z/aN_B^\nu)^\delta]$ with $\delta$ around 5/2. That means the points in Fig. 3 should lie on straight lines at large argu-

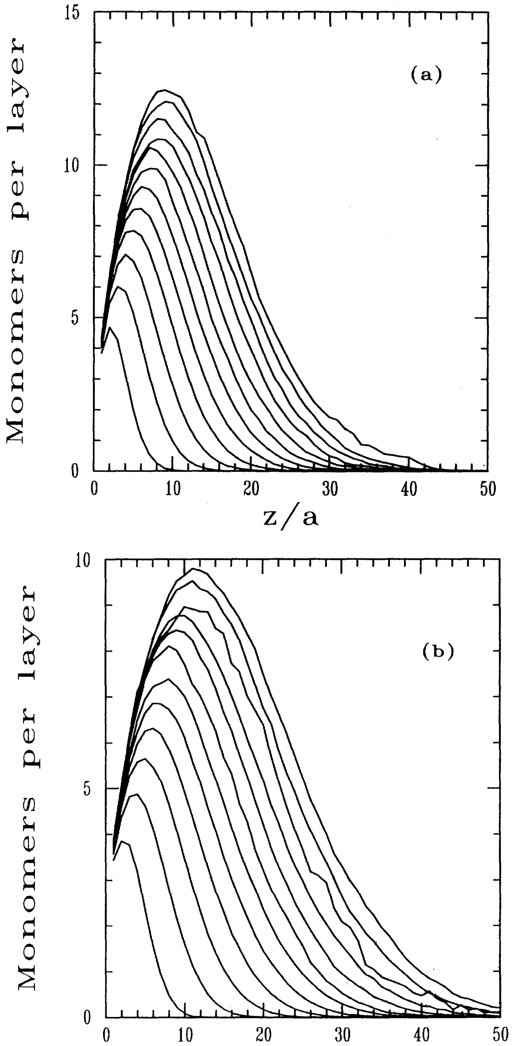

FIG. 1. The segment density $n(z)$ in monomers per layer is shown as a function of the layer number $z/a$ for anchored chains of length $20 \leq N_B \leq 240$ in increments of 20. In (a) the monomers are noninteracting, and in (b) the nearest-neighbor interaction parameter, or Flory-Huggins parameter, is $U_{BB}/kT = 2$. Longer molecules on average are at larger $z/a$.

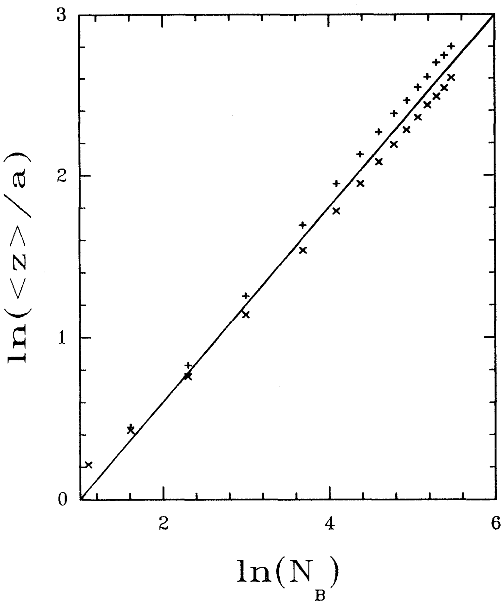

FIG. 2. The mean distance of a monomer from the substrate, in units of $a$, is shown against the chain length in a log-log plot for anchored noninteracting chains ($\times$) and for anchored chains with $U/kT = 2$ (+). The diagonal line through the figure has slope 0.6.

ment, and they do in fact have pretty nearly this behavior. A more detailed analysis, based on making a log-log plot relative to what is given in Fig. 3 and including one parameter chosen to produce the best straight line from the data, indicates that an exponent $\delta$ somewhat below 5/2 (between 2.2 and 2.4) gives a slightly better fit. The uncertainty in this result, however, is large enough that the difference from 5/2 is probably not significant.

We have also attempted to determine the scaling function at small $z$, where it has been predicted [22] that $n \sim z^{2/3}$; however, the range of $z$ over which we are in the appropriate regime is so small as to make it impossible to test this prediction; that is, we cannot distinguish any simple power law in our data at small $z$.

As a final example using anchored chains, we consider a case with $U_{BB} = -U < 0$ and $V_B = 0$. Now there are effective attractive interactions between monomers, corresponding to a relatively poor solvent, and the chain will collapse onto itself at large $U/kT$. This collapse in solution was studied in some detail by us in Ref. [20] and also by Szleifer, O'Toole, and Panagiotopoulos in Ref. [19], who, among other things, extracted the dependence of the $\Theta$ point on the chain length. When the attached chain collapses, although it is not actually attracted to the substrate, it will be localized close by because of the anchor. Of course, if there were an attractive monomer-substrate interaction $V_B < 0$, the behavior would be similar even in the absence of an attractive monomer-monomer effective interaction. Figures 4(a) and 4(b) display the segment density distributions for chains of lengths 120 and 240, respectively, at three relative coupling parameters $U/kT$. At the largest coupling, $U/kT = 2$, the chain is collapsed close to the substrate with essentially no depletion region so that the maximum in the density is almost adjacent to the substrate. As the effective coupling $U/kT$ decreases, the maximum in $n(z)$ moves to larger $z$. Figure 5 shows $\langle z\rangle/a$ as a function of $kT/U$ for chains with $40 \leq N_B \leq 200$ in increments of 40. One can see that the mean distance of a monomer from the substrate varies smoothly as the polymer changes from the collapsed configuration to an extended one. As the $U/kT$ goes to zero, $\langle z\rangle$ approaches the behavior found for the noninteracting chain, $\langle z\rangle \sim N_B^{0.6}$.

We look next at the behavior of $AB$ copolymers when

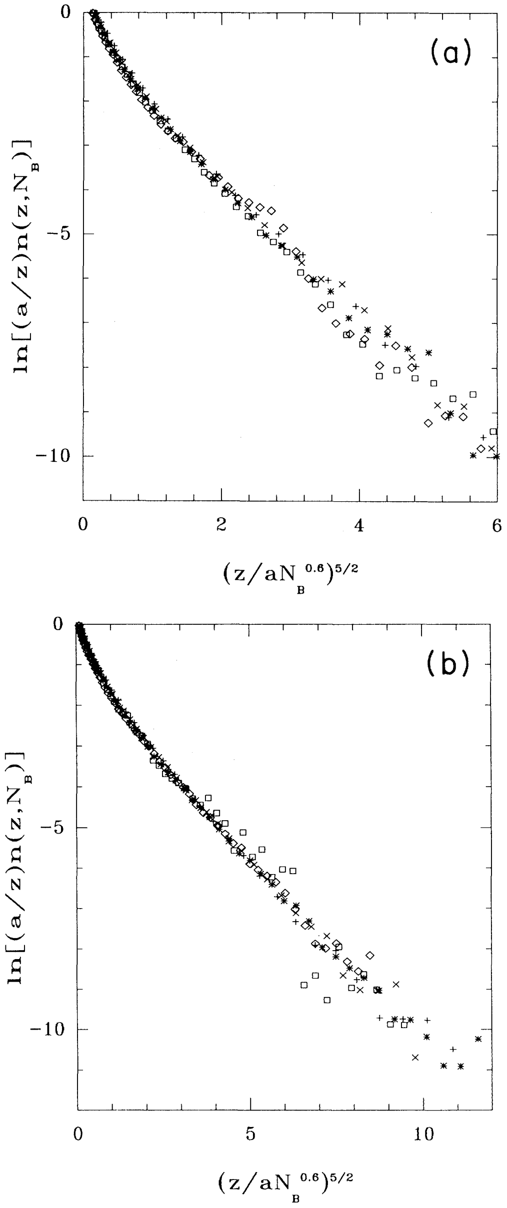

FIG. 3. For anchored chains, $\ln[(a/z)n(z,N_B)]$ is plotted against $[(z/a)/N_B^{0.6}]^{5/2}$ for (a) noninteracting chains and (b) ones with $U_{BB}/kT = 2$. The values of $N_B$ are 80 (+), 120 ($\times$), 160 ($*$), 200 ($\square$), and 240 ($\Diamond$).

the $A$ monomers are sufficiently strongly attracted to the substrate that they will be adsorbed; in other words, $V_A = -V < 0$ and $V/kT$ is large enough to produce strong adsorption of the $A$'s. Specifically, we choose $V/kT = 2$. We also take $U_{AA} = -V$ while the remaining effective interactions $U_{BB}$, $U_{AB}$, and $V_B$ are equal to zero. Under these conditions the $A$ block will collapse either in solution or in the adsorbed state [20] while the $B$ monomers interact with nothing aside from the condition of single occupancy of a lattice site.

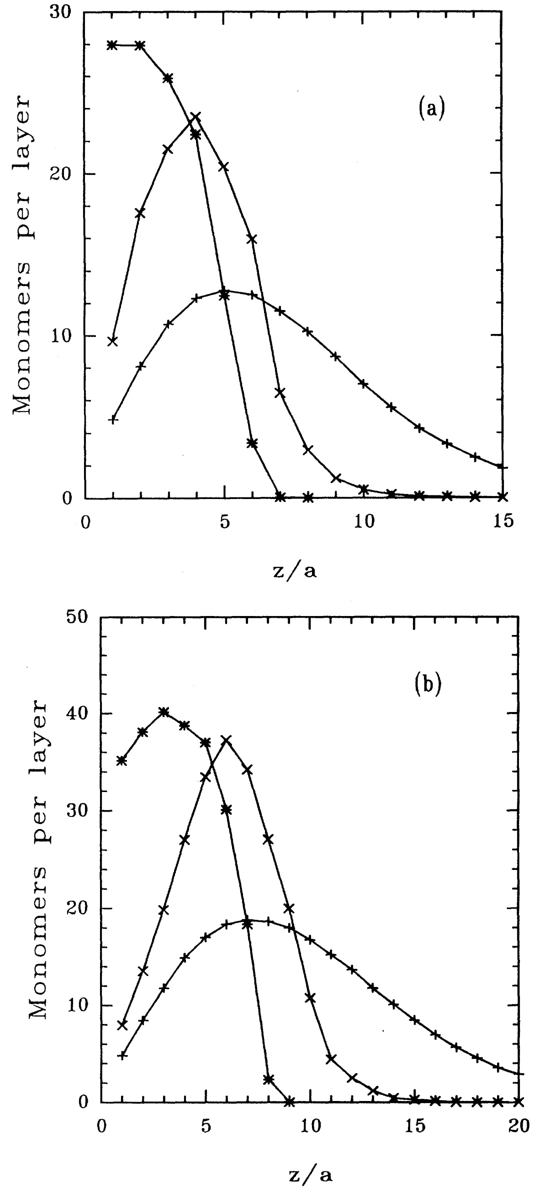

FIG. 4. The density in monomers per layer is shown as a function of the layer number $z/a$ for anchored chains with an attractive interaction $-U$ between monomers. The individual cases are (a) $N_B = 120$ at $U/kT = 2$ ($*$), $2/3$ ($\times$), and $1/3$ ($+$); and (b) $N_B = 240$ at $U/kT = 2$ ($*$), $4/7$ ($\times$), and $1/3$ ($+$). The solid lines serve as a guide to the eye.

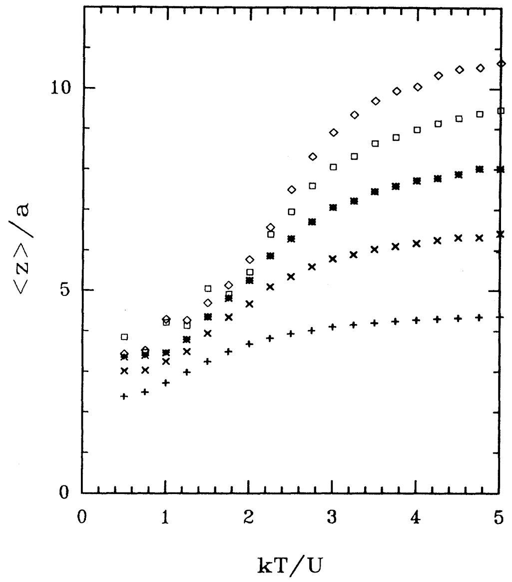

FIG. 5. The mean distance $\langle z \rangle / a$ of a monomer from the substrate is shown as a function of $kT/U$ for anchored chains of monomers with an attractive effective monomer-monomer interaction $-U$. The chains have length 40 ($+$), 80 ($\times$), 120 ($*$), 160 ($\square$), and 200 ($\Diamond$).

Figure 6 displays the segment density distribution of the $B$ block as a function of $z/a$ for $40 \le N_B \le 200$ in increments of 40. One can see that the behavior is not significantly different from what we found for an anchored chain of the same length $N_B$ and with the same interactions (none) between $B$ monomers. Figure 7 makes

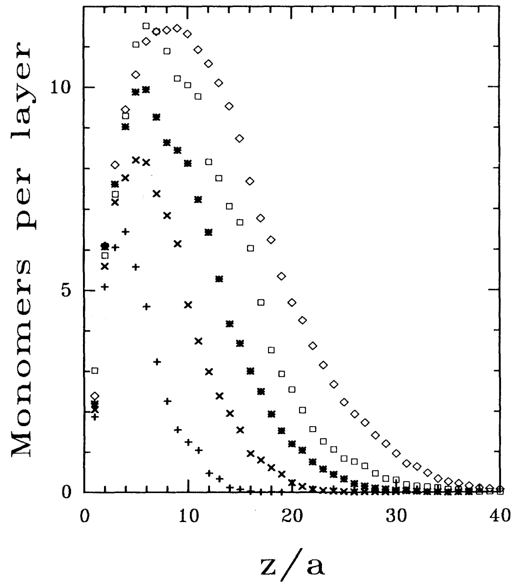

FIG. 6. The segment density distribution of the $B$ block of an $AB$ copolymer is shown as a function of layer number $z/a$. The interaction parameters are $V_A/kT = U_{AA}/kT = -2$ and $V_B = U_{AB} = U_{BB} = 0$. The points are for $N_B = 40$ ($+$), 80 ($\times$), 120 ($*$), 160 ($\square$), and 200 ($\Diamond$); $N_A = 20$ throughout.

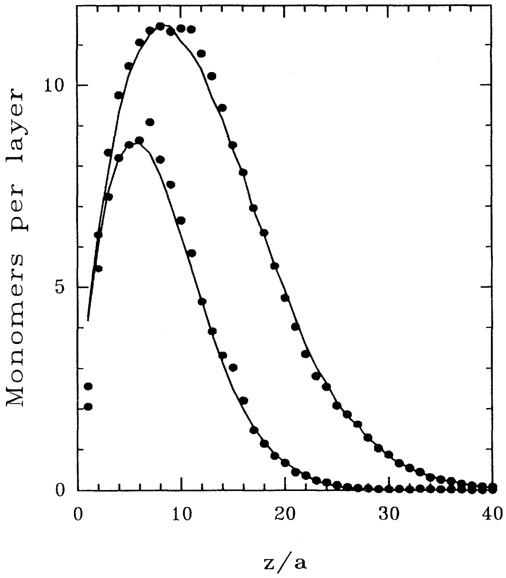

FIG. 7. The densities in monomers per layer of noninteracting anchored chains with lengths 100 and 200 (solid lines) are compared with the densities (●) of the $B$ monomers in adsorbed $AB$ copolymers with $N_B = 100$ and 200, $N_A = 20$, and all interactions equal to zero other than $U_{AA}/kT = -2 = V_A/kT$ for the copolymer.

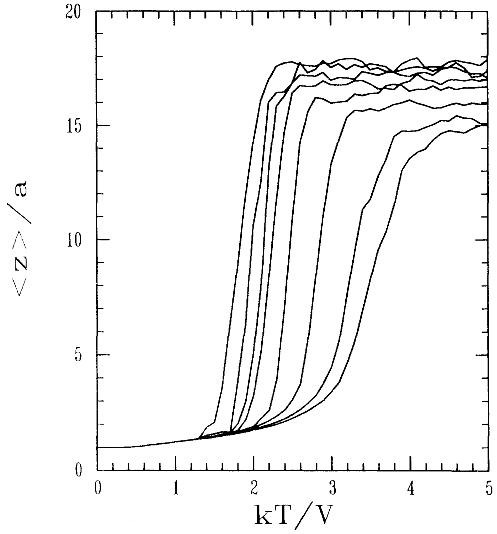

FIG. 8. The mean distance from the substrate of the $A$ monomers is shown as a function of $kT/V$ for a $BAB$ triblock copolymer with $N_A = 20$, $N = 48$, and $B$ blocks of lengths 1, 2, 5, 10, 15, 20, 25, and 30. The $A$ block desorbs at increasing temperature with decreasing $B$ block length. Interaction parameters are $V_A = U_{AA} = -V$ and $V_B = U_{AB} = U_{BB} = 0$.

this point very clearly; it presents a direct comparison of the densities of $B$ monomers for these two systems (the anchored block of $B$'s and the $AB$ copolymer) with $N_B = 100$ and 200. Except very close to the substrate, where one system has an $A$ block and the other does not, the results for a particular $N_B$ are identical for all practical purposes; the $B$ block of the copolymer is pushed out just a bit relative to the anchored polymer as a consequence of the presence of the $A$ block.

The similarity of the segment density distribution of the $B$ block in an $AB$ copolymer with a strongly adsorbed $A$ block to the anchored chain is not really surprising and suggests that for many purposes one need study just the latter, simpler system and can claim that the results carry over to the block copolymer. For that reason we present no further studies of $AB$ copolymers in the regime where the $A$'s are strongly adsorbed but simply refer to the results for a single anchored block. Instead, we turn next to a study of the transition between the adsorbed and nonadsorbed state for block copolymers.

Given $V_A = -V < 0$, and $V_B \geq 0$ while $U_{BB} \geq 0$ and $U_{AB} \geq 0$, an $AB$ or $BAB$ copolymer will undergo a change from a completely dissolved state to one in which the $A$ block is adsorbed as the temperature is decreased or, more properly, as the ratio of the temperature to $V$ is decreased. One may get a clear qualitative picture of this change by studying the mean distance $\langle z\rangle$ of the $A$ monomers from the substrate as a function of $kT/V$. Figure 8 is a plot of $\langle z\rangle/a$ against $kT/V$ for a $BAB$ triblock copolymer with $N_A = 20$ and $N_B$ ranging from 1 to 30, using $V_B = -V$ and $U_{AA} = -V$, while the other coupling parameters are zero and the number of layers in the lattice is $N = 48$. The change from the adsorbed to nonadsorbed state is a fairly sharp function of temperature, especially for the larger values of $N_B$. Also, the temperature at which this change takes place is more sensitive to $N_B$ for the smaller values of $N_B$. At the larger values a given change in $N_B$ produces a relatively smaller effect. If we adopt the simple criterion [20] that $\langle z\rangle/a = 10$ defines the adsorption temperature $T_a$, then we may easily extract $T_a$ as a function of $N_B$ from Fig. 8.

For other sets of coupling parameters, the general behavior of $\langle z\rangle$ is much the same. Increasingly negative $V_A$ will produce adsorption at correspondingly higher temperatures, and the introduction of repulsive interactions between the $B$ monomers and the substrate or between $B$'s and $A$'s will discourage adsorption somewhat but not very much. In Fig. 9 we show the adsorption temperature as a function of $N_B$ for $N_A = 20$ with four different sets of coupling parameters. The salient features of the figure are, first, that the adsorption temperature rises with decreasing $N_B$, and, second, that it is not particularly sensitive to the presence or absence of repulsive interactions between the $B$ monomers themselves, or between $B$ monomers and $A$ monomers; $T_a$ is somewhat more sensitive to the presence of repulsive interactions $V_B$ and decreases with increasing $V_B$. Finally, $T_a$ is naturally quite sensitive to the strength of the attraction between the $A$ monomers and the substrate.

In the adsorbed state, one may study the distribution of $B$ monomers as a function of various coupling parameters, $N_B$, and the temperature. Generally speaking the behavior is not much different from what we have already explored for the simple case of a block of $B$'s anchored to the substrate, and hence we shall not give any further re-

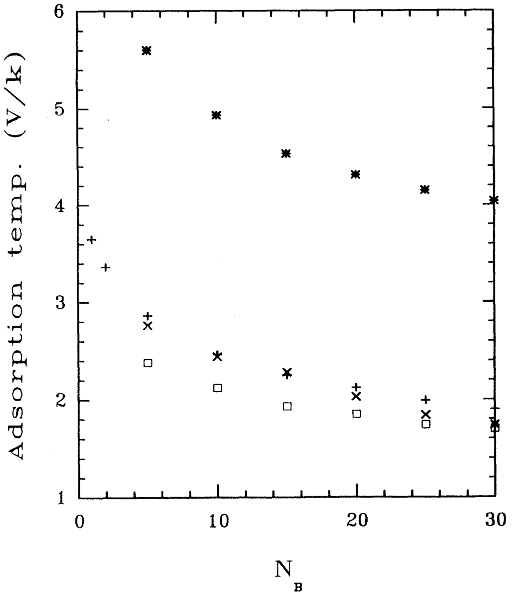

FIG. 9. The reduced adsorption temperature $kT_a/V$ is shown as a function of $N_B$ for $BAB$ triblock copolymers with $N_A = 20$, $N = 48$, and four different sets of interaction parameters. (i) $U_{AA} = V_A = -V$, $U_{AB} = U_{BB} = V_B = 0$ (+); (ii) $U_{AA} = -V$, $V_A = -2V$, $U_{AB} = U_{BB} = V_B = 0$ (∗); (iii) $U_{AA} = V_A = -U_{AB} = -U_{BB} = -V$, $V_B = 0$, (×); and (iv) $U_{AA} = V_A = -V_B = -V$, $U_{AB} = U_{BB} = 0$ (□).

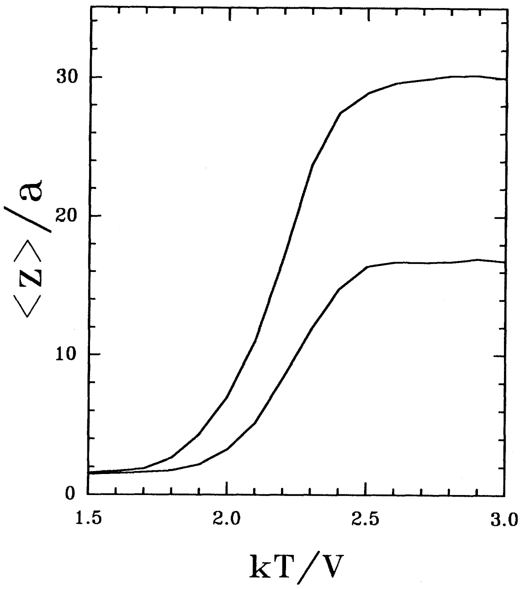

FIG. 10. The mean distance from the substrate of the $A$ monomers is shown as a function of $kT/V$ for a $BAB$ triblock copolymer with $N_A = 20$ and $N_B = 15$. Interaction parameters are the same as for Fig. 8. The two cases shown are for $N = 48$ and $N = 96$, demonstrating the downward shift of the adsorption temperature as system size is increased.

sults here. As for the properties of the copolymers under conditions in which the $A$ block is not adsorbed, these will be presented elsewhere.

The temperature at which adsorption occurs will depend on the width $N$ of the system normal to the substrate. One may estimate this dependence as follows. The change from dissolved to adsorbed behavior takes place at temperature $T$ such that the probabilities of the polymer's being in one or the other type of state is about the same, $\mathcal{N}_b \exp(-\beta E_b) \approx \mathcal{N}_s \exp(-\beta E_s)$ where $\mathcal{N}_b$ is the number of bulk (dissolved) states of the molecule, $\mathcal{N}_s$ is the number of surface (adsorbed) states, and $E_b$ and $E_s$ are typical energies of bulk or surface states which are accessed by the molecule at the temperature $kT = 1/\beta$. If one changes $N$ to $N'$, the number of surface states is unaffected while the number of bulk states scales roughly as $N'/N$, to the extent that $N$ and $N'$ are much larger than the diameter of the molecule in a bulk state. Applying this argument to the two system sizes $N$ and $N'$ and comparing, one finds that $\beta' E' - \beta E \approx \ln(N'/N)$ where $\beta' = 1/kT'$ is the adsorption temperature in the system of size $N'$, and $E$ and $E'$ are, respectively, $E_b - E_s$ and $E'_b - E'_s$, i.e., the differences between typical bulk and surface state energies at temperatures $T$ and $T'$. From our simulations, and not surprisingly, we find that this energy difference varies linearly with $\beta$ at temperatures around the adsorption temperature; most of the variation comes from changes in $E_b$. Moreover, the relative change in $E$ is on the same order as the relative change in $\beta$, or $\delta E/E = f\delta\beta/\beta$ where $f \approx 1$. Given that the shift in the adsorption temperature when $N \to N'$ is small compared to $T$ itself, which means $N'$ is not too different from $N$, we have

$$\frac{\delta T}{T} = \frac{kT}{(1+f)E} \ln\left(\frac{N}{N'}\right), \tag{6}$$

where $\delta T = T' - T$ is the shift in the adsorption temperature when the size of the system changes from $N$ to $N'$. A typical example may be taken from Fig. 8, specifically the system with $N_B = 15$ for which the simulations give $E \approx 10V$, $kT/V \approx 2.3$, and $f \approx 1$. Then $\delta(kT)/V \approx 0.25 \ln(N/N')$. In Fig. 10 we compare values of $\langle z\rangle/a$ for systems with $N = 48$ and $N' = 96$, demonstrating that the adsorption temperature is indeed shifted by about the amount predicted, $\delta(kT)/V \approx -0.2$. Because the shift depends only logarithmically on $N'$, it is relatively insensitive to the system size. Finally, notice in the figure that for the dissolved molecules (large $T$), $\langle z\rangle$ is about twice as big in the larger system as in the smaller one.

## IV. DISCUSSION AND SUMMARY

In this paper we have presented results from simulations of a lattice model for the adsorption of copolymers and results from simulations of a lattice model for a homopolymer anchored at one end to a substrate. Comparison of these under conditions such that one particular block of the copolymer, the $A$ block, is strongly adsorbed to the substrate demonstrates that the behavior of the nonadsorbed block is much the same in both types of systems. Consequently, we have emphasized results for the anchored chain as being representative of the behavior of the $B$ block in a block copolymer such that the $A$ block is strongly adsorbed. In particular, we have looked in some detail at the density distribution of the $B$ monomers as a function of the interactions between these monomers and the length $N_B$ of the $B$ block. From such distributions we have found the mean distance $\langle z \rangle$ of a monomer from the substrate as a function of $N_B$ and have demonstrated that it is close to obeying the relation $\langle z \rangle \sim N_B^{0.6}$, which is predicted from scaling arguments [22] for SAW's. We have found this result for both $U_{BB} = 0$ and $U_{BB} > 0$. Moreover, the density distribution for given interactions and different $N_B$ is not too far from obeying the scaling relation function $n(z, N_B) = zf(z/N_B^{0.6})$. The general behavior of the density as a function of $z$ when the monomers are not attracted to the substrate or to each other very strongly, displayed in Fig. 1, has been found in numerous other studies based on both mean-field theories and simulations [2,7,13,14,23,24].

For $U_{BB} = -U < 0$, we have looked at the density distribution and mean distance from the substrate of $B$'s as a function of $kT/U$ and of $N_B$, finding in particular that $\langle z \rangle$ decreases smoothly with decreasing $kT/U$ as the chain forms a collapsed "globule" adjacent to the substrate. At high temperatures the chain forms an expanded "coil." The temperature at which the collapse occurs increases with increasing $N_B$, as one would expect from an argument based on the behavior of the energy and entropy as functions of the temperature and $N_B$. In the absence of attractive interactions between the monomers and substrate, this collapse is much the same as would be observed for a polymer in solution given attractive monomer-monomer effective interactions, with the difference being that the presence of the substrate inhibits somewhat the formation of the globule.

The other point emphasized in our work is the change from adsorption to nonadsorption of a $BAB$ block copolymer as a function of temperature and $N_B$ at fixed $N_A$ and the various couplings given that the $A$ monomers are attracted to the substrate (and to each other, which is less important) and the $B$ monomers are not. Specifically, we have computed $\langle z \rangle$ for the $A$ monomers from which a clear switch between the two types of states is determined. Using a simple criterion for deciding when a polymer is adsorbed, we then can determine the adsorption temperature $T_a$ as a function of $N_B$. One should emphasize that the change from adsorption to nonadsorption is not a phase transition; the molecule is finite and there is no singular behavior in any of the thermodynamic quantities. Thus if one makes a "phase diagram" such as in the plots of $kT_a/V$ against $N_B$ in Fig. 9, the lines do not represent phase boundaries but merely separate qualitatively regions of adsorbed and nonadsorbed states.

Because the system simulated contains but a single molecule, we are clearly unable to investigate the competition between adsorption and micelle formation that takes place around the critical micelle concentration (CMC). Our results must be understood as being relevant only to adsorption at polymer concentrations below the CMC. The behavior in this or any regime will depend on the relative abundance of surface or adsorbed states and bulk or nonadsorbed states of the polymer. The parameter in our model that controls this ratio is the width $N$ of the system in the $z$ direction. The probability that the molecule is in a surface state is greater for smaller values of $N$, other things (the effective interactions) being equal. Thus Figs. 8 and 9, which demonstrate the temperature at which a molecule becomes adsorbed, would change if different values of $N$ were employed. We have given a simple estimate of the magnitude of this change as a function of $N$ and have simulated one case, shown in Fig. 10, which serves to verify the estimate. Our results are perhaps best interpreted as being relevant for polymer adsorption in relatively narrow channels or capillaries, comparable in width to the length of a fully stretched polymer.

On the experimental side, there are a number of measurements [25–29] done on different block copolymers in selective solvents, of the variation of the "brush" thickness $t$, analogous to $\langle z \rangle$ in our work, with the lengths of the anchoring block and soluble block. Generally speaking, one finds that $t \sim N^{\nu}$ where $N$ is the length of the soluble block and $\nu$ ranges from about 0.5 to 0.7. The reasons for the observed variation in $\nu$ presumably have to do in part with the density (coverage) of the polymers on the adsorbing surface, the quality of the solvent for the two blocks, and the relative size of the anchor and "buoy." These points are discussed clearly and in some detail in Ref. [7]. Cosgrove and co-workers [25], in their neutron reflectivity measurements, also are able to infer the shape of $n(z)$, that is, whether it is monotonically decreasing in an exponential or parabolic fashion or whether it contains a maximum at some finite $z$. The evidence suggests that under some conditions for diblock polystyrene-poly(2-vinylpyridine) polymers in toluene there is a maximum in $n(z)$ in qualitative agreement with the results found here and in other theoretical treatments.

There are numerous other interesting properties of block copolymer molecules that may be obtained from simulations such as ours. For example, one may study the configurations and relative configurations of the different blocks that are found in various collapsed or condensed states, both in bulk and adsorbed states, as functions of the different coupling parameters. Work along these lines is continuing.

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* Present address: Department of Computer Science, George Mason University, Fairfax, VA 22030.

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