Effect of Heterogeneous Energies on Adsorption Properties: Adsorption of Copolymers, Comb Polymers, and Stars onto a Surface

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ABSTRACT: With a view to understanding how a dilute sprinkling of strong hydrogen bonds affect the bulk properties and the colligative properties of polymers, we examine three polymer adsorption problems. They are (1) a copolymer between two adsorbing plates, (2) a comb polymer between two adsorbing surfaces, and (3) a star polymer between two absorbing surfaces. Matrix methods are used to solve each of these problems. Numerical results for a block copolymer with a periodic repeat of a single strong bond and *r* weak bonds show that the adsorption is not well represented by a model which replaces the segments by those of an average energy. This means that the specifics of molecular architecture cannot be ignored as has been done in so much of the previously published work on adsorption. Because the matrices do not commute, block polymers and random copolymers of the same composition are expected to show different adsorption profiles.

1. Introduction

We are interested generally in how a relatively few but very strong bonds affect the properties of polymer systems.[1] One example is a two-component polymer blend that has a few hydrogen bonds per molecule between the unlike polymers. The hydrogen bonds have the effect of compatibilizing the polymers.[2] Another example is a bulk copolymer which contains a few strong bonds per molecule that act as cross-links between the chains, thus creating a rubbery material rather than just a viscous material.[3] Each of these systems is important industrially.

In order to gain further insight into the sparse but strong bonds problem (SBSB) in bulk systems, we thought it best to proceed methodically by treating the two-molecule problem, then the three-molecule problem, and so on until the n-molecule problem is solved. However, even the two-molecule problem is difficult as one sees readily since the two-molecule problem is closely related to the double-strained DNA problem (imperfect matching model). The imperfect matching DNA model has been solved when the bonds are all the same strength,[4] and the perfect matching model has been solved for copolymers,[5] but for the case of a sparse sprinkling of strong bonds (the copolymer problem) the imperfect matching model is not solved. So we thought it best to gain insight by looking for any exactly solvable problem that contains SBSB. It is to be stressed that we are looking for exact solutions; mean-field treatments will miss the characteristic features of the SBSB problem.

The adsorption of a polymer lying between two parallel plates is an exactly solvable lattice model problem[6] (self-excluded volume is not treated). A trivial generalization of this model allows us to treat the general linear copolymer problem exactly, and by choosing a copolymer with only a few A monomers that are strongly adsorbed and many B monomers that are weakly adsorbed, we immediately have an entry into an exactly solvable SBSB problem.

We have also extended the lattice model of a chain between two parallel plates to architectures other than pure linear since for these materials also the SBSB problem is important. There are three general problems involving polymers adsorbed between two plates that we shall solve analytically in this paper: (1) a linear copolymer adsorbed onto a surface, (2) a comb molecule adsorbed onto a surface, and (3) an adsorbed star polymer. A fourth architecture, that of polymer rings, was solved previously.[7] In each of these problems an isolated molecule is adsorbed between two surfaces when the energies of attraction of monomer for the surfaces are of two types, weak and strong. If the weak and strong monomers are distributed periodically, we have a block copolymer, while if they are distributed randomly, we have a random copolymer. Thus, we now have a large class of exactly solvable problems for which we can treat the SBSB problem. However, all of our numerical work in this paper will be restricted to elucidating the properties of linear block copolymers.

There are some important questions that we shall begin to answer in this paper. Can one replace the copolymer by homopolymer with some sort of average energy (the answer as we shall see is no), and if not, does the actual sequence matter, or is the composition only important? We shall see not only that must we treat the system as a copolymer but also that the sequence itself as well as the overall composition is important. What is the importance of the architecture and the microstructure of the architecture on the transition properties of the absorption? Our figures will give us an insight into these questions.

For the specific case of the SBSB problem we shall study, we shall discover that when the relative number of weak monomers is large compared to the plate separation, we can choose the ratio of weak to strong energy small enough so that the adsorption curves show an interesting double plateau. One can never get this plateau by using an average energy for each monomer. The adsorption of a copolymer on a line is also an interesting SBSB problem and may be solvable by the methods of Rubin,[8] although we have not made the attempt.

The authors are not aware of any experimental technique, other than so-called "critical chromatography" that allows us to test the single chain theory directly. In critical chromatography all the action is with isolated molecules that are adsorbing onto and desorbing from surfaces. Our results are directly applicable to so-called "critical liquid chromatography"[9] or

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polymer chromatography[10] at the adsorption transition in that our partition functions can be identified with the partition coefficients K in the formula for elution volume V_e in

$$V_e = V_f + KV_s \tag{1.1}$$

where V_f is the flowing volume and V_s is the stagnant volume. We are hopeful that this relatively new chromatographic method will enable us to identify different polymer species and different architectures by chromatographic means. Recent work by the authors discusses these questions.[10,11]

The problem of the adsorption of copolymers onto surfaces is an active area of research. Both the isolated copolymer at a surface problem and the problem of copolymers crowded onto a surface have been studied. We discuss them separately. A useful general reference for the problem of polymers at interfaces is the book edited by Sanchez.[12]

Mostly Bulk Systems. Fleer and co-workers have made extensive use of their lattice model treatment for crowded molecules near a surface. Quite recently van der Linden, van Lent, Leermakers, and Fleer have investigated the adsorption of linear block copolymers onto "chemically rough" or patchy surfaces.[13] Earlier Evers, Scheutjens, and Fleer had made extensive calculations on copolymers on smooth surfaces.[14,15] Van Lent and Scheutjens have been able, using lattice methods, to treat copolymers in geometries other than planar.[16] Balazs and co-workers have also made extensive computer investigations of linear block copolymers onto patchy surfaces.[17] A very recent paper by Donley and Fredrickson should also be mentioned.[18] These mean-field treatments of bulk and concentrated polymers require the properties of the isolated polymers as input, but it is difficult to see how much of the non-mean-field characteristics of the isolated chain survive the mean-field approximations necessary to the treatment of crowded molecules.

Mostly Isolated Polymers. There is much merit in the view that the isolated polymer chain problem should be understood in its full generality before application to bulk systems is made. Cosgrove, Finch, and Webster[19] have performed Monte Carlo calculations on a linear block copolymer. Li, Yeung, Jasnow, and Balazs have treated an alternating copolymer at a fluid–fluid interface.[20] Marques and Joanny have a treatement much like our paper with the intent in that it treats a copolymer of mostly B molecules with a few sticker molecules.[21] However, they are mainly concerned with the density profile of these chains on the surface. They do not consider the effect on the thermodynamics or transition temperature that we consider. The latter two papers are continuum treatments, and in continuum treatments certain energy regimes are not nearly as accessible as they are in the lattice treatment. A recent Monte Carlo investigation into the adsorption of block copolymers that also have the option of self-assembling further illustrates the complexity of the problem.[22] Finally, the polymer between two plates problem introduces the added complexity of polymer bridges. The adsorption of telechelic polymers between two parallel plates has been investigated by Misra and Mattice.[23] The existence of these added complexities and the existence of various polymer architectures argue strongly for solving the isolated polymer problem in as general a way as possible. The matrix method of our paper is such a treatment.

In section 2 we shall offer general solutions for copolymers of any possible size and architecture adsorbed onto the surfaces between two parallel plates. In section 3 we shall present a numerical study for the SBSB problem of an infinite linear block copolymer with one strong bond and $r - 1$ weak bonds between two plates repeated indefinitely. In future papers we shall examine finite molecular weight systems, random copolymers, and various other architectures.[11]

2. Theory

2.1. Solution of the Linear Copolymer Problem. The copolymer problem can be solved using a method developed previously[6] to solve the homopolymer problem. The copolymer is confined to M parallel layers labeled 1 to M. We use a lattice of coordination number z such that $za/2$ of the nearest-neighbor bonds are away from the surface, $za/2$ are toward the surface, and $z(1 - a)$ are parallel to the surface. Thus, in a three-dimensional cubic lattice, for example, $a = 1/3$, while in a three-dimensional body-centered-cubic lattice, $a = 1$. Let each of the copolymer molecules be identical; the sequence of A and B monomers in each molecule is identical. An A monomer has an energy of contact with surface 1 of $\Delta\epsilon_{A1}$ ($-\Delta\epsilon_{A1}/kT = \theta_{A1}$), and with surface M of $\Delta\epsilon_{AM}$ ($-\Delta\epsilon_{AM}/kT = \theta_{AM}$). Similar expressions hold for the B monomer. Contacts with the second to $M - 1$ layers are energetically neutral. There are no interactions of the monomers with each other, which is to say we ignore the excluded-volume problem as well as the collapse problem. For a homopolymer which is confined between two parallel plates a distance $M - 1$ apart but which can begin and end anywhere, we have[6] for the partition function Q_{N+1}

$$Q_{N+1} = \mathbf{U}^{\mathrm{T}}\mathbf{A}^{\mathrm{N}}\mathbf{P}(0) \tag{2.1}$$

where $\mathbf{U}^{\mathrm{T}}$ is the unit row vector (1, 1, ... 1), $\mathbf{P}(0)$ is the column vector ($e^{\theta_{A1}}$, 1, ... 1, $e^{\theta_{AM}}$), and the matrix A is

$$A(\theta_1,\theta_M) = \begin{vmatrix} (1-a)e^{\theta_{A1}} & {}^1\!/_2 a e^{\theta_{A1}} & & & & & & \\ {}^1\!/_2 a & 1-a & {}^1\!/_2 a & & & & & \\ & {}^1\!/_2 a & 1-a & {}^1\!/_2 a & & & & \\ & & {}^1\!/_2 a & 1-a & & & & \\ & & & & \ddots & & & \\ & & & & & 1-a & {}^1\!/_2 a & \\ & & & & & {}^1\!/_2 a & 1-a & {}^1\!/_2 a \\ & & & & & & {}^1\!/_2 a e^{\theta_{AM}} & (1-a)e^{\theta_{AM}} \end{vmatrix} \tag{2.2}$$

For a copolymer the only change is that the matrices **A** and **B** appear as a product in the same sequence as in the polymer. For example, suppose that we have $r - s$ A type monomer units followed by s B type and that this is repeated N times. The partition function for this block copolymer is

$$\mathbf{Q}_{N+1} = U^{\mathrm{T}}(\mathbf{A}^{r-s}\mathbf{B}^{s})^{\mathrm{N}}\mathbf{P}(0) \tag{2.3}$$

where the matrix **B** is just like **A** except that θ_B replaces θ_A. For large N only the largest eigenvalue λ of the

$$C(\theta_1,\theta_M) = \left(\begin{array}{lllll}
(1-a)e^{\theta_{A1}}Q(1,J) & {}^1\!/_2 a e^{\theta_{A1}}Q(1,J) & & & \\
{}^1\!/_2 aQ(2,J) & (1-a)Q(2,J) & {}^1\!/_2 aQ(2,J) & & \\
 & {}^1\!/_2 aQ(3,J) & (1-a)Q(3,J) & {}^1\!/_2 aQ(3,J) & \\
 & \cdot & & & \\
 & & \cdot & & \\
 & & \cdot & & \\
 & & (1-a)Q(M-2,J) & {}^1\!/_2 aQ(M-2,J) & \\
 & & {}^1\!/_2 aQ(M-1,J) & (1-a)Q(M-1,J) & {}^1\!/_2 aQ(M-1,J) \\
 & & & {}^1\!/_2 a e^{\theta_{AM}}Q(M,J) & (1-a)e^{\theta_{AM}}Q(M,J)
\end{array}\right) \qquad (2.8)$$

matrix $\mathbf{A}^{r-s}\mathbf{B}^{s}$ is of importance and the partition function is equal to

$$Q = \lambda^N \qquad (2.4)$$

By making r large and θ_B large compared to θ_A, we can investigate the effect of a few strong bonds on adsorption.

The fact that we are using a polymer between plates rather than a semiinfinite space (one plate) allows us to use the matrix method rather than the more cumbersome recurrence relation techniques. We effectively obtain the semiinfinite case by choosing θ_{AM} and θ_{BM} to be neutral and M large. This presents no difficulties, as we shall see in the numerical analysis section.

The extension to random copolymers is obvious. If a given sequence of mers in a random copolymer is ABAAB..., then the partition function for the copolymer is given by

$$Q\{\text{ABAAB...}\} = \mathbf{U}^{\mathrm{T}}\text{ABAAB...}\mathbf{P}(0) \qquad (2.5)$$

$Q\{s\}$ is the partition function for a mole of polymers with this exact sequence s = ABAAB.... Such polymers are often found in biological macromolecules but seldom in synthetic macromolecules. The more common occurrence in synthetic macromolecules is that a fraction f of A-mers and $1 - f$ of B-mers occur randomly in the polymers, with all sequences being possible. For this case the partition function is

$$Q = \prod_s [Q\{s\}] \qquad (2.6)$$

where the product is taken over all possible sequences s. For each sequence the matrix $\mathbf{A}$ must be replaced by the matrix $f\mathbf{A}$ and the matrix $\mathbf{B}$ by $(1 - f)\mathbf{B}$. This weights the chains correctly. The method of Lehman and Mctague,[5] or, equivalently, replica theory,[24] must be used to evaluate eq 2.6.

Obviously neither of the above can be solved analytically unless the matrices commute. Once the sequence is specified, eq 2.5 can be evaluated numerically. Because the matrices do not commute, we expect the results to be dependent on the sequence, not just on the relative numbers of A- and B-mers. A numerical Monte Carlo evaluation of the product in eq 2.6 is feasible.

2.2. Theory for Comblike Polymers. Suppose that for every r monomers we have a side group consisting of J monomers of energy of attraction for the surface of $\Delta\epsilon_C$. Then the partition function for the comblike polymer is given by

$$\mathbf{Q}_{N+1} = U^{\mathrm{T}}(\mathbf{A}^{r-1}\mathbf{C})^N\mathbf{P}(0) \qquad (2.7)$$

where $\mathbf{C}$ is given by eq 2.8.

$Q(m,J)$ is the partition function for a polymer of length J which is forced to start at level m. Each of its segments has an energy of interaction with the surface of value $\Delta\epsilon_C$. For small J it is best to write the functions down directly by means of recurrence relations.

$$Q(1,1) = z(1-a)e^{\theta_C} + za/2,$$
$$Q(2,1) = z(1-a) + zae^{\theta_C}/2 + za/2, \quad Q(3,1) = z$$
$$Q(1,2) = z(1-a)e^{\theta_C}Q(1,1) + Q(2,1)za/2$$
$$Q(2,2) = (zae^{\theta_C}/2)Q(1,1) + z(1-a)Q(2,1) + (za/2)Q(3,1)$$
$$Q(3,2) = (za/2)Q(2,1) + z(1-a)Q(3,1) + (za/2)Q(4,1) \qquad (2.9)$$

These equations relate an n-step partition function to an $(n-1)$-step partition function by taking a first step toward, parallel to, or away from a surface. The general recurrence term is obtained if we first define θ_m as the energy that a segment sees at level m. Then

$$Q(m,J) = (za/2)\exp(\theta_{c(m-1)})Q(m-1,J-1) + z(1-a)\exp(\theta_{cm})Q(m,J-1) + (za/2)\exp(\theta_{c(m+1)})Q(m+1,J-1) \qquad (2.10)$$

This equation includes all values of m and J if we let $Q(0,J) = Q(M+1,J) = 0$ and use eq 9 for $Q(m,1)$.

An interesting question is whether a comblike molecule gives a second-order or a first-order transition as the lengths of the branches are increased to infinity. We believe that for small branch length the effect is to broaden the transition, just as in the block copolymer. But for long branch lengths we expect the transition to become sharper and perhaps even first order.

It is obvious by an extension of the discussion at the end of section 2.1 that the backbone could be a block or random copolymer as described above and/or each graft could be different.

2.3. Theory for Star Polymers. Let $Q(i,m,N_i)$ be the partition function for the ith chain of the star, which consists of N_i segments and which begins at level m. Then the partition function for the star is

$$Q(\text{star}) = \sum_m \prod_i Q(i,m,N_i) \qquad (2.11)$$

Each arm of the star can be a homopolymer, a copolymer, or a comb polymer. The appropriate partition functions are obtained from eqs 1, 3, or 7, with the only additional feature being that $\mathbf{P}(0)$ is given by a column vector that has zero at every place except for the mth place which is given by $\exp(\theta_m)$.

2.4. Other Solvable Problems. By now the power of the matrix method should be evident. We describe here additional problems that are easily solved.

We can solve the problem of a polymer in an arbitrary field, $V(m)$, by multiplying each element of each row of the matrix by the Boltzmann factor $\exp(-V(m)/kT)$.

We can solve the constant force ensemble problem where a force f perpendicular to the plates is applied to the unattached end by multiplying each element of the mth row of the last matrix (only the last matrix) by $\exp(-fmd/kT)$, where f is the force and d is the layer spacing. We also choose $\mathbf{P}(0)$ so that the other end of the polymer is always fixed at some given level. This problem has recently been solved exactly in the continuum limit by Gorbunov and Skvortsov,[25] who note that their exact solution violates the analyticity assumptions usual to the Landau model.

We can solve the problem of a copolymer at the interface of two liquids by modifying the two matrices **A** and **B** as follows. Multiply each element of the upper $M/2$ rows of matrix **A** by $\exp(-\Delta\epsilon_{\mathrm{AU}}/kT)$ and the elements of the lower rows by $\exp(-\Delta\epsilon_{\mathrm{AL}}/kT)$. Similarly for matrix **B** we use $\exp(-\Delta\epsilon_{\mathrm{BU}}/kT)$ and $\exp(-\Delta\epsilon_{\mathrm{BL}})$.

Excluded volume can be taken into account by a procedure previously published and used successfully for star molecules as well as for linear polymers.[26]

3. Numerical Analysis of the Many Weak Bond–Few Strong Bond Case: Linear Copolymer System

The above development allows a variety of models on which we could calculate detailed results. However, since we are interested in the SBSB model, we shall consider in the remainder of this paper a model of a copolymeric chain with one single strong bond of energy $\Delta\epsilon_{\mathrm{s}}$ ($\Theta_{\mathrm{s}} = -\Delta\epsilon_{\mathrm{s}}/kT$) and $r - 1$ weak bonds of energy $\Delta\epsilon_{\mathrm{w}}$ ($\Theta_{\mathrm{w}} = -\Delta\epsilon_{\mathrm{w}}/kT$) all repeated N times. For the infinite molecular weight calculations, we need only obtain the largest eigenvalue, λ, of the matrix $\mathbf{A}^{r-1}\mathbf{B}$ from which all thermodynamic information is obtained. The number of weak bonds per segment $\langle n_{\mathrm{w}}\rangle$, or the number of strong bonds per segment $\langle n_{\mathrm{s}}\rangle$, is given by

$$\langle n_i\rangle = (1/r)\,\mathrm{d}\ln(\lambda)/\mathrm{d}\Theta_i \tag{3.1}$$

where i = s or w. The average energy per segment is given by

$$(1/r)kT^2\,\mathrm{d}\ln(\lambda)/\mathrm{d}T = \langle n_{\mathrm{s}}\rangle\Delta\epsilon_{\mathrm{s}} + \langle n_{\mathrm{w}}\rangle\Delta\epsilon_{\mathrm{w}} = \langle E\rangle \tag{3.2}$$

Equivalently, $\langle n_{\mathrm{s}}\rangle\Theta_{\mathrm{s}} + \langle n_{\mathrm{w}}\rangle\Theta_{\mathrm{w}} = \langle E\rangle/kT$. These three formulas are derived by writing the partition function as

$$Q = \lambda^N = \sum W(n,m)\,(\mathrm{e}^{\Theta_{\mathrm{s}}})^n(\mathrm{e}^{\Theta_{\mathrm{w}}})^m \tag{3.3}$$

where n and m are the numbers of strong and weak contacts with the surface, and then performing the indicated differentiations. Earlier work on adsorption of the homopolymer in the two-plate system by Di Marzio and Rubin[6] showed a second-order phase transition behavior for infinite plate separation when the value of the Θ reached $U/kT^* = 0.18232$, T^* being the transition temperature for the three-dimensional cubic lattice system, but the curves were not highly structured. As we shall now see there is much more structure to the copolymer system.

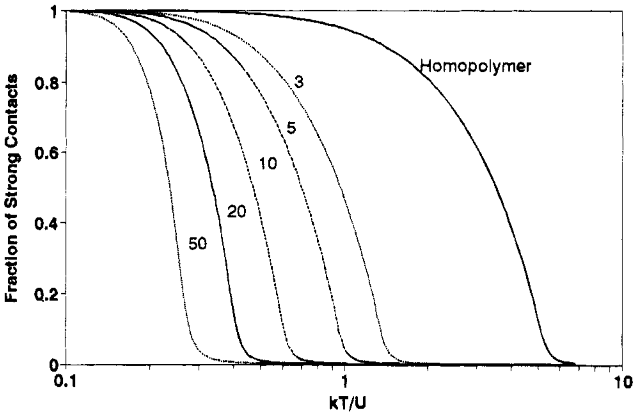

Figure 1. Adsorption profile of an infinitely long block copolymer consisting of $r - 1$ weak bonds alternating with one strong bond. The adsorption is onto the interior surfaces between two infinite parallel plates located at layers 1 and 50 in a simple cubic lattice. The weak monomers have a zero energy of attraction for the surfaces, while the strong monomer has an energy of U for each surface. The ordinate is the fraction of the strong monomers that are adsorbed, and the abscissa is temperature. The curves are labeled by $r - 1$ values.

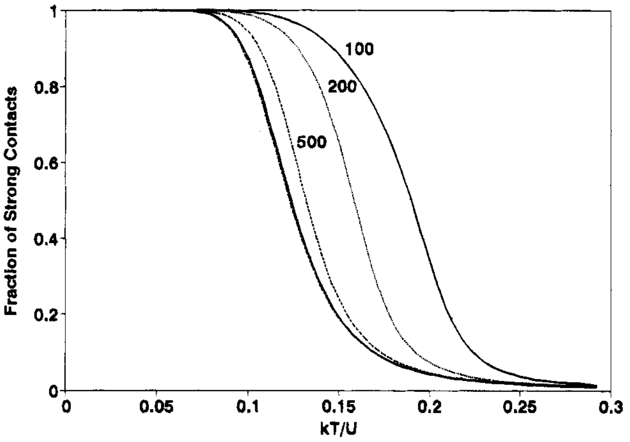

Figure 2. Same as Figure 1 but different $r - 1$. The unlabeled line is for $r - 1$ = 1000, 2000, and 4000.

3.1. Case of $\Theta_{\mathrm{w}} = 0$. 3.1.1. Transition Behavior. For our first calculations we consider the case of zero adsorption energy for the weak bond, while that of the strong bond is given by Θ_{s}. Figure 1 gives the fraction of the strong bonds attached to the surface, $r^{-1}\,\langle n_{\mathrm{s}}\rangle$, versus kT/U for the following values of $r - 1$ and the homogeneous chain, 3, 5, 10, 20, and 50. The wall separation, M, is 50. Figure 2 continues the $r^{-1}\langle n_{\mathrm{s}}\rangle$ versus kT/U display of data for the homogeneous chain and $r - 1$ = 100, 200, 500, 1000, 2000, and 4000. The wall separation, M, is again 50.

We define the transition temperature as the intercept of the line of maximum slope with $\langle n_{\mathrm{t}}\rangle = 0$. The homogeneous chain has a true transition temperature of second-order in the Eherenfest sense. This means that there is a discontinuity in slope of the extensive variables, E, S, and V. But this occurs only for infinite plate separation;[6,27] for finite plate separation the transition is rounded as the curve for the homogeneous chain in our first two figures indeed shows.

There is an interesting progression of the transition temperature as the number of weak type monomer units increases. We wish to understand it. In Figure 3 we

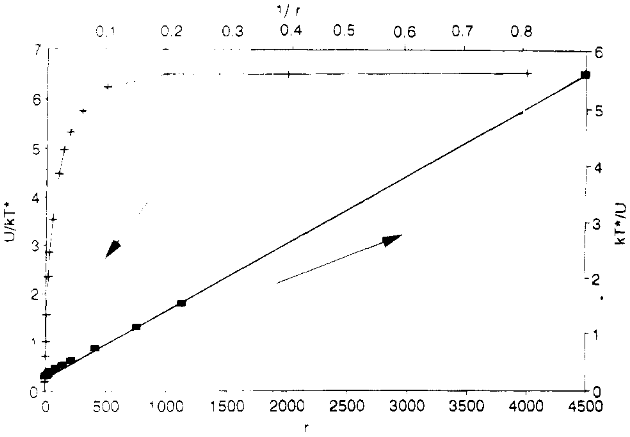

Figure 3. Plot of the scaled transition temperature T^*/kU versus $r - 1$ obtained from the first two figures. The lower plot shows that an average energy approximation (see text) is valid for small r, while the upper curve shows that this approximation fails for large r.

plot the transition temperature kT^*/U vs number of monomers in the A-block, r, in two ways. The upper curve is for U/kT^* vs r, while the lower curve plots kT^*/U vs r^{-1}. Two simple models are envisioned to mimic this system; the first is for low values of r the second for its higher values.

The simplest form of a mean-field model for a system with $r - 1$ weak bonds and one strong bond is a homogeneous model with an average energy of $(\Delta\epsilon_s + (r - 1)\Delta\epsilon_w)/r$. For $\Delta\epsilon_w = 0$, on a cubic lattice, the transition temperature of this model in which each segment has $1/r$ of the energy is

$$r/\Theta_s = 5.48 \qquad (3.4)$$

Thus, a plot of the transition temperature as a function of $1/r$ should yield a straight line with slope 5.48. The bottom curve of Figure 3 shows $1/r$ versus kT^*/U; the slope on this curve is 5.32, quite close to the correct value. In this plot the small r are emphasized and we can say that we explain the small r region adequately. However, the plot of U/kT^* versus r as in the upper curve of Figure 3 does not show a straight line. This plot emphasizes large values of r. Thus we would suggest for small r a mean energy model is sensible. But as r becomes large the mean energy model, as expected, fails.

Another estimate of the transition temperature can be made by use of the zippering–unzippering model treated in Appendix A. If we treat the one adsorbed strong bond plus the $r - 1$ weak bonds as the basic zippering–unzippering unit, then the transition temperature which would occur in the ordinary zippering–unzippering model at $x = z \exp(-\Delta\epsilon/kT^*) = 1$ now occurs at

$$x = (z^2 r^{3/2}) \exp(-\Theta_s^*) = 1 \qquad (3.5)$$

where we have written $(z^r r^{-3/2})$ for the number of configurations of a loop in the continuum approximation.[28] We expect this value for the loop to be valid for large r which is where we shall use it. In pulling a loop off of a surface we go from $(z^r r^{-3/2})$ configurations to z^{r+2} configurations. In Figure 4 we show a plot of U/kT^* versus $\ln(r)$ for three separate wall conditions. The bottom curve and the top curve are for plate separations of 50 and 150, respectively. The middle curve is for a plate separation of 50, but one of the plates has zero adsorption energy for each kind of segment.

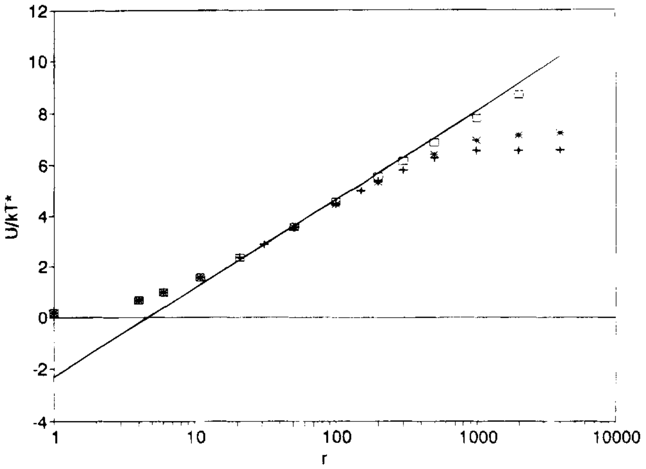

Figure 4. Plot of the transition temperature versus $\ln(r)$. The plate separation is 50 (lowest curve) and 100 (highest curve). For the middle curve the plate separation is 50, but the strong monomer is attracted only to the bottom plate. For all three curves the ratio of weak to strong energies is zero. An explanation of the logarithmic dependence of $T^*(r)$ for moderate to large r is given in the text.

We have also plotted the straight line representing eq 3.5. The slope of the straight line best representing the data for moderate r is 1.22 instead of the expected 1.5. The agreement is surprisingly good considering the simplicity of the model.

We should also like to explain why the transition temperature becomes independent of r for very large r. The fact that the leveling off occurs later with larger plate separation suggests that the formula for the number of configurations of a loop becomes independent of r for extremely large r. This is the case, since the configurations of segments in the interior of the loop are completely unaffected by the location of the ends. We would expect that the value of r at which leveling off begins is proportional to the square of the plate separation. Summing up, we see that we have arrived at a semiquantitative understanding of the $kT^*(r)/U$ curves over the complete range of r.

3.1.2. Number of Weak Contacts per Strong Contact. We again consider the case of $\Delta\epsilon_w = 0$. We count how many monomer units of the weak type lie on the surface. At temperatures much lower than the transition temperature all the strong type monomers are bound to the surface. We wish to know how many of the weak monomers adjacent to the strongly bound monomers along the chain are pulled down to the surface. Because the interaction of the weak bonds is zero, a first expectation would be that few or none are at the surface. Figure 5 shows the number of weak bonds per strong bond as a function of r for separations of 50 and 150. We see that as r gets larger the number of weak bonds per strong bond approaches a fixed value at about 10 weak bonds per strong bond. We notice this result holds well beyond $r = 500$, the r at which the transition temperature for the separation of 50 has come to a constant. This value of 10 weak bonds per strong bond is independent of plate separation for large plate separation since the result at a separation of 150 steps is identical to that at 50 steps.

The cause of this may be seen from a very simple model. For each strong monomer bound to the surface the probability that a few adjacent or near-adjacent weak monomers touch the surface is very high. This

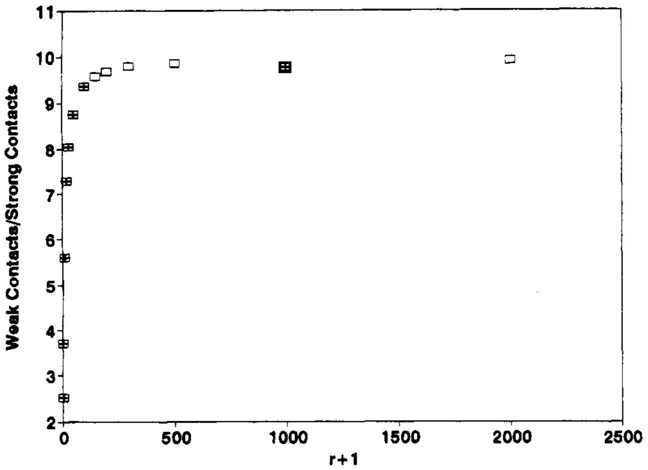

Figure 5. Ratio of the number of weak segment contacts with the surface to strong segment contacts at low temperatures (or large U) versus $r - 1$. For large loop sizes each strong bond pulls down 10 weak segments onto the surface. (□) $M = 50$; (+) $M = 150$. See text for explanation.

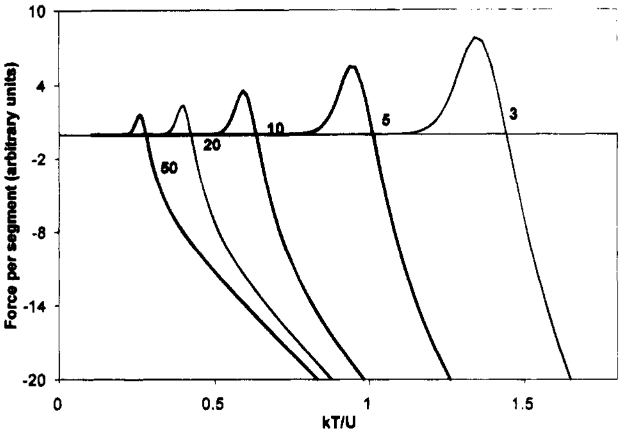

Figure 6. Force between plates versus temperature versus r at a plate separation of 50. Positive force corresponds to plate attraction. For large T the confinement entropy pushes the plates apart. As the temperature is lowered, bridges form between the plates pulling them together. As the temperature is lowered further, the ratio of bridges to loops gets very small, resulting in a maximum in the attractive force. See text for a more detailed explanation of these curves.

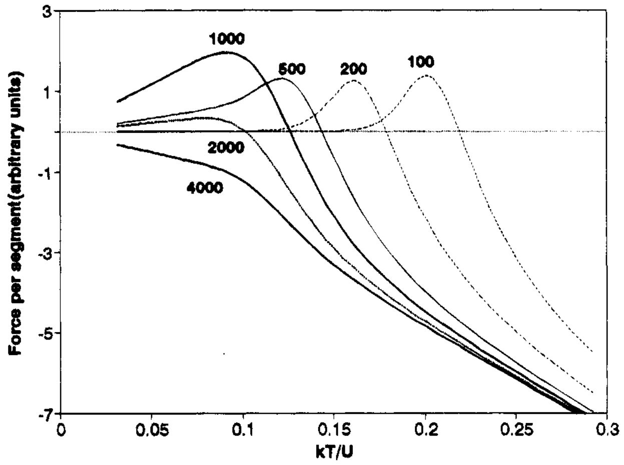

Figure 7. Force between plates versus temperature for various $r - 1$ at a plate separation of 50, but for other values of $r - 1$. At extremely large r the force is always repulsive because for large r even a bridge pushes the plates apart.

can be easily seem by drawing out the first few graphs for a chain terminally attached to the surface. Clearly most of the first few steps from the attached segment are on the surface. A simple model which allows us to calculate the number of attached week monomers is as follows. The probability that a chain remains on the surface rather than walks freely is given by

$$Z = p + p^2 + p^3 \ldots = \sum p^j \qquad (3.6)$$

where p is $4/5$ for the cubic lattice. That is, the probability that the first segment is on the surface is $4/5$. Of those steps $4/5$ of those remain on the surface, etc. Thus, $Z = p/(1 - p)$, and

$$\langle n_w \rangle = p \, \mathrm{d} \ln(Z)/\mathrm{d}p = 1/(1 - p) = 5 \qquad (3.7)$$

for a cubic lattice.

For two walks from each adsorbed strong segment we get 10 steps which is close to the asymptotic value in Figure 5. Thus, the model shows us the local structure we should expect around a single strong bond. This effect is expected to be increasingly important for combs and stars.

3.1.3. Force on the System with $\Delta\epsilon_w = 0$. We defined the force, f, as

$$f = \mathrm{d}F/\mathrm{d}M \qquad (3.8)$$

where F is the free energy per segment. This force between the plates is positive when the plates pull together. Figures 6 and 7 show the force per segment with $\Delta\epsilon_w = 0$ at $M = 50$ for various r as a function of kT/U. There is an interesting richness of structure.

For all r except $r \geq 1000$ the curves have the same general shape which we now explain by reference to the $r = 3$ curve. At temperatures much lower than the transition temperature the force is zero since all the chains are adsorbed onto one wall. There are no bridges because this would imply unattached strong monomers which is energetically forbidden at small T. As kT/U increases, bridges between plates (ties) form which create a force pulling the plates together. Positive force in this sense favors pulling the plates together. This positive force reaches a maximum due to the increasing importance of the entropy contribution to the force which acts to push the plates apart (negative force). This negative force can be viewed as due to a thermal bombardment on the walls from the segments unattached to the walls. As the entropy contribution becomes more negative, the force becomes zero near the transition point, kT^*/U, and finally goes negative. At very large temperatures the entropy contribution $-T\,\partial S/\partial M$ becomes linear in T. We note we have calculated the force on a chain with no attachments allowed on one of the two walls and found there is no positive force at all. We find only the negative forces for this case. This supports our argument that bridges cause the positive force.

The value of the maximum force decreases as r increases simply because of the dilution effect of the strong bonds. If there were no strong bonds, there would be no positive force at all. For very large $r = 4000$ the force is always negative because even bridges exert a negative force, tending to force the plates apart. When the dilution effect reduces the number of strong bonds, we can expect that the number of bridges to loops is proportionally higher. Thus it is conceivable that these two effects cause a shallow minimum in the value of the maximum force.

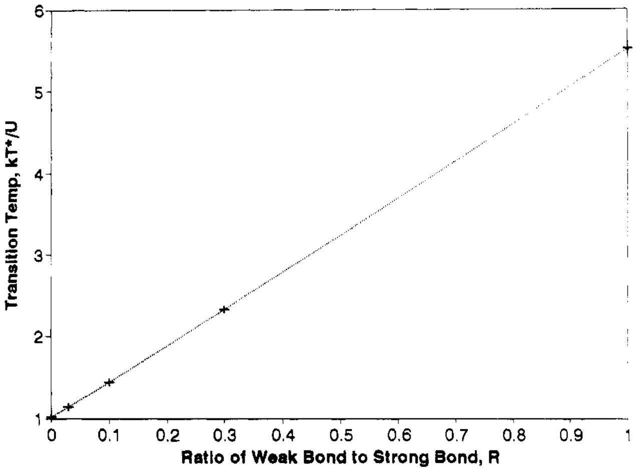

Figure 8. Transition temperature for various ratios of weak to strong segment adsorption energy, R, for the value of $r - 1 = 5$. For this small value of r compared to the plate separation, $M = 50$, the plot shows that we have a mean-field model to explain the phase behavior of these systems. The line fit through the data in this figure has slope of 4.50 compared to the one predicted by mean field of 4.58 and a constant of 0.997 compared to the predicted value of 0.917.

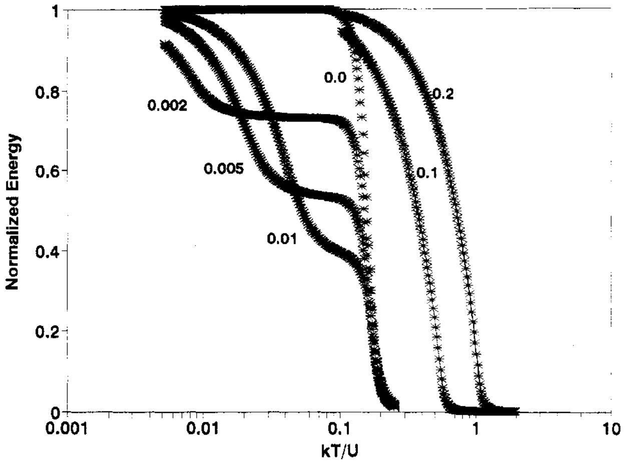

Figure 9. Normalized energy of absorption versus the temperature for various values of the ratio of the weak to strong segment absorption energy, R, for a plate separation of $M = 200$. Values of R are shown on figures near the curves. For R near 1 we see a single transition. As R get smaller, we get two transitions. For small R the transition at the highest temperature is identical to that at $R = 0$.

Thus we have explained qualitatively (1) the general shape of the force curve and (2) why there is a decrease in the maximum force with increasing r. We really do not have a feel for the existence of the minimum in the maximum force at about $r = 200$ but have pointed out two opposing effects which could be its cause.

3.2. Effect of Nonzero $\Delta\epsilon_w$ on the Shape of the Transition Curves. From our earlier studies on $\Delta\epsilon_w = 0$ we found that for small r compared to the plate separation, M, a mean-field model worked to explain the transition point data. As we vary the ratio of the weak to the strong energy ($R = \Delta\epsilon_w/\Delta\epsilon_s$) for small r compared to M, we see only a single transition and that transition is approximated by a mean-field model of the system. In Figure 8 we show the plot of the transition temperature versus $\Delta\epsilon_w$. This plot is linear in $\Delta\epsilon_w$ and verifies the mean-field approach for small r.

For r much larger than M, shown in Figure 9, we show two different effects. For R near 1 we have a single transition. However, for small R the adsorption curves are highly structured. There is a plateau which can be raised or lowered, depending on the ratio of the energies. The value of the plateau can be estimated by assuming that the weak and strong transition are independent of each other. For a normalized energy, the plateau should occur at $1/(r^*R + 1)$. For $R = 0.005$ and $r = 200$ in Figure 9 the plateau occurs at 0.538 and is predicted by the assumption of complete independence to occur at 0.5. For $R = 0.002$ the predicted plateau is at 0.73, while the actual value is at 0.71. The strong transition occurs at the value of the transition for the transition of the $\Delta\epsilon_w = 0$ case found in section 3.1.1. The transition due to the weak bonds seems to be controlled by the value of the weak bond itself.

The highly structured region seems to occur when the total mean-field transition temperature becomes less than the transition found for $R = 0$ in section 3.1.1. This structure is thus a result of the decoupling of the weak and strong transition.

The general features of these curves are very similar to those of DNA which also shows a double plateau when it is treated as a copolymer with differing C−G and A−T hydrogen bond energies. Montroll and Goel[29] were able to vary the plateau level widely by varying the relative number of C−G and A−T pairs and their energies.

4. Results and Discussion

We have obtained formulas for the adsorption of copolymers, combs, and stars between plates. The copolymers can be random or block, as can also the arms of the combs or stars. Our matrix method is easily adapted to the computer, and we have obtained numerical results for linear block copolymers. The adsorption curves display a surprising amount of structure which have important physical consequences.

First, the modeling of a copolymer by a homopolymer with an adsorption energy that is *any* kind of average of the copolymer adsorption energies *cannot* reproduce the adsorption curves for copolymers. This means that one is forced to consider the copolymer case in its own right—one cannot reduce the two-parameter adsorption energy space to just one. It also means that mean-field methods for bulk copolymer systems should pay more careful attention to the proper incorporation into the theory of the properties of the isolated copolymer. Further, a third energy corresponding to chain stiffness can be introduced as was done for the polymer ring problem.[7] The implications of this energy cannot be ignored.

Second, as a quick perusal of the figures shows, there is a highly significant structure in the adsorption curves for block copolymers. When we add to this observation the observation that random copolymers will have their own different significant structure, as will also comb and star molecules, then we can expect that the adsorption profiles themselves can be used to infer the architecture. Thus, we can at least hope that the experimental results from various chromatographic techniques can be used to infer molecular architecture.[9] A recent preprint applies our methods to chromatography near the adsorption transition.[10]

Both of these consequences are at present largely unexplored.

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5. Appendix A

5.1. Theory of the Zippering a Copolymer off of a Line. In this paper we have approached the adsorption problem of copolymers from the matrix method of Di Marzio and Rubin. One may consider the much simpler problem of the zippering and unzippering of a copolymer off a line. In a previous paper the authors considered the zippering–unzippering transition for a homopolymer and were able to get some insights into hydrogen-bonded systems.[1] We will now examine unzippering in copolymer systems.

Let us first consider a copolymer that has the sequence $r - 1$ monomers of type A and one monomer of type B, repeated N times. The end B unit is fixed to the surface and the remainder of the chain can zipper off of the surface one unit at a time, beginning at the end. It zippers down onto the surface by reversing the process. There are no loops in the unzippering model. If z is the freedom gained and $\Delta\epsilon$ is the energy lost when a type A monomer is desorbed, $x = z\exp(-\Delta\epsilon_A/kT)$, and similarly for type B monomer, $x_B = z_B\exp(-\Delta\epsilon_B/kT)$. Then if we zipper the copolymer off of a surface or a line, then the partition function Q is

$$\begin{aligned}Q &= 1 + x + x^2 + x^3 \ldots + x^{r-1} + x_B x^{r-1}(1 + x + x^2 + \\ &\quad x^3 \ldots + x^{r-1}) + (x_B x^{r-1})^2(1 + x + x^2 + x^3 \ldots + x^{r-1}) \\ &= (1 + x_B x^{r-1} + (x_B x^{r-1})^2 + \ldots) \times \\ &\qquad (1 + x + x^2 + x^3 \ldots + x^{r-1}) \\ &= (1 + x_B x^{r-1} + (x_B x^{r-1})^2 + \ldots)\{(1 - x^r)/(1 - x)\} \\ &= \{(1 - (x_B x^{r-1})^N)/(1 - x_B x^{r-1})\}\{(1 - x^r)/(1 - x)\} = \\ &\qquad Q(\text{A at end})\end{aligned}$$

which shows two transitions rather than just one first-order transition as in the homopolymer case.

A second easily solved problem is when both end monomers are of the B type, one of which is attached permanently to the surface, so that a B monomer is the first to peel off. Then we obtain

$$\begin{aligned}&Q(\text{B at end}) = \\ &\quad 1 + x_B\{(1 - (x_B x^{r-1})^N)/(1 - x_B x^{r-1})\}\{(1 - x^r)/(1 - x)\}\end{aligned}$$

which shows distinctly different behavior from the case where the free end begins with an A.

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