Macromolecules 1988, *21*, 1411–1421

Microscopic Structure and Thermodynamic Properties of Bulk Copolymers and Surface-Active Polymers at Interfaces. 1. Theory

Doros N. Theodorou

Department of Chemical Engineering, University of California, Berkeley, California 94720, and Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720. *Received May 27, 1987; Revised Manuscript Received October 23, 1987*

ABSTRACT: A lattice model is developed for the quantitative description of the interfacial behavior of bulk polymers, consisting of two types of segments, with different affinity for the surface. The model is an extension of previous work on bulk homopolymers[1] and is inspired by Scheutjens and Fleer's[2] formulation for polymer solutions. Techniques are introduced for the exploration of microscopic structural characteristics (chain conformation, bond orientation) and macroscopically observable thermodynamic properties (interfacial tension, surface tension). The approach is general and can be used for bulk systems of any degree of polymerization, any proportion and sequence of the two types of segments along the chains, and any relative affinity of these segment types for the surface. Applications to block and random copolymers and to systems of flexible molecules with a surface active head are described in an accompanying paper.

Introduction

Understanding the microscopic structure and thermodynamic properties of bulk polymers and copolymers at interfaces with solid or gaseous phases is a prerequisite for the optimal design of composite materials, adhesive systems, and surfaces with controlled wetting properties. Specific interactions and entropic constraints present at an interface cause the conformation of chains, hence local values of mechanical and thermodynamic properties, to deviate from those of the isotropic polymer bulk. Quantitatively describing interfacial structure and properties as a function of the chemical architecture of constituent chains is a very desirable goal.

In preceding papers[1] we examined the mathematical structure of lattice models, a particularly simple category of models that, nevertheless, can adequately represent the salient features of structure and thermodynamic properties of polymers at interfaces. A site model for bulk homopolymers, based on Scheutjens and Fleer's formulation for solutions,[2] was derived and used to explore bond orientation characteristics and interfacial tension.

Here we extend our site lattice model approach to the case of bulk polymers consisting of two different types of segments that can interact differently with the surface. The model is cast into a generalized form, applicable for any chain length, any proportion and sequence of the two types of segments along the chain, and any relative affinity of these segment types for the surface. A robust algorithmic procedure is developed for its numerical solution.

The objective of this paper is to present the theoretical analysis, leading to a set of equations that describe the interfacial characteristics of a bulk system of chains, composed of two types of segments, arranged in a given sequence. Techniques introduced in ref 1 for the quantitative exploration of bond orientation as a function of distance from the interface are refined and extended. A new method is developed for the exploration of chain shape and size characteristics in the interfacial region. Also, an expression is derived for the interfacial energy in terms of molecular characteristics (chain size and composition, segment–segment and segment–surface interaction energies). Application of the model to some representative chain architectures will be the subject of an accompanying paper.

Formulation of the System of Equations. We consider a monodisperse linear polymer, whose chains consist of two types of segments, A and B, arranged in a given sequence. Let r_A (r_B) be the total number of A (B) segments per chain. The total chain length will then be equal to

$$r = r_A + r_B \tag{1}$$

A directionality is defined along a chain, by choosing one of its ends as the start and numbering segments successively from 1 to r. The choice of the start segment is essentially arbitrary but consistent for all chains in a given bulk system, which are assumed identical. By "chain structure" or "chain architecture" we mean the sequence of segment types

$$\{t(s)\} \qquad 1 \le s \le r \tag{2}$$

for all segments, taken successively in the forward direction; $t(s)$ can assume the values of A or B.

Our theoretical development is based on the lattice model system introduced in ref 1. A bulk copolymer phase is envisioned, between two identical infinite plane surfaces. Local structure is assumed to vary from layer to layer along the z-direction. We focus on a portion of the interfacial system, having L sites on each layer. If $M = 2m$ is the total number of layers between the surfaces, average properties in the system are symmetric with respect to the midplane between layers m and $(m + 1)$. In this work the number of layers M is taken sufficiently large, relative to the chain length, r, so that the polymer in the central region between the two surfaces is indistinguishable from the unconstrained bulk. The model is then representative of a semiinfinite domain of bulk polymer adjacent to a single plane surface. Following ref 2 and 1 we define a conformation c by the ordered sequence of layer numbers, in which successive chain segments find themselves:

$$\{k(s,c)\} \qquad 1 \le s \le r \tag{3}$$

There are a number of different chain arrangements in the lattice corresponding to the same conformation, given by

$$Lz^{r-1} \prod_{s=1}^{r-1} (\lambda_{s,s+1})_c = Lz^{r-1}\omega_c \tag{4}$$

where

$$\begin{aligned}(\lambda_{s,s+1})_c &= \lambda_0, \quad \text{if} \quad k(s,c) = k(s+1,c) \\ &= \lambda_1, \quad \text{if} \quad |k(s,c) - k(s+1,c)| = 1\end{aligned} \tag{5}$$

All calculations in this paper will refer to a simple cubic lattice, for which $\lambda_0 = {}^2/_3$, $\lambda_1 = {}^1/_6$.

The total number of chains in the considered model system, n, is related to the numbers of chains in each conformation by the balance condition:

0024-9297/88/2221-1411$01.50/0

$$n = \sum_c n_c \tag{6}$$

Our lattice model rests on the following assumptions.

(I) Full occupancy of the lattice by chain segments is assumed. Segment density variations in the direction perpendicular to the surface, as well as density fluctuations within the bulk polymer phase, are ignored. This assumption, introduced for simplicity, can be readily relaxed, as will be discussed in a subsequent publication. Mathematically it is expressed as

$$L = \sum_c r_{i,c} n_c \tag{7}$$

(II) The Bragg–Williams approximation of random mixing is employed for estimating configurational entropy in the multichain polymer system. To obtain the number of ways in which a given set of conformations $\{n_c\}$ can be arranged on the lattice, a Flory process of filling the lattice by sequential placement of chains in a segment by segment fashion is envisioned.[1] At each step of this filling procedure all sites within a given layer have the same probability of accommodating an added segment; this probability is equal to the fraction of unoccupied sites in the considered layer.

(III) In calculating the potential energy for a given configuration of the lattice model system, only nearest-neighbor interactions between segments and between segments and the surface are considered. There are three characteristic segment–segment interaction energies (w_{AA}, w_{AB}, w_{BB}) and two characteristic adsorbed segment–surface interaction energies (w_{AS}, w_{BS}). Segment–segment interactions are active both between nonbonded and between bonded segments.

(IV) Whatever their chemical architecture may be, polymer chains are considered as flexible, freely jointed sequences of segments.

(V) All interfacial systems we examine in this work are assumed to be in thermodynamic equilibrium with an unconstrained bulk polymer phase of infinite extent. The unconstrained bulk polymer is taken as completely homogeneous and isotropic. This implies that the interaction energies w_{AA}, w_{AB}, and w_{BB} are sufficiently close, so that phenomena of phase separation, development of micellar structures, or any other kind of molecular organization in the bulk are not favored (see below).

Choosing the unconstrained bulk polymer as a reference state, we write the value of the partition function of our interfacial lattice model system, for a given set $\{n_c\}$ of conformations,[1] as a product of an entropic (combinatorial) and an energy (residual) term

$$Q[M,L,T,\{n_c\}] = (\Omega/\Omega^*)\, e^{-U/kT} \tag{8}$$

where Ω is the number of ways of arranging the considered set of conformations $\{n_c\}$ on the lattice in the interfacial system, Ω^* is the number of ways of arranging n chains on the lattice in the bulk polymer, and U is the potential energy of the interfacial system under the set of conformations $\{n_c\}$, relative to a system of n chains in the unconstrained bulk:

$$U = U_{\text{interf}}[\{n_c\}] - U_{\text{bulk}}(n) \tag{9}$$

The combinatorial term in expression 8 is evaluated by a Flory procedure of laying chains one by one in the lattice. Since it is only the connectivity, and not the chemical architecture of chains, that plays a role in this procedure, the analysis presented in ref 1 for the case of a homopolymer is valid here, leading to the expression

$$\ln\,[\Omega/\Omega^*] = n \ln\left[\frac{n}{M}\right] - \sum_c n_c \ln\,[n_c/\omega_c] \tag{10}$$

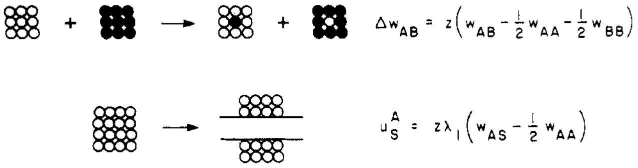

Figure 1. Physical meaning of the interchange energy Δw_{AB} and the adsorption energy $u_S{}^A$.

Let φ_{Ai} (φ_{Bi}) symbolize the volume fraction of type A (type B) segments in layer i. By assumption I,

$$\varphi_{Ai} + \varphi_{Bi} = 1 \qquad 1 \le i \le M \tag{11}$$

Moreover, an overall segment balance demands

$$L\sum_{i=1}^{M} \varphi_{Ii} = n r_I \qquad I = A, B \tag{12}$$

We define the site volume fractions[2] $\langle\varphi_{Ai}\rangle$ and $\langle\varphi_{Bi}\rangle$ by

$$\langle\varphi_{Ii}\rangle = \sum_{j=1}^{M} \lambda_{j-i}\varphi_{Ij} \qquad 1 \le i \le M;\ I = A, B \tag{13}$$

where

$$\begin{aligned} \lambda_{j-i} &= \lambda_{|j-i|} && \text{for } |j-i| \le 1 \\ &= 0 && \text{for } |j-i| > 1 \end{aligned} \tag{14}$$

As a result of the above definitions,

$$\langle\varphi_{Ai}\rangle + \langle\varphi_{Bi}\rangle = 1 - \lambda_1(\delta_{i1} + \delta_{iM}) \tag{15}$$

The potential energy U, under a given set of conformations $\{n_c\}$, is obtained in a mean-field approximation, by an enumeration of interacting segment pairs in the interfacial system, as well as in the unconstrained bulk polymer, which we use as a reference. A detailed derivation is presented in Appendix A. The result is

$$U = LkT\chi\left(\sum_{i=1}^{M}\varphi_{Ai}\langle\varphi_{Bi}\rangle - \frac{nr_Ar_B}{Lr}\right) + L[(\varphi_{A1} + \varphi_{AM})u_S{}^A + (\varphi_{B1} + \varphi_{BM})u_S{}^B] \tag{16}$$

where the χ factor has been defined as a dimensionless "interchange energy"[3,4] between segments A and B,

$$\chi = \frac{\Delta w_{AB}}{kT} = \frac{z}{kT}\left[w_{AB} - \frac{1}{2}w_{AA} - \frac{1}{2}w_{BB}\right] \tag{17}$$

and the absorption energy $u_S{}^I$ is the energy required for splitting a hypothetical pure fluid of type I segments to create two interfaces per site on the interfaces created (see Figure 1):

$$u_S{}^I = z\lambda_1\left[w_{IS} - \frac{1}{2}w_{II}\right] \qquad I = A, B \tag{18}$$

From (8), (10), and (16) one obtains for the partition function Q:

$$\ln Q[M,L,T,\{n_c\}] = n \ln\left[\frac{n}{M}\right] - \sum_c n_c \ln\left[\frac{n_c}{\omega_c}\right] - L\chi\left(\sum_{i=1}^{M}\varphi_{Ai}\langle\varphi_{Bi}\rangle - \frac{nr_Ar_B}{Lr}\right) - L\left[\frac{u_S{}^A}{kT}(\varphi_{A1} + \varphi_{AM}) + \frac{u_S{}^B}{kT}(\varphi_{B1} + \varphi_{BM})\right] \tag{19}$$

According to assumption V all chains in the interfacial system must have the same chemical potential, equal to the chemical potential of the polymer in the unconstrained bulk. As shown in ref 1, this implies that ln Q must remain invariant under changes in the configuration of the interfacial system that modify the occupancy of some conformational categories. The quantity $\ln Q$ must be at a *maximum* with respect to the distribution of conformations $\{n_c\}$, under the full occupancy constraints (7):

$$G_i[\{n_c\}] \equiv \sum_c [r_{\mathrm{A}i,c} + r_{\mathrm{B}i,c}]n_c - L = 0 \qquad (20)$$

The quantities $r_{\mathrm{I}i,c}$ in eq 20 stand for the numbers of I-type segments that conformation c has in the i-th layer. They are related to volume fractions via the balance conditions

$$\sum_c r_{\mathrm{I}i,c}n_c = L\varphi_{\mathrm{I}i} \qquad \mathrm{I} = \mathrm{A, B} \qquad (21)$$

Introducing a Lagrange multiplier ζ_i for each constraint of the type (20) we require that the function

$$F = \ln Q[M,L,T,\{n_c\}] - \sum_{i=1}^{M} \zeta_i G_i[\{n_c\}] \qquad (22)$$

have a stationary point with respect to the conformation distribution $\{n_c\}$ at equilibrium. This implies

$$\left.\frac{\partial F}{\partial n_c}\right|_{M,L,T,n_d \neq n_c} = \left.\frac{\partial \ln Q}{\partial n_c}\right|_{M,L,T,n_d \neq n_c} - \sum_{i=1}^{M} \zeta_i \left.\frac{\partial G_i}{\partial n_c}\right|_{M,L,T,n_d \neq n_c} = 0 \qquad \text{for all conformations } c \quad (23)$$

$$-\frac{\partial F}{\partial \zeta_i} = G_i[\{n_c\}] = \sum_c [r_{\mathrm{A}i,c} + r_{\mathrm{B}i,c}]n_c - L = 0 \qquad (20)$$

From eq 19, taking into account eq 21,

$$\left.\frac{\partial \ln Q}{\partial n_c}\right|_{M,L,T,n_d \neq n_c} = -\ln\left[\frac{n_c}{\omega_c}\right] - 1 - L\chi\left\{\frac{1}{L}\sum_{i=1}^{M} r_{\mathrm{A}i,c}\langle\varphi_{\mathrm{B}i}\rangle + \sum_{i=1}^{M}\varphi_{\mathrm{A}i}\sum_{j=1}^{M}\lambda_{j-i}\frac{r_{\mathrm{B}j,c}}{L}\right\} - L\left[\frac{1}{L}[r_{\mathrm{A}1,c} + r_{\mathrm{A}M,c}]\frac{u_{\mathrm{S}}{}^{\mathrm{A}}}{kT} + \frac{1}{L}[r_{\mathrm{B}1,c} + r_{\mathrm{B}M,c}]\frac{u_{\mathrm{S}}{}^{\mathrm{B}}}{kT}\right] = -\ln\left[\frac{n_c}{\omega_c}\right] - 1 - \chi[\sum_{i=1}^{M} r_{\mathrm{A}i,c}\langle\varphi_{\mathrm{B}i}\rangle + \sum_{i=1}^{M} r_{\mathrm{B}i,c}\langle\varphi_{\mathrm{A}i}\rangle] - [r_{\mathrm{A}1,c} + r_{\mathrm{A}M,c}]\frac{u_{\mathrm{S}}{}^{\mathrm{A}}}{kT} - [r_{\mathrm{B}1,c} + r_{\mathrm{B}M,c}]\frac{u_{\mathrm{S}}{}^{\mathrm{B}}}{kT} \qquad (24)$$

On the other hand,

$$\left.\frac{\partial G_i}{\partial n_c}\right|_{M,L,T,n_d \neq n_c} = r_{\mathrm{A}i,c} + r_{\mathrm{B}i,c}$$

Hence (23) becomes

$$-\ln\left(\frac{n_c}{\omega_c}\right) - 1 + \sum_{i=1}^{M} r_{\mathrm{A}i,c}[\chi_{\mathrm{S}}{}^{\mathrm{A}}(\delta_{i1} + \delta_{i\mathrm{M}}) - \chi\langle\varphi_{\mathrm{B}i}\rangle - \zeta_i] + \sum_{i=1}^{M} r_{\mathrm{B}i,c}[\chi_{\mathrm{S}}{}^{\mathrm{B}}(\delta_{i1} + \delta_{iM}) - \chi\langle\varphi_{\mathrm{A}i}\rangle - \zeta_i] = 0 \qquad (25)$$

where we have defined the dimensionless quantities $\chi_{\mathrm{S}}{}^{\mathrm{I}}$ as

$$\chi_{\mathrm{S}}{}^{\mathrm{I}} = -u_{\mathrm{S}}{}^{\mathrm{I}}/kT \qquad \mathrm{I} = \mathrm{A, B} \qquad (26)$$

Introducing the free segment probabilities for segment types A and B in layer i by the equations

$$\ln P_{\mathrm{A}i} = -\zeta_i + \chi_{\mathrm{S}}{}^{\mathrm{A}}(\delta_{i1} + \delta_{iM}) - \chi\langle\varphi_{\mathrm{B}i}\rangle = -\zeta_i + (\chi_s{}^{\mathrm{A}} + \lambda_1\chi)(\delta_{i1} + \delta_{iM}) + \chi\langle\varphi_{Ai}\rangle - \chi \qquad (27\mathrm{a})$$

$$\ln P_{\mathrm{B}i} = -\zeta_i + \chi_{\mathrm{S}}{}^{\mathrm{B}}(\delta_{i1} + \delta_{iM}) - \chi\langle\varphi_{\mathrm{A}i}\rangle \qquad (27\mathrm{b})$$

we can rewrite (25) as

$$\frac{n_c}{L} = \frac{1}{Le}\omega_c\prod_{i=1}^{M} P_{\mathrm{A}i}{}^{r_{\mathrm{A}i,c}}P_{\mathrm{B}i}{}^{r_{\mathrm{B}i,c}} \qquad (28)$$

This conformation distribution identifies the model as a site model.[1] By analogy to the pure homopolymer case,[1] we define the unnormalized conformation probability for conformation c as

$$P(r)_c = \omega_c\prod_{i=1}^{M} P_{\mathrm{A}i}{}^{r_{\mathrm{A}i,c}}P_{\mathrm{B}i}{}^{r_{\mathrm{B}i,c}} = \omega_c\prod_{s=1}^{r} P_{t(s),k(s,c)} \qquad (29)$$

The "chain probability" $P(r)$ is introduced as a normalization factor,

$$P(r) = \sum_c P(r)_c = nLe \qquad (30)$$

The (unnormalized) probability that the sth segment of a chain in conformation c finds itself in layer i is simply

$$\begin{aligned} P(s,i;r)_c &= P(r)_c, && \text{if } k(s,c) = i \\ &= 0, && \text{otherwise} \end{aligned} \qquad (31)$$

The probability of finding the sth segment of any chain on layer i is

$$P(s,i;r) = \sum_c P(s,i;r)_c \qquad (32)$$

The definitions (30), (31), and (32) are identical with those introduced in ref 1. One obtains from them the normalization condition

$$\sum_{i=1}^{M} P(s,i;r) = P(r) \qquad (33)$$

A simple relationship exists between volume fractions $\varphi_{\mathrm{I}i}$ and the segment probabilities $P(s,i;r)$. From division of eq 21 for I = A by the sum of eq 20 over all i and use of the distribution (28), together with the definitions (29)–(33),

$$\frac{L\varphi_{\mathrm{A}i}}{\sum_{i=1}^{M} L} = \frac{\sum_c r_{\mathrm{A}i,c}P(r)_c}{\sum_{i=1}^{M}[\sum_c (r_{\mathrm{A}i,c} + r_{\mathrm{B}i,c})P(r)_c]} = \frac{\sum_c\sum_{s=1}^{r}\delta_{ik(s,c)}\delta_{\mathrm{A},t(s)}P(r)_c}{\sum_{i=1}^{M}[\sum_c\sum_{s=1}^{r}\delta_{i,k(s,c)}P(r)_c]} = \frac{\sum_{s=1}^{r}\delta_{\mathrm{A},t(s)}\sum_c\delta_{ik(s,c)}P(r)_c}{\sum_{i=1}^{M}[\sum_{s=1}^{r}\sum_c P(s,i;r)_c]} = \frac{\sum_{s=1}^{r}\delta_{\mathrm{A},t(s)}P(s,i;r)}{\sum_{i=1}^{M}\sum_{s=1}^{r}P(s,i;r)} = \frac{\sum_{s=1}^{r}\delta_{\mathrm{A},t(s)}P(s,i;r)}{\sum_{s=1}^{r}\sum_{i=1}^{M}P(s,i;r)}$$

or

$$\varphi_{\mathrm{A}i} = \frac{M}{rP(r)}\sum_{s=1}^{r}\delta_{\mathrm{A},t(s)}P(s,i;r) \qquad 1 \le i \le M \qquad (34)$$

where the Kronecker delta serves as a segment type selector. Similarly, for I = B,

$$\varphi_{\mathrm{B}i} = \frac{M}{rP(r)}\sum_{s=1}^{r}\delta_{\mathrm{B},t(s)}P(s,i;r) \qquad 1 \le i \le M \qquad (35)$$

Our objective now is to relate the probabilities $P(s,i;r)$ to the free segment probabilities of eq 27, in order to arrive at a closed system of equations for the interfacial model. In the homopolymer[1] case this objective was achieved by introducing end-segment probabilities, which were found to conform to convenient recursive relationships. A similar approach is followed here, with the only difference that the asymmetric, in general, architecture necessitates the introduction of *two types* of end segment probabilities.

We will use the superscript + to denote the positive direction (start to end, direction of increasing segment order) along one of our chains; similarly, we will use the superscript − to denote the negative direction.

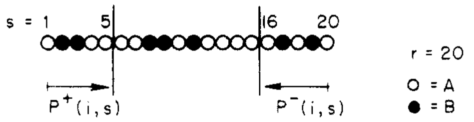

Figure 2. Definition of end-segment probabilities in the forward (+) and backward (−) direction; $r = 20$, $s = 5$.

We define the *end segment probability* for an s-segment subchain in the *positive direction* by the equation

$$P^+(i,s) = \sum_{\text{all } c(s)} P^+(i,s)_c \equiv \sum_{\substack{\text{all } c(s)\\ \text{such that}\\ k(s,c)=i}} [\omega_c \prod_{u=1}^{s} P_{t(u),k(u,c)}] \quad (36)$$

Here $P^+(i,s)$ stands for the probability that the end segment of a subchain of s segments, having a structure identical with that of the first s-segment portion of our reference chain (taken from the start forward), will lie in layer i (compare Figure 2). The summation in eq 36 is taken over all conformations of the s-segment subchain.

We define the *end segment probability* for an s-segment subchain *in the negative direction* by the equation

$$P^-(i,s) = \sum_{\text{all } c(s)} P^-(i,s)_c \equiv \sum_{\substack{\text{all } c(s)\\ \text{such that}\\ k(s,c)=i}} [\omega_c \prod_{u=1}^{s} P_{t(r-u+1),k(u,c)}] \quad (37)$$

The subchain considered in eq 37 has a structure identical with that of the last s-segment portion of our reference chain (taken in the reverse direction, terminal segment first). The summations are again taken over all conformations of the s-segment subchain.

From definitions (36) and (37) and eq 33 one immediately obtains

$$P^+(i,r) = P(r,i;r), \qquad P^-(i,r) = P(1,i;r)$$

and

$$\sum_{i=1}^{M} P^+(i,r) = \sum_{i=1}^{M} P^-(i,r) = P(r) \quad (38)$$

By construction the end segment probabilities obey the recursive relation

$$P^+(i,s) = \sum_j \lambda_{j-i} P_{t(s)i} P^+(j,s-1) \qquad 2 \le s \le r \quad (39)$$

$$P^-(i,s) = \sum_j \lambda_{j-i} P_{t(r-s+1)i} P^-(j,s-1) \qquad 2 \le s \le r \quad (40)$$

with

$$P^+(i,1) = P_{t(1)i} \qquad P^-(i,1) = P_{t(r)i} \quad (41)$$

In eq 39 (40) we visualize the chain growing in the positive (negative) direction.

To establish a connection between free segment probabilities and the probabilities $P(s,i;r)$ we consider our r-segment copolymer chain as consisting of two subchains, of length s and $r - s + 1$ segments, having segment number s in common. From the product form of conformation probabilities (29) and the reciprocity of the quantities λ_{ij} (eq 5) one obtains

$$P(s,i;r) = \frac{P^+(i,s)P^-(i,r-s+1)}{P_{t(s)i}} \quad (42)$$

Equations 34 and 35 then become

$$\varphi_{Ai} = \frac{M}{rP(r)} \frac{1}{P_{Ai}} \sum_{s=1}^{r} \delta_{A,t(s)} P^+(i,s)P^-(i,r-s+1) \quad (43)$$

$$\varphi_{Bi} = 1 - \varphi_{Ai} = \frac{M}{rP(r)} \frac{1}{P_{Bi}} \sum_{s=1}^{r} \delta_{B,t(s)} P^+(i,s)P^-(i,r-s+1) \quad (44)$$

Equations 27, 38–41, 43, and 44 constitute a formulation of the lattice model.

It is convenient to cast the problem in terms of reduced probabilities, defined with respect to the unconstrained bulk. Again, we emphasize that the term "probability" is used here loosely.[1] In the unconstrained bulk limit free segment probabilities P_{Ai} and P_{Bi}, as well as the Lagrange multipliers ζ_i, become layer-number independent; we symbolize them by $P^*{}_A$, $P^*{}_B$, and ζ^*, respectively. We define the reduced free segment probabilities by

$$p_{Ii} = P_{Ii}/P^*{}_I \qquad I = A, B \quad (45)$$

and the reduced end segment probabilities by

$$p^+(i,s) = \frac{P^+(i,s)}{\prod_{u=1}^{s} P^*{}_{t(u)}} \qquad p^-(i,s) = \frac{P^-(i,s)}{\prod_{u=1}^{s} P^*{}_{t(r-u+1)}} \quad (46)$$

With these definitions, eq 39–41 are readily converted into their lower-case counterparts. Equation 27 for the bulk becomes

$$\ln P^*{}_A = -\zeta^* + \chi\frac{r_A}{r} - \chi \qquad \ln P^*{}_B = -\zeta^* - \chi\frac{r_A}{r} \quad (47)$$

Subtracting (47) from (27) and defining ξ_i by

$$\ln \xi_i = -(\zeta_i - \zeta^*) \quad (48)$$

we obtain

$$p_{Ai} = \xi_i \exp\left[(\chi_S{}^A + \lambda_1\chi) \times (\delta_{i1} + \delta_{iM}) + \chi\left(\langle\varphi_{Ai}\rangle - \frac{r_A}{r} \right)\right] \qquad 1 \le i \le M \quad (49)$$

$$p_{Bi} = \xi_i \exp\left[(\chi_S{}^B + \lambda_1\chi) \times (\delta_{i1} + \delta_{iM}) - \chi\left(\langle\varphi_{Ai}\rangle - \frac{r_A}{r} \right)\right] \qquad 1 \le i \le M \quad (50)$$

The segment balance equations (43) and (44) can be written in terms of reduced probabilities as

$$\varphi_{Ai} = \frac{M}{r} \frac{(P^*{}_A)^{r_A}(P^*{}_B)^{r_B}}{P(r)} \frac{1}{p_{Ai}} \sum_{s=1}^{r} \delta_{A,t(s)} p^+(i,s)p^-(i,r-s+1) \quad (51)$$

$$\varphi_{Bi} = 1 - \varphi_{Ai} = \frac{M}{r} \frac{(P^*{}_A)^{r_A}(P^*{}_B)^{r_B}}{P(r)} \frac{1}{p_{Bi}} \sum_{s=1}^{r} \delta_{B,t(s)} p^+(i,s)p^-(i,r-s+1) \quad (52)$$

In the unconstrained bulk all reduced probabilities assume a value of unity and (51) becomes

$$\varphi^*{}_A = \frac{r_A}{r} = \frac{M}{r} \frac{(P^*{}_A)^{r_A}(P^*{}_B)^{r_B}}{P(r)} r_A$$

or

$$\frac{M}{r} \frac{(P^*{}_A)^{r_A}(P^*{}_B)^{r_B}}{P(r)} = \frac{1}{r} \quad (53)$$

Substituting (53) into (51) and (52) one obtains

$$\varphi_{Ai} p_{Ai} = \frac{1}{r} \sum_{s=1}^{r} \delta_{A,t(s)} p^+(i,s)p^-(i,r-s+1) \qquad 1 \le i \le M \quad (54)$$

$$(1 - \varphi_{Ai})p_{Bi} = \frac{1}{r} \sum_{s=1}^{r} \delta_{B,t(s)} p^+(i,s)p^-(i,r-s+1) \qquad 1 \le i \le M \quad (55)$$

Chart I

$$p_{\mathrm{A}1} = p_{\mathrm{B}1} \exp\left[(\chi_s + \lambda_1\chi) + 2\chi\left(\lambda_0\varphi_{\mathrm{A}1} + \lambda_1\varphi_{\mathrm{A}2} - \frac{r_{\mathrm{A}}}{r} \right) \right] \tag{57}$$

$$p_{\mathrm{A}i} = p_{\mathrm{B}i} \exp\left[2\chi\left(\lambda_1\varphi_{\mathrm{A}i-1} + \lambda_0\varphi_{\mathrm{A}i} + \lambda_1\varphi_{\mathrm{A}i+1} - \frac{r_{\mathrm{A}}}{r} \right) \right] \quad 2 \le i \le M-1 \tag{58}$$

$$p_{\mathrm{A}M} = p_{\mathrm{B}M} \exp\left[(\chi_{\mathrm{s}} + \lambda_1\chi) + 2\chi\left(\lambda_1\varphi_{\mathrm{A}M-1} + \lambda_0\varphi_{\mathrm{A}M} - \frac{r_{\mathrm{A}}}{r} \right) \right] \tag{59}$$

$$\begin{bmatrix} p^+(1,s) \\ p^+(2,s) \\ \vdots \\ p^+(i,s) \\ \vdots \\ p^+(M-1,s) \\ p^+(M,s) \end{bmatrix} = \begin{bmatrix} \lambda_0 p_{t(s)1} & \lambda_1 p_{t(s)1} & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1 p_{t(s)2} & \lambda_0 p_{t(s)2} & \lambda_1 p_{t(s)2} & \cdot & & & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \lambda_1 p_{t(s)i} & \lambda_0 p_{t(s)i} & \lambda_1 p_{t(s)i} & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & \cdot & \lambda_1 p_{t(s)M-1} & \lambda_0 p_{t(s)M-1} & \lambda_1 p_{t(s)M-1} \\ 0 & \cdot & \cdot & \cdot & & \lambda_1 p_{t(s)M} & \lambda_0 p_{t(s)M} \end{bmatrix} \begin{bmatrix} p^+(1,s-1) \\ p^+(2,s-1) \\ \vdots \\ p^+(i,s-1) \\ \vdots \\ p^+(M-1,s-1) \\ p^+(M,s-1) \end{bmatrix} \quad 2 \le s \le r \tag{60}$$

$$\text{with} \qquad p^+(i,1) = p_{t(1)i} \quad 1 \le i \le M \tag{61}$$

$$\begin{bmatrix} p^-(1,s) \\ p^-(2,s) \\ \vdots \\ p^-(i,s) \\ \vdots \\ p^-(M-1,s) \\ p^-(M,s) \end{bmatrix} = \begin{bmatrix} \lambda_0 p_{t(r-s+1)1} & \lambda_1 p_{t(r-s+1)1} & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1 p_{t(r-s+1)2} & \lambda_0 p_{t(r-s+1)2} & \lambda_1 p_{t(r-s+1)2} & \cdot & & & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \lambda_1 p_{t(r-s+1)i} & \lambda_0 p_{t(r-s+1)i} & \lambda_1 p_{t(r-s+1)i} & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & \cdot & \lambda_1 p_{t(r-s+1)M-1} & \lambda_0 p_{t(r-s+1)M-1} & \lambda_1 p_{t(r-s+1)M-1} \\ 0 & \cdot & \cdot & \cdot & 0 & \lambda_1 p_{t(r-s+1)M} & \lambda_0 p_{t(r-s+1)M} \end{bmatrix} \begin{bmatrix} p^-(1,s-1) \\ p^-(2,s-1) \\ \vdots \\ p^-(i,s-1) \\ \vdots \\ p^-(M-1,s-1) \\ p^-(M,s-1) \end{bmatrix} \quad 2 \le s \le r \tag{62}$$

$$\text{with} \qquad p^-(i,1) = p_{t(r)i} \quad 1 \le i \le M \tag{63}$$

$$\varphi_{\mathrm{A}i} p_{\mathrm{A}i} = \frac{1}{r} \sum_{s=1}^{r} \delta_{\mathrm{A},t(s)} p^+(i,s) p^-(i,r-s+1) \quad 1 \le i \le M \tag{54}$$

$$\varphi_{\mathrm{A}i} p_{\mathrm{A}i} + (1 - \varphi_{\mathrm{A}i}) p_{\mathrm{B}i} = \frac{1}{r} \sum_{s=1}^{r} p^+(i,s) p^-(i,r-s+1) \quad 1 \le i \le M \tag{64}$$

The system of model equations now comprises the $2rM$ equations (39)–(41), written in terms of reduced (lower case) probabilities, the $2M$ equations (49) and (50), the M components of (13) for I = A, and the $2M$ equations (54) and (55). The quantities $\varphi_{\mathrm{A}i}$, $\langle\varphi_{\mathrm{A}i}\rangle$, $p_{\mathrm{A}i}$, $p_{\mathrm{B}i}$, and ξ_i ($1 \le i \le M$), as well as the $2rM$ quantities $p^+(i,s)$ and $p^-(i,s)$ ($1 \le i \le M$, $1 \le s \le r$), appear as unknowns. We thus have a set of $(2r + 5)M$ equations in $(2r + 5)M$ variables. As the quantities ξ_i, derived from Lagrange multipliers, are relatively uninteresting, we chose to eliminate them from eq 49 and 50. This permits a reduction of the number of model parameters by one, since $\chi_{\mathrm{S}}^{\mathrm{A}}$ and $\chi_{\mathrm{S}}^{\mathrm{B}}$ only appear together in the term $\chi_{\mathrm{S}}^{\mathrm{A}} - \chi_{\mathrm{S}}^{\mathrm{B}}$.

We define the dimensionless difference in adsorption energies between segments A and B as

$$\chi_s = \chi_{\mathrm{S}}^{\mathrm{A}} - \chi_{\mathrm{S}}^{\mathrm{B}} = -\frac{u_{\mathrm{S}}^{\mathrm{A}} - u_{\mathrm{S}}^{\mathrm{B}}}{kT} \tag{56}$$

The quantity χ_s is a measure of the differential affinity of A and B for adsorption on the surface. The greater the value of χ_s, the greater the tendency for A segments to adsorb preferentially over B segments.

Using χ_s and substituting $\langle\varphi_{\mathrm{A}i}\rangle$ from eq 13, we cast our system of model equations in the final form shown in Chart I. In eq 64 we have replaced the B-segment balance (55) with a total segment balance, by adding eq 54 and 55 together. The recursive equations (60) and (62) can be written, in abbreviated form, as

$$\mathbf{p}^+(s) = \mathbf{w}_{t(s)}{}^{+}\mathbf{p}^+(s-1) \tag{60}$$

$$\mathbf{p}^-(s) = \mathbf{w}_{t(s)}{}^{-}\mathbf{p}^-(s-1) \tag{62}$$

In contrast to the homopolymer case, the matrices $\mathbf{w}_{t(s)}{}^{+}$ and $\mathbf{w}_{t(s)}{}^{-}$ are segment-order-dependent. Each can assume either of two values ($\mathbf{w}_{\mathrm{A}}{}^{+}$ or $\mathbf{w}_{\mathrm{B}}{}^{+}$, $\mathbf{w}_{\mathrm{A}}{}^{-}$ or $\mathbf{w}_{\mathrm{B}}{}^{-}$), depending on the architecture of the chain.

The $(2r + 3)M$ equations (54) and (57)–(64) comprise a system in the $(2r + 3)M$ unknowns $\varphi_{\mathrm{A}i}$, $p_{\mathrm{A}i}$, $p_{\mathrm{B}i}$, $p^+(i,s)$, and $p^-(i,s)$ ($1 \le i \le M$, $1 \le s \le r$). Equations 57–59 provide explicit expressions for calculating $\{p_{\mathrm{A}i}\}$ as a function of $\{\varphi_{\mathrm{A}i}\}$ and $\{p_{\mathrm{B}i}\}$. Equations 60–63 provide expressions for calculating $p^+(i,s)$ and $p^-(i,s)$ as functions of $\{p_{\mathrm{A}i}\}$ and $\{p_{\mathrm{B}i}\}$. Thus, the set of equations (54) and (64) can be viewed as a system of $2M$ equations in the $2M$ unknowns $\{\varphi_{\mathrm{A}i}\}$ and $\{p_{\mathrm{B}i}\}$. The numerical solution strategy we developed relies on this approach. Our solution algorithm is based on a straight forward Newton–Raphson scheme, with analytical calculation of the Jacobian. Advantage was taken of the symmetry of the problem, to reduce the number of equations and the number of unknowns by a factor of 2. The performance of the algorithm was remarkably good, in all cases studied. Numerical solution procedures are discussed in Appendix B.

A simple-cubic lattice was used in all calculations. Inputs to the model are the chain architecture (chain length, number, and exact sequence of A and B segments), the parameter χ, characteristic of the interaction between A and B segments, and the parameter χ_s, characteristic of the difference in affinity of A and B segments for the surface. Input parameters can be estimated with good accuracy from available data for particular physical systems; as output from the model one obtains the segment volume fraction and reduced free segment probability profiles, as well as reduced end segment probabilities. How these quantities can be used to extract valuable information on the interfacial tension and the microscopic structure of our system is examined below.

Interfacial Tension. At equilibrium the distribution of conformations is given by expression 28. Using definition 45 and eq 30 and 53 we can recast this expression into the following form, involving reduced free segment probabilities:

$$n_c = n\frac{\omega_c}{M}\prod_{i=1}^{M} p_{\mathrm{A}i}{}^{r_{\mathrm{A}i,c}} p_{\mathrm{B}i}{}^{r_{\mathrm{B}i,c}} \qquad (65)$$

The value of the partition function at equilibrium is obtained by substituting the distribution (65) in eq 19. From the partition function the Helmholtz energy of the model system is calculated as

$$\frac{A}{LkT} = -\frac{1}{L}\ln Q = \frac{2u_{\mathrm{S}}{}^{\mathrm{B}}}{kT} - (\chi_s + \lambda_1\chi)(\varphi_{\mathrm{A}1} + \varphi_{\mathrm{A}M}) + \sum_{i=1}^{M}[\varphi_{\mathrm{A}i}\ln p_{\mathrm{A}i} + (1 - \varphi_{\mathrm{A}i})\ln p_{\mathrm{B}i}] + \chi\left[\sum_{i=1}^{M}\varphi_{\mathrm{A}i}(1 - \langle\varphi_{\mathrm{A}i}\rangle) - M\frac{r_{\mathrm{A}}r_{\mathrm{B}}}{r^2}\right] \qquad (66)$$

A derivation of eq 66 is given in Appendix C. Since the unconstrained bulk was used as a reference state in our analysis, the Helmholtz energy (66) is purely interfacial,

$$\frac{A}{LkT} = \frac{2\gamma a}{kT} \qquad (67)$$

where γ is the interfacial tension, a is the area per surface site, and the factor 2 is due to the two surfaces present. Combining eq 66 and 67 and taking the symmetry of the model system into account, we reach the following expression for γ, in which the adsorption energy of a pure B segment is used as a reference:

$$\frac{\gamma a}{kT} = \frac{u_{\mathrm{S}}{}^{\mathrm{B}}}{kT} - (\chi_s + \lambda_1\chi)\varphi_{\mathrm{A}1} + \sum_{i=1}^{m}[\varphi_{\mathrm{A}i}\ln p_{\mathrm{A}i} + (1 - \varphi_{\mathrm{A}i})\ln p_{\mathrm{B}i}] + \chi\left[\sum_{i=1}^{m}\varphi_{\mathrm{A}i}(1 - \langle\varphi_{\mathrm{A}i}\rangle) - m\frac{r_{\mathrm{A}}r_{\mathrm{B}}}{r^2}\right] \qquad (68)$$

This expression permits evaluation of the surface or interfacial tension from the profiles $\{\varphi_{\mathrm{A}i}\}$, $\{p_{\mathrm{A}i}\}$, and $\{p_{\mathrm{B}i}\}$ obtained by solution of the model. In the following we will use the symbol ϵ to denote the dimensionless difference

$$\epsilon = \frac{\gamma a}{kT} - \frac{u_s{}^{\mathrm{B}}}{kT} \qquad (69)$$

A limiting case to which eq 68 can be applied is that of a pure homopolymer, consisting exclusively of A-type segments. In this case, $\varphi_{\mathrm{A}i} = 1$ $(1 \le i \le m)$, $r_{\mathrm{B}} = 0$, and

$$\left[\frac{\gamma a}{kT}\right]_{\mathrm{A}_r} = \frac{u_{\mathrm{S}}{}^{\mathrm{B}}}{kT} - (\chi_s + \lambda_1\chi) + \sum_{i=1}^{m}\ln p_{\mathrm{A}i} + \lambda_1\chi = \frac{u_{\mathrm{S}}{}^{\mathrm{B}}}{kT} - \chi_s + \sum_{i=1}^{m}\ln p_{\mathrm{A}i}$$

and, by the definition 56,

$$\left[\frac{\gamma a}{kT}\right]_{\mathrm{A}_r} = \frac{u_s{}^{\mathrm{A}}}{kT} + \sum_{i=1}^{m}\ln p_{\mathrm{A}i} \qquad (70)$$

which is identical with the expression derived in ref 1 for the interfacial tension of a pure homopolymer.

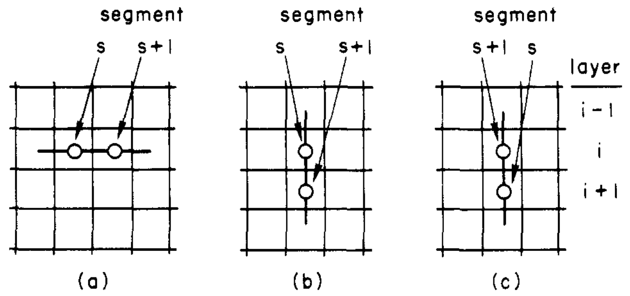

Figure 3. Cases considered for the enumeration of bonds in various directions, having one of their ends in layer i.

On the other hand for the case of a pure homopolymer, consisting exclusively of B segments, $\varphi_{\mathrm{A}i} = 0$ $(1 \le i \le m)$, $r_{\mathrm{A}} = 0$, and eq 68 gives

$$\left[\frac{\gamma a}{kT}\right]_{\mathrm{B}_r} = \frac{u_s{}^{\mathrm{B}}}{kT} + \sum_{i=1}^{m}\ln p_{\mathrm{B}i} \qquad (71)$$

which is identical in form with (70).

Bond Orientation. As pointed out in ref 1, the spatial distribution of bond orientations crucially affects local mechanical properties and the response of a composite interface to deformation. A new method for quantitatively characterizing bond orientation at a bulk homopolymer interface was introduced in ref 1. Conditional stepping probabilities for a bond starting in layer i to propagate in the direction of increasing layer numbers (forward stepping), to remain in layer i (side stepping), or to propagate in the direction of decreasing layer numbers (back stepping) in the lattice were determined.

This analysis is readily transplanted to the copolymer case. We follow the reasoning described in ref 1 and use eq 42 and the normalization conditions (54) and (55). Let b_i^+ (q_i^+, f_i^+) be the conditional stepping probability for a segment to lie in layer $i - 1$ $(i, i + 1$, respectively), provided that the segment *preceding* it, in the sense defined by the positive direction along the chain, lies in layer i. Then

$$b_i^+ = \frac{\lambda_1}{r - p^+(i,r)}\sum_{s=1}^{r-1}p^+(i,s)p^-(i-1,r-s) \qquad 2 \le i \le M \qquad (72a)$$

$$q_i^+ = \frac{\lambda_0}{r - p^+(i,r)}\sum_{s=1}^{r-1}p^+(i,s)p^-(i,r-s) \qquad 1 \le i \le M \qquad (72b)$$

$$f_i^+ = \frac{\lambda_1}{r - p^+(i,r)}\sum_{s=1}^{r-1}p^+(i,s)p^-(i+1,r-s) \qquad 1 \le i \le M - 1 \qquad (72c)$$

with $b_1^+ = f_M^+ = 0$. Similarly, the conditional probabilities b_i^-, q_i^-, and f_i^- for a segment to lie in layer $i - 1$, i, and $i + 1$, respectively, provided that the segment *following* it, in the sense defined by the positive direction along the chain, lies in layer i, are

$$b_i^- = \frac{\lambda_1}{r - p^-(i,r)}\sum_{s=1}^{r-1}p^+(i-1,s)p^-(i,r-s) \qquad 2 \le i \le M \qquad (73a)$$

$$q_i^- = \frac{\lambda_0}{r - p^-(i,r)}\sum_{s=1}^{r-1}p^+(i,s)p^-(i,r-s) \qquad 1 \le i \le M \qquad (73b)$$

$$f_i^- = \frac{\lambda_1}{r - p^-(i,r)}\sum_{s=1}^{r-1}p^+(i+1,s)p^-(i,r-s) \qquad 1 \le i \le M - 1 \qquad (73c)$$

Normalization of the probabilities defined by (72) and (73) follows from eq 54, 55, 60, and 62. The order parameters associated with the above conditional probability definitions are[1]

$$S_i^+ = \tfrac{1}{2}[3(f_i^+ + b_i^+) - 1] = \tfrac{1}{2}[2 - 3q_i^+] \qquad (74)$$

$$S_i^- = \tfrac{1}{2}[3(f_i^- + b_i^-) - 1] = \tfrac{1}{2}[2 - 3q_i^-] \qquad (75)$$

S values of 1, $-^1/_2$ and 0 correspond to situations of perfect perpendicularity to the surface, perfect parallelity, and completely random orientation, respectively.

When the chain structure possesses a center of symmetry (i.e., the segment type sequence is the same, whether taken in the positive or in the negative direction), probabilities b_i^+ and b_i^-, q_i^+ and q_i^-, and f_i^+ and f_i^- are identical. The bulk homopolymer is a particular instance of this. In the general case of an asymmetric chain architecture, however, probabilities in the positive and negative directions, and the associated order parameters, are different.

A more complete methodology is introduced here for probing bond orientation characteristics, which is free of this problem of asymmetry upon inversion of chain direction. We start by realizing that what is immediately related to the local mechanical properties of interest is not the conditional stepping probabilities but rather the absolute numbers of bonds lying in and between layers. Let $n_{\mathrm{b}i}{}^{\mathrm{T}}$ be the number of bonds per surface site that connect layers i and $i + 1$; let also $n_{\mathrm{b}i}{}^{\mathrm{L}}$ be the number of bonds per surface site lying flat in layer i. Our objective will be to find expressions for $n_{\mathrm{b}i}{}^{\mathrm{T}}$ and $n_{\mathrm{b}i}{}^{\mathrm{L}}$ in terms of the volume fraction and segment probability profiles given by the model.

Consider a particular bond, s, connecting segments s and $(s + 1)$ of one of our copolymer chains (segment orders defined in the positive direction). The bond divides the chain into two subchains, s and $(r - s)$ segments long. We focus on a situation where bond s has one of its terminal segments in layer i (Figure 3a). The absolute probability that bond s will lie flat in layer i is proportional to the quantity

$$\lambda_0 p^+(i,s)p^-(i,r-s) \qquad (76)$$

The absolute probability that bond s will connect layers i and $i + 1$ in the direction $s \rightarrow (s + 1)$ (Figure 3b) is proportional to the quantity

$$\lambda_1 p^+(i,s)p^-(i+1,r-s) \qquad (77)$$

The absolute probability that bond s will connect layers i and $i + 1$ in the direction $(s + 1) \rightarrow s$ (Figure 3c) is proportional to the quantity

$$\lambda_1 p^+(i+1,s)p^-(i,r-s) \qquad (78)$$

The total probability, for all possible locations and orientations of bond s in the model system, is proportional to

$$p_{\mathrm{b}}(s) = \lambda_0 \sum_{i=1}^{M} p^+(i,s)p^-(i,r-s) + \lambda_1 \sum_{i=1}^{M-1} p^+(i,s)p^-(i+1,r-s) + \lambda_1 \sum_{i=1}^{M-1} p^+(i+1,s)p^-(i,r-s) \qquad (79)$$

There is a total number of $n = ML/r$ bonds of order s in the model of M layers. From (76)–(79) the numbers of s-bonds per surface site lying flat in layer i, and connecting layers i and $i + 1$, will be

$$n_{\mathrm{b}i}{}^{\mathrm{L}}(s) = \frac{M}{r}\lambda_0 \frac{p^+(i,s)p^-(i,r-s)}{p_{\mathrm{b}}(s)} \qquad 1 \le i \le M \qquad (80)$$

$$n_{\mathrm{b}i}{}^{\mathrm{T}}(s) = \frac{M}{r}\lambda_1 \frac{p^+(i,s)p^-(i+1,r-s) + p^+(i+1,s)p^-(i,r-s)}{p_{\mathrm{b}}(s)} \qquad 1 \le i \le M-1 \qquad (81)$$

The total numbers of bonds per surface site, irrespective of order, lying flat in layer i and connecting layers i and $i + 1$, will be

$$n_{\mathrm{b}i}{}^{\mathrm{L}} = \frac{M}{r}\lambda_0 \sum_{s=1}^{r-1} \frac{p^+(i,s)p^-(i,r-s)}{p_{\mathrm{b}}(s)} \qquad 1 \le i \le M \qquad (82)$$

$$n_{\mathrm{b}i}{}^{\mathrm{T}} = \frac{M}{r}\lambda_1 \sum_{s=1}^{r-1} \frac{p^+(i,s)p^-(i+1,r-s) + p^+(i+1,s)p^-(i,r-s)}{p_{\mathrm{b}}(s)} \qquad 1 \le i \le M-1 \qquad (83)$$

Equations 79, 82, and 83 permit obtaining absolute numbers of bonds in and between layers from the segment probability profiles; they are invariant under reversal of chain direction. Use is made of the symmetry of the model system in the computation of $n_{\mathrm{b}i}{}^{\mathrm{L}}$ and $n_{\mathrm{b}i}{}^{\mathrm{T}}$ (compare Appendix B). Significant simplification of the computations is afforded by the realization that the normalizing factor $p_{\mathrm{b}}(s)$, defined in eq 79, is actually bond-order-independent and equal to M. A proof is given in Appendix D.

The bond numbers $n_{\mathrm{b}i}{}^{\mathrm{L}}$ and $n_{\mathrm{b}i}{}^{\mathrm{T}}$ conform to the obvious normalization:

$$\sum_{i=1}^{M} n_{\mathrm{b}i}{}^{\mathrm{L}} + \sum_{i=1}^{M-1} n_{\mathrm{b}i}{}^{\mathrm{T}} = \frac{n}{L}(r-1) = M\frac{r-1}{r} \qquad (84)$$

We define the *absolute* orientation probabilities b_i^{abs}, that a bond emanating from i will connect layers $i - 1$ and i; q_i^{abs}, that it will lie flat in layer i; and f_i^{abs}, that it will connect layers i and $i + 1$, in terms of the absolute numbers $n_{\mathrm{b}i}{}^{\mathrm{T}}$ and $n_{\mathrm{b}i}{}^{\mathrm{L}}$:

$$b_i^{\mathrm{abs}} = \frac{n_{\mathrm{b}i-1}{}^{\mathrm{T}}}{n_{\mathrm{b}i-1}{}^{\mathrm{T}} + n_{\mathrm{b}i}{}^{\mathrm{T}} + 2n_{\mathrm{b}i}{}^{\mathrm{L}}} \qquad 2 \le i \le M \qquad (85a)$$

$$q_i^{\mathrm{abs}} = \frac{2n_{\mathrm{b}i}{}^{\mathrm{L}}}{n_{\mathrm{b}i-1}{}^{\mathrm{T}} + n_{\mathrm{b}i}{}^{\mathrm{T}} + 2n_{\mathrm{b}i}{}^{\mathrm{L}}} \qquad 1 \le i \le M \qquad (85b)$$

$$f_i^{\mathrm{abs}} = \frac{n_{\mathrm{b}i}{}^{\mathrm{T}}}{n_{\mathrm{b}i-1}{}^{\mathrm{T}} + n_{\mathrm{b}i}{}^{\mathrm{T}} + 2n_{\mathrm{b}i}{}^{\mathrm{L}}} \qquad 1 \le i \le M-1 \qquad (85c)$$

$$b_1^{\mathrm{abs}} = f_M^{\mathrm{abs}} = 0 \qquad (85d)$$

The factor of 2 multiplying $n_{\mathrm{b}i}{}^{\mathrm{L}}$ in these definitions is due to the fact that a bond lying flat in layer i is shared by two segments in that layer, so it must be counted twice for correct assessment of the orientational environment around a segment of that layer (Equivalently, a bond connecting layers i and $i + 1$ is shared by both layers, so it should be weighted by a factor of $^1/_2$ relative to a bond lying entirely in layer i.)

Probabilities (85) do not, in general, satisfy the reciprocity conditions:

$$f_i^{\mathrm{abs}} = b_{i+1}^{\mathrm{abs}} \qquad 1 \le i \le M-1 \qquad (86)$$

The reason is that the total number of bonds emanating from a layer, $n_{\mathrm{b}i-1}{}^{\mathrm{T}} + n_{\mathrm{b}i}{}^{\mathrm{T}} + 2n_{\mathrm{b}i}{}^{\mathrm{L}}$, varies from layer to layer, reflecting chain termination. The reciprocity relation would be strictly valid for infinite chains (compare discussion in ref 1).

We define the order parameter S_i for layer i, based on absolute bond numbers, as

$$S_i = \frac{1}{2}[3(b_i^{\mathrm{abs}} + f_i^{\mathrm{abs}}) - 1] = \frac{1}{2}\left(3\frac{n_{\mathrm{b}i-1}{}^{\mathrm{T}} + n_{\mathrm{b}i}{}^{\mathrm{T}}}{n_{\mathrm{b}i-1}{}^{\mathrm{T}} + n_{\mathrm{b}i}{}^{\mathrm{T}} + 2n_{\mathrm{b}i}{}^{\mathrm{L}}} - 1\right) \qquad (87)$$

For chains of *symmetric* structure one can prove that definitions 72, 73, and 85 become equivalent, as do definitions 74, 75, and 87. In particular,

$$S_i^+ = S_i^- = S_i \qquad \text{symmetric chains} \qquad (88)$$

This equality was confirmed by our numerical computations. In the unperturbed bulk limit, in a cubic lattice, $n_i{}^{\mathrm{T}}$, $n_i{}^{\mathrm{L}}$, and S_i assume the values

$$\lim_{i\to m} n_{\mathrm{b}i}{}^{\mathrm{T}} = \frac{\lambda_1 z}{3}\,\frac{r-1}{r} = \frac{1}{3}\,\frac{r-1}{r} \qquad (89a)$$

$$\lim_{i\to m} n_{\mathrm{b}i}{}^{\mathrm{L}} = \frac{\lambda_0 z}{6}\,\frac{r-1}{r} = \frac{2}{3}\,\frac{r-1}{r} \qquad (89b)$$

$$\lim_{i\to m} S_i = 0 \qquad (89c)$$

This asymptotic behavior was observed in all cases studied.

Chain Shape as a Function of Distance from the Interface. As a result of the special conditions prevailing in the interfacial region, the overall spatial extent and the shape of individual chains will deviate from what they are in the unconstrained bulk. It is very interesting to explore these conformational characteristics of chains in the interfacial region as a function of molecular architecture, as they are intimately related to macroscopic properties. In this section we develop a methodology for the quantitative characterization of average chain size and shape as a function of distance from the surface, based on two quantities. The first of these quantities is the number of chains per surface site passing through a given layer i, which we symbolize by n_i. The second is the average number of segments that a chain passing through layer i has in that layer; we will symbolize it by n_{si}. The quantities n_i and n_{si} are simply related by the equation

$$n_{si} = 1/n_i \qquad (90)$$

Consider a chain conformation, c', that has *none* of its segments in layer i. By eq 29 the reduced probability of such a conformation will be equal to

$$p'_{(i)}(r)_{c'} = \omega_{c'}\prod_{s=1}^{r} p_{t(s),k(s,c')}, \qquad k(s,c') \neq i \qquad 1 \leq s \leq r \qquad (91)$$

The reduced chain probability for a chain not passing through layer i will be

$$p'_{(i)}(r) = \sum_{c'} p'_{(i)}(r)_{c'} \qquad (92)$$

By definition, $p'_{(i)}(r)$ will be a sum of products of the form (91), none of which contains the factor $p_{\mathrm{A}i}$ or $p_{\mathrm{B}i}$. Such a sum can readily be generated by a successive multiplication scheme, similar to that of eq 60. Let

$$\mathbf{p}'_{(i)\mathrm{A}} = \mathrm{col}\,(p_{\mathrm{A}1}, p_{\mathrm{A}2}, ..., p_{\mathrm{A}i-1}, 0, p_{\mathrm{A}i+1}, ..., p_{\mathrm{A}M}) = \mathbf{p}_{\mathrm{A}} - p_{\mathrm{A}i}\boldsymbol{C}_i$$

$$\mathbf{p}'_{(i)\mathrm{B}} = \mathrm{col}\,(p_{\mathrm{B}1}, p_{\mathrm{B}2}, ..., p_{\mathrm{B}i-1}, 0, p_{\mathrm{B}i+1}, ..., p_{\mathrm{B}M}) = \mathbf{p}_{\mathrm{B}} - p_{\mathrm{B}i}\boldsymbol{C}_i \qquad (93)$$

Let also $\mathbf{w}^{+\prime}{}_{(i)\mathrm{A}}$ and $\mathbf{w}^{+\prime}{}_{(i)\mathrm{B}}$ be modifications of the matrices $\mathbf{w+}_{\mathrm{A}}$ and $\mathbf{w}^{+}{}_{\mathrm{B}}$ (eq 60), in which the entire i-th row is replaced by zeros.

$$\mathbf{w}^{+\prime}{}_{(i)t(s)} = \left[\begin{array}{ccccccc}
\lambda_0 p_{t(s)1} & \lambda_1 p_{t(s)1} & 0 & \cdot & \cdot & \cdot & 0 \\
\lambda_1 p_{t(s)2} & \lambda_0 p_{t(s)2} & \lambda_1 p_{t(s)2} & \cdot & & & \cdot \\
0 & \cdot & \cdot & \cdot & \cdot & & \cdot \\
\cdot & \cdot & 0 & 0 & 0 & \cdot & \cdot \\
\cdot & & \cdot & \cdot & \cdot & \cdot & 0 \\
\cdot & & & \cdot & \lambda_1 p_{t(s)M-1} & \lambda_0 p_{t(s)M-1} & \lambda_1 p_{t(s)M-1} \\
0 & \cdot & \cdot & \cdot & & \lambda_1 p_{t(s)M} & \lambda_0 p_{t(s)M}
\end{array}\right] \qquad (94)$$

Introducing the symbolism

$$\mathbf{p}^{+\prime}{}_{(i)}(s) = \mathrm{col}\,[p^{+\prime}{}_{(i)}(1,s), p^{+\prime}{}_{(i)}(2,s), ..., p^{+\prime}{}_{(i)}(M,s)] \qquad (95)$$

with

$$\mathbf{p}^{+\prime}{}_{(i)}(s) = \mathbf{w}^{+\prime}{}_{(i)t(s)}\mathbf{p}^{+\prime}{}_{(i)}(s-1) \qquad \mathbf{p}^{+\prime}{}_{(i)}(1) = \mathbf{p}'_{(i)t(1)} \qquad (96)$$

we express the reduced probability for not passing through layer i as

$$p'_{(i)}(r) = \sum_{j=1}^{M} p^{+\prime}{}_{(i)}(j,r) \qquad (97)$$

The total reduced chain probability, $p(r)$, irrespective of whether a chain passes through layer i or not, is obtained from (60) as

$$p(r) = \sum_{j=1}^{M} p^{+}(j,r) \qquad (98)$$

Note that estimates of $p'_{(i)}(r)$ and $p(r)$ remain unchanged, if calculations in eq 94–98 are performed in the negative direction along the chain.

The reduced probability for a chain *passing* through layer i will be equal to the difference

$$p_{(i)}(r) = p(r) - p'_{(i)}(r) \qquad (99)$$

Equations 93–99 provide a scheme for calculating the reduced probability $p_{(i)}(r)$ of a chain passing through layer i. This scheme is a generalization of that proposed by Scheutjens and Fleer[2] for calculating chain adsorption probabilities. As pointed out in ref 2, a numerically more accurate modification of eq 99 can be obtained by introducing the probabilities

$$\mathbf{p}^{+}{}_{(i)}(s) = \mathbf{p}^{+}(s) - \mathbf{p}^{+\prime}{}_{(i)}(s) \qquad (100)$$

By eq 60, 94, and 96, these satisfy the recursive relationship

$$\mathbf{p}^{+}{}_{(i)}(s) = \mathbf{w}^{+\prime}{}_{(i)t(s)}\mathbf{p}^{+}{}_{(i)}(s-1) + p^{+}(i,s)\boldsymbol{C}_i \qquad 2 \leq s \leq r \qquad (101)$$

with $\mathbf{p}^{+}{}_{(i)}(1) = p_{t(1)i}\boldsymbol{C}_i$, and allow the calculations of $p_{(i)}(r)$ as

$$p_{(i)}(r) = \sum_{j=1}^{M} p^{+}{}_{(i)}(j,r) \qquad (102)$$

The total number of chains per surface site in the model system is

$$n/L = M/r$$

The desired number of chains per surface site passing through layer i is then obtained from the probabilities $p_{(i)}(r)$ and $p(r)$ as

$$n_i = \frac{M}{r}\,\frac{p_{(i)}(r)}{p(r)} \qquad (103)$$

and the average number of segments per chain in layer i, n_{si}, is obtained as the inverse of n_i (eq 90).

The quantity n_{si} is a sensitive measure of local structure. A high value of n_{si} reflects a tendency of chains to lie flat in a layer. A low value of n_{si} indicates a crowded situation, where chains compete for sites in the considered layer and are therefore elongated in a direction perpendicular to the surface. For a given chain length, n_{si} varies between the obvious limits

$$1 \leq n_{si} \leq r \qquad (104)$$

According to assumption V, far from a surface n_{si} assumes an asymptotic value, which is independent of the details of chain architecture and is a function solely of chain length. We will denote this value by

$$\lim_{i\to m} n_{si} = n_{s\infty}(r) \qquad (105)$$

Acknowledgment. Financial support provided in the course of this work by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098, and computing resources offered by Academic Computing Services at Berkeley are deeply appreciated. Support from the Shell Companies Foundation, in the form of a Faculty Career Initiation Fund, is gratefully acknowledged.

Appendix A: Derivation of Equation 16 for the Total Potential Energy of the Interfacial System, Relative to the Unconstrained Bulk

The desired potential energy U for a given configuration $\{n_c\}$ of the interfacial system is obtained as a difference between actual and reference states, according to eq 9.

In the unconstrained bulk, assuming full occupancy of the lattice by polymer segments, the volume fraction of I-type segments will be uniform and equal to

$$\varphi^*_{\mathrm{I}} = r_{\mathrm{I}}/r \qquad \mathrm{I} = \mathrm{A, B} \tag{A.1}$$

The numbers of AA, AB, and BB pairs will be equal to $^1/_2 nr_{\mathrm{A}}\varphi^*_{\mathrm{A}}$, $nr_{\mathrm{A}}\varphi^*_{\mathrm{B}}$, and $^1/_2 nr_{\mathrm{B}}\varphi^*_{\mathrm{B}}$, respectively, where the factors of $^1/_2$ have been introduced to avoid double counting. Thus, by definition of the interaction energies,

$$U_{\mathrm{bulk}}(n) = \frac{1}{2}\left[nr_{\mathrm{A}}z\left(w_{\mathrm{AA}}\frac{r_{\mathrm{A}}}{r} + w_{\mathrm{AB}}\frac{r_{\mathrm{B}}}{r}\right) + nr_{\mathrm{B}}z\left(w_{\mathrm{AB}}\frac{r_{\mathrm{A}}}{r} + w_{\mathrm{BB}}\frac{r_{\mathrm{B}}}{r}\right)\right] \tag{A.2}$$

In the interfacial system segment volume fractions are layer number-dependent. The total numbers of contacts are given by

AA contacts

$$\tfrac{1}{2}zL\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\sum_{j=1}^{M}\lambda_{j-i}\varphi_{\mathrm{A}j} = \tfrac{1}{2}zL\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{A}i}\rangle$$

AB contacts

$$zL\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\sum_{j=1}^{M}\lambda_{j-i}\varphi_{\mathrm{B}j} = zL\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{B}i}\rangle$$

BB contacts

$$\tfrac{1}{2}zL\sum_{i=1}^{M}\varphi_{\mathrm{B}i}\sum_{j=1}^{M}\lambda_{j-i}\varphi_{\mathrm{B}j} = \tfrac{1}{2}zL\sum_{i=1}^{M}\varphi_{\mathrm{B}i}\langle\varphi_{\mathrm{B}i}\rangle \tag{A.3}$$

Note that, by definitions 13 and 14,

$$\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{B}i}\rangle = \sum_{i=1}^{M}\varphi_{\mathrm{B}i}\langle\varphi_{\mathrm{A}i}\rangle \tag{A.4}$$

Moreover, $z\lambda_1L\varphi_{\mathrm{A}1}$ and $z\lambda_1L\varphi_{\mathrm{A}M}$ A segments on each wall contribute an interaction energy w_{AS}; similarly, $z\lambda_1L\varphi_{\mathrm{B}1}$ and $z\lambda_1L\varphi_{\mathrm{B}M}$ B segments on each wall contribute an interaction energy w_{BS}. The total potential energy in the interfacial system will then be

$$U_{\mathrm{interf}}[\{n_c\}] = \tfrac{1}{2}zLw_{\mathrm{AA}}\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{A}i}\rangle + \tfrac{1}{2}zLw_{\mathrm{BB}}\sum_{i=1}^{M}\varphi_{\mathrm{B}i}\langle\varphi_{\mathrm{B}i}\rangle + zLw_{\mathrm{AB}}\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{B}i}\rangle + z\lambda_1L\varphi_{\mathrm{A}1}w_{\mathrm{AS}} + z\lambda_1L\varphi_{\mathrm{A}M}w_{\mathrm{AS}} + z\lambda_1L\varphi_{\mathrm{B}1}w_{\mathrm{BS}} + z\lambda_1L\varphi_{\mathrm{B}M}w_{\mathrm{BS}} \tag{A.5}$$

Taking the difference between eq A.5 and A.2 and using eq 15 to substitute homopair in terms of heteropair volume fraction products, we have, by eq 9,

$$U = \tfrac{1}{2}zLw_{\mathrm{AA}}\left[\sum_{i=1}^{M}\varphi_{\mathrm{A}i}[1 - \langle\varphi_{\mathrm{B}i}\rangle - (\delta_{1i} + \delta_{Mi})\lambda_1] - \frac{nr_{\mathrm{A}}^2}{Lr}\right] + \tfrac{1}{2}zLw_{\mathrm{BB}}\left[\sum_{i=1}^{M}\varphi_{\mathrm{B}i}[1 - \langle\varphi_{\mathrm{A}i}\rangle - (\delta_{1i} + \delta_{Mi})\lambda_1] - \frac{nr_{\mathrm{B}}^2}{Lr}\right] + zLw_{\mathrm{AB}}\left[\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{B}i}\rangle - \frac{nr_{\mathrm{A}}r_{\mathrm{B}}}{Lr}\right] + z\lambda_1Lw_{\mathrm{AS}}[\varphi_{\mathrm{A}1} + \varphi_{\mathrm{A}M}] + z\lambda_1Lw_{\mathrm{BS}}[\varphi_{\mathrm{B}1} + \varphi_{\mathrm{B}M}]$$

From the above, by using eq 12,

$$U = zL[w_{\mathrm{AB}} - \tfrac{1}{2}w_{\mathrm{AA}} - \tfrac{1}{2}w_{\mathrm{BB}}]\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{B}i}\rangle + z\lambda_1L[w_{\mathrm{AS}} - \tfrac{1}{2}w_{\mathrm{AA}}][\varphi_{\mathrm{A}1} + \varphi_{\mathrm{A}M}] + z\lambda_1L[w_{\mathrm{BS}} - \tfrac{1}{2}w_{\mathrm{BB}}][\varphi_{\mathrm{B}1} + \varphi_{\mathrm{B}M}] + \tfrac{1}{2}zLw_{\mathrm{AA}}\frac{nr_{\mathrm{A}}}{L}\left[1 - \frac{r_{\mathrm{A}}}{r}\right] + \tfrac{1}{2}zLw_{\mathrm{BB}}\frac{nr_{\mathrm{B}}}{L}\left[1 - \frac{r_{\mathrm{B}}}{r}\right] - zLw_{\mathrm{AB}}\frac{nr_{\mathrm{A}}r_{\mathrm{B}}}{Lr}$$

and, by employing eq 1,

$$U = Lz[w_{\mathrm{AB}} - \tfrac{1}{2}w_{\mathrm{AA}} - \tfrac{1}{2}w_{\mathrm{BB}}]\left[\sum_{i=1}^{M}\varphi_{\mathrm{A}i}\langle\varphi_{\mathrm{B}i}\rangle - \frac{nr_{\mathrm{A}}r_{\mathrm{B}}}{Lr}\right] + Lz\lambda_1[w_{\mathrm{AS}} - \tfrac{1}{2}w_{\mathrm{AA}}][\varphi_{\mathrm{A}1} + \varphi_{\mathrm{A}M}] + Lz\lambda_1[w_{\mathrm{BS}} - \tfrac{1}{2}w_{\mathrm{BB}}][\varphi_{\mathrm{B}1} + \varphi_{\mathrm{B}M}] \tag{A.6}$$

Introducing defintions 17 and 18 in eq A.6, one obtains expression 16 for the potential energy U.

Appendix B: Numerical Solution of the System of Model Equations (54) and (57)-(64)

Use is made of the symmetry of the model interfacial system, to reduce the size of the problem. For identical surfaces, adjacent to layers 1 and M (as was assumed in all cases studied) the following conditions hold:

$$\varphi_{\mathrm{A}i} = \varphi_{\mathrm{A}M-i+1} \qquad 1 \le i \le m \tag{B.1}$$

$$p_{\mathrm{B}i} = p_{\mathrm{B}M-i+1} \qquad 1 \le i \le m \tag{B.2}$$

In view of the model equations, these further imply

$$p_{\mathrm{A}i} = p_{\mathrm{A}M-i+1} \qquad 1 \le i \le m \tag{B.3}$$

$$p^+(i,s) = p^+(M-i+1,s) \qquad 1 \le i \le m,\ 1 \le s \le r \tag{B.4}$$

$$p^-(i,s) = p^-(M-i+1,s) \qquad 1 \le i \le m,\ 1 \le s \le r \tag{B.5}$$

By virtue of the above symmetry conditions we confined ourselves to the half-domain $1 \le i \le m$.

Equations 57 and 58 for $2 \le i \le m - 1$ were kept as they appear in section 1. Equation 58 for $i = m$ was written as

$$p_{\mathrm{A}m} = p_{\mathrm{B}m}\exp\left[2\chi\left(\lambda_1\varphi_{\mathrm{A}m-1} + (\lambda_0 + \lambda_1)\varphi_{\mathrm{A}m} - \frac{r_{\mathrm{A}}}{r}\right)\right] \tag{B.6}$$

Equation 58 for $m + 1 \le i \le M$, as well as eq 59, was omitted. Equation 60 was modified as in eq B.7. Equation 62 was similarly modified. Equations 54 and 64

$$\begin{bmatrix} p^+(1,s) \\ p^+(2,s) \\ \vdots \\ p^+(\mathrm{i},s) \\ \vdots \\ p^+(m-1,s) \\ p^+(m,s) \end{bmatrix} = \begin{bmatrix} \lambda_0p_{t(s)1} & \lambda_1p_{t(s)1} & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1p_{t(s)2} & \lambda_0p_{t(s)2} & \lambda_1p_{t(s)2} & \cdot & & & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \lambda_1p_{t(s)i} & \lambda_0p_{t(s)i} & \lambda_1p_{t(s)i} & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & \cdot & \lambda_1p_{t(s)m-1} & \lambda_0p_{t(s)m-1} & \lambda_1p_{t(s)m-1} \\ 0 & \cdot & \cdot & \cdot & & \lambda_1p_{t(s)m} & (\lambda_0+\lambda_1)p_{t(s)m} \end{bmatrix} \begin{bmatrix} p^+(1,s-1) \\ p^+(2,s-1) \\ \vdots \\ p^+(i,s-1) \\ \vdots \\ p^+(m-1,s-1) \\ p^+(m,s-1) \end{bmatrix} \qquad 2 \le s \le r \tag{B.7}$$

were taken into account for the m first layers only. The resulting system is a set of $(2r + 3)m$ equations in the unknowns φ_{Ai}, p_{Ai}, p_{Bi}, $p^+(i,s)$, $p^-(i,s)$, $1 \le i \le m$, $1 \le s \le r$; it is completely analogous in structure to the original system.

The solution strategy is based on considering the variables p_{Ai}, $p^+(i,s)$, and $p^-(i,s)$ as functions of φ_{Ai} and p_{Bi}, given by eq 57–63, and on treating the $2m$ equations (54) and (64) as a set in the $2m$ unknowns φ_{Ai} and p_{Bi}.

A Newton–Raphson numerical solution scheme with analytical calculation of the Jacobian, analogous to the one discussed in ref 1, was implemented. Equations 57, 58, and B.6 were differentiated to arrive at analytical expressions for the derivatives $\partial p_{Ai}/\partial \varphi_{Aj}$ and $\partial p_{Ai}/\partial p_{Bj}$. Equation B.7 and its counterparts, obtained from equation 62, were differentiated to obtain recursive relations that permit the calculation of derivatives $\partial p^+(i,s)/\partial \varphi_{Aj}$, $\partial p^+(i,s)/\partial p_{Bj}$, $\partial p^-(i,s)/\partial \varphi_{Aj}$, and $\partial p^-(i,s)/\partial p_{Bj}$. The elements of the Jacobian matrix were evaluated from the above derivatives of segment probabilities, using analytical expressions derived by differentiation of the residuals defined by eq 54 and 64.

This analytical scheme was somewhat laborious to implement and considerably demanding in computation time, due to the recursive calculations required for obtaining the derivatives of end segment probabilities. These limitations are by far outweighed by its excellent convergence characteristics. In the applications, described in a companion publication, a uniform volume fraction profile ($\varphi_{Ai} = r_A/r$, $1 \le i \le m$) and a uniform free B-segment probability profile ($p_{Bi} = 1$, $1 \le i \le m$) were used as an initial guess. For our surface-active polymer studies a zeroth order continuation scheme in the parameter χ_s was implemented; calculations for a given chain length were started at $\chi_s = 0$ (pure homopolymer case) and proceeded to progressively increasing values of χ_s, using the solution obtained in each case as an initial guess for the next one. A step size $\Delta\chi_s = 1$ proved adequate for computations up to high χ_s values.

In all calculations, A was chosen as the less abundant segment species. By exchanging the roles of A and B in some test cases (with an accompanying sign inversion in χ_s) it was confirmed that the model coverges to the same solution, irrespective of how segment types are defined. Five iterations were typically required for reducing the maximum norm of the vector of residuals to less than 10^{-8}.

Computation time for an iteration was found to scale approximately linearly with chain length (r) and quadratically with the number of layers employed (m). For given r and m values the copolymer code is slower than the homopolymer code, discussed in ref 1, by a factor of 5.8. The fact that the copolymer model involves twice as many equations and variables gives rise to a fourfold increase in the size of the Jacobian; in addition, calculations for obtaining a single Jacobian element are inherently more elaborate than in the homopolymer case. The CPU time per iteration for a $m = 100$, $r = 100$ copolymer system on a VAXstation II, running ULTRIX 32m (f77 compiler, 64 bit real arithmetic), is 1015 s.

Appendix C: Derivation of Equation 66 for the Helmholtz Energy

Substituting the equilibrium distribution (65) into expression 19 for the partition function we obtain

$$\ln Q = n \ln [n/M] - \sum_c n_c \ln [n/M] - \sum_c n_c \sum_{i=1}^{M} [r_{Ai,c} \ln p_{Ai} + r_{Bi,c} \ln p_{Bi}] - L\chi \left[\sum_{i=1}^{M} \varphi_{Ai} \langle \varphi_{Bi} \rangle - \frac{n r_A r_B}{Lr} \right] - L \left[\frac{u_S{}^A}{kT} [\varphi_{A1} + \varphi_{AM}] + \frac{u_S{}^B}{kT} [\varphi_{B1} + \varphi_{BM}] \right] \quad (C.1)$$

Furthermore, from eq 6, 11, 15, and 56,

$$\ln Q = \sum_{i=1}^{M} [(\sum_c n_c r_{Ai,c}) \ln p_{Ai} + (\sum_c n_c r_{Bi,c}) \ln p_{Bi}] - L\chi \left[\sum_{i=1}^{M} \varphi_{Ai}(1 - \langle \varphi_{Ai} \rangle) - \frac{n r_A r_B}{Lr} \right] + L\chi\lambda_1(\varphi_{A1} + \varphi_{AM}) - L\frac{2u_S{}^B}{kT} + L\chi_s(\varphi_{A1} + \varphi_{AM}) \quad (C.2)$$

Addition of eq 20 for all layers leads to the full occupancy condition:

$$nr = ML \quad (C.3)$$

Using eq 21 and C.3 in eq C.2 we obtain

$$-\frac{1}{L} \ln Q = \frac{2u_S{}^B}{kT} - (\chi_s + \lambda_1\chi)(\varphi_{A1} + \varphi_{AM}) + \sum_{i=1}^{M} [\varphi_{Ai} \ln p_{Ai} + (1 - \varphi_{Ai}) \ln p_{Bi}] + \chi \left(\sum_{i=1}^{M} \varphi_{Ai}(1 - \langle \varphi_{Ai} \rangle) - M\frac{r_A r_B}{r^2} \right)$$

which is eq 66.

Appendix D: Simplification of Expression 79 for the Normalization Factor $p_b(s)$

We prove here that the normalization factor $p_b(s)$, defined by eq 79 and used in the calculation of absolute numbers of bonds perpendicular and parallel to the surface, is bond-order independent and equal to the number of lattice layers M. Physically this means that, in our simple lattice model, the total probability for a particular bond of a chain to lie somewhere within the interfacial system is independent of where this bond is located along the chain.

Isolating the terms corresponding to $i = 1$ and $i = M$ from the first sum in eq 79, the $i = 1$ term from the second sum, and the $i = M$ term from the third sum and reindexing the third sum in that equation, we obtain

$$p_b(s) = \lambda_0 p^+(1,s)p^-(1,r-s) + \lambda_0 p^+(M,s)p^-(M,r-s) + \lambda_0 \sum_{i=2}^{M-1} p^+(i,s)p^-(i,r-s) + \lambda_1 p^+(1,s)p^-(2,r-s) + \lambda_1 \sum_{i=2}^{M-1} p^+(i,s)p^-(i+1,r-s) + \lambda_1 \sum_{i=2}^{M-1} p^+(i,s)p^-(i-1,r-s) + \lambda_1 p^+(M,s)p^-(M-1,r-s) = p^+(1,s)[\lambda_0 p^-(1,r-s) + \lambda_1 p^-(2,r-s)] + \sum_{i=2}^{M-1} p^+(i,s)[\lambda_1 p^-(i-1,r-s) + \lambda_0 p^-(i,r-s) + \lambda_1 p^-(i+1,r-s)] + p^+(M,s)[\lambda_1 p^-(M-1,r-s) + \lambda_0 p^-(M,r-s)] \quad (D.1)$$

By virtue of the recursive relations (62) between end segment probabilities in the negative direction,

$$\lambda_0 p^-(1,r-s) + \lambda_1 p^-(2,r-s) = p^-(1,r-s+1)/p_{t(s)1}$$

$$\lambda_1 p^-(i-1,r-s) + \lambda_0 p^-(i,r-s) + \lambda_1 p^-(i+1,r-s) = p^-(i,r-s+1)/p_{t(s)i} \qquad 2 \le i \le M - 1$$

$$\lambda_1 p^-(M-1,r-s) + \lambda_0 p^-(M,r-s) = \frac{p^-(M,r-s+1)}{p_{t(s)M}} \quad (D.2)$$

By combination of (D.1) and (D.2),

$$p_b(s) = \sum_{i=1}^{M} \frac{p^+(i,s)p^-(i,r-s+1)}{p_{t(s)i}} = \frac{1}{(P^*{}_A)^{r_A}(P^*{}_B)^{r_B}} \sum_{i=1}^{M} \frac{P^+(i,s)P^-(i,r-s+1)}{P_{t(s)i}} \quad (D.3)$$

where the definitions (46) have been used to revert from lower case to upper case probability notation.

By use of 42 and 53 in eq D.3,

$$p_b(s) = \frac{M}{P(r)}\sum_{i=1}^{M} P(s,i;r) \qquad \text{(D.4)}$$

which, by definition 33 of the normalizing factor $P(r)$, becomes $p_b(s) = M$, independent of bond order s, QED.

List of Symbols

a	area per surface lattice site
A	Helmholtz energy
b_i	bond backstepping probability in layer i
c	index for conformations
$\mathbf{C}_i$	the M-long vector col (0, 0, ..., 0, 1, 0, ..., 0) with unit in ith position
f_i	forward stepping probability in layer i
F	augmented objective function, incorporating Lagrange multipliers, used for constrained optimization
G_i	constraint arising from full occupancy requirement in layer i
i	index for layers
k	Boltzmann constant
$k(s,c)$	layer number in which segment s of conformation c finds itself
L	number of sites per layer
m	half of the number of layers M
M	number of layers of model interfacial system
n	number of chains
n_{bi}	number of bonds per surface site in layer i
n_c	number of chains belonging to conformation c
n_i	number of chains per surface site passing through layer i
n_{si}	average number of segments per surface site that a chain passing through layer i has in that layer
p	probability in the site model, reduced by the corresponding value for the unconstrained bulk
$\mathbf{p}^+(s)$, $\mathbf{p}^-(s)$	vectors of reduced end segment probabilities $p^+(i,s)$ and $p^-(i,s)$, respectively
$p_b(s)$	total reduced probability, for all possible locations and orientations of bond s in model system
$P^+(i,s)$	end segment probability for an s-segment long subchain on layer i, in the positive direction along the chain
$P^-(i,s)$	end segment probability for an s-segment long subchain on layer i, in the negative direction along the chain
$P(s,i;r)$	probability that sth segment of a chain r segments long is in layer i
$P(s,i;r)_c$	probability that sth segment of a chain r segments long, belonging to conformation c, is in layer i
$P(r)$	chain probability (normalization factor)
$P(r)_c$	probability of conformation c in site model
P_{Ii}	free segment probability of species I in layer i
q_i	side-stepping probability in layer i
Q	canonical partition function
r	number of segments per chain
$r_{i;c}$	number of segments of a chain belonging to conformation c in layer i
r_I	number of I-type segments per chain (I = A, B)
$r_{Ii,c}$	number of I-type segments of a chain belonging to conformation c in layer i (I = A, B)
s	index for segments and bonds along a chain
S_i	bond order parameter in layer i
$t(s)$	type of sth segment along the chain (may assume the values A, B)
T	temperature
$u_S{}^I$	adsorption energy of a segment of type I, defined in eq 18
U	potential energy of interfacial system relative to unconstrained bulk
$U_{bulk}(n)$	potential energy of a system of n chains in the unconstrained bulk
$U_{interf}[\{n_c\}]$	potential energy of the interfacial system under the set of conformations $\{n_c\}$
$\mathbf{w}_I$	matrix, characteristic of type-I segment, appearing in recursive relations 60 and 62
w_{IJ}	interaction energy between nearest neighbor I- and J-type segments (I, J = A, B)
w_{IS}	interaction energy between adsorbed I-type segment and the surface
z	lattice coordination number

Greek Symbols

γ	surface tension; interfacial tension
Δw_{AB}	interchange energy, defined by eq 17
ϵ	dimensionless interfacial free energy relative to a pure monomeric fluid of B segments, defined by eq 69
ζ_i	Lagrange multiplier, corresponding to full occupancy constraint in layer i
λ_0	fraction of nearest-neighbor sites to a given site lying in same layer as the considered site
λ_1	fraction of nearest-neighbor sites to a given site lying in layer above (i.e., nearer the surface) the layer of the considered site; also, fraction of nearest-neighbor sites to a given site lying in layer below the layer of the considered site
ξ_i	quantity $\exp[-(\zeta_i - \zeta^*)]$
φ_{Ii}	volume fraction of I-type segments in layer i (I = A, B)
$\langle\varphi_{Ii}\rangle$	site volume fraction of I-type segments on layer i, defined by eq 13
χ	Flory interaction parameter expressing the difference in interaction energy between unlike and like pairs of segments, defined in eq 17
$\chi_S{}^I$	dimensionless adsorption energy for an I-type segment, defined by eq 26
χ_s	surface interaction parameter, expressing the difference in affinities of the two types of segments for the surface, defined by eq 56
ω_c	factor proportional to the number of arrangements of conformation c in the lattice
Ω	number of ways of arranging a given set of conformations $\{n_c\}$ in the lattice

Superscripts

abs	probability defined in terms of absolute bond numbers
A	pertaining to A-type segments
B	pertaining to B-type segments
L	longitudinal (in direction parallel to surface)
T	transverse (in direction perpendicular to surface)
+	positive direction along the chain (head to tail)
−	negative direction along the chain (tail to head)
′	negation
*	unconstrained bulk polymer

Subscripts

A	A-type segment
b	bond
B	B-type segment
c	conformation
i	pertaining to layer i
(i)	chain passing through layer i
s	segment; surface
S	surface
∞	unconstrained bulk polymer, in the absence of interfaces

References and Notes

(1) Theodorou, D. N. *Macromolecules*, first of four papers in this issue. Theodorou, D. N. *Macromolecules*, second of four papers in this issue.

(2) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619–1635.; **1980**, *84*, 178–190; *Macromolecules* **1985**, *18*, 1882–1900.

(3) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986; p 295. Denbigh, K. *The Principles of Chemical Equilibrium*, 4th ed.; Cambridge University Press: Cambridge, 1981; p 245.

(4) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.