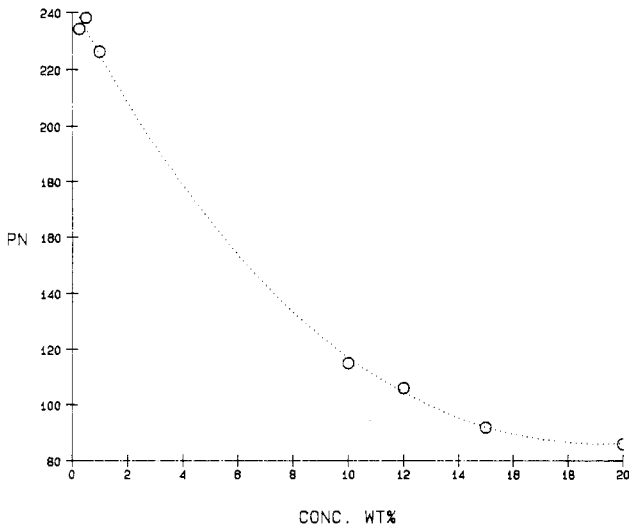

Figure 7. Plot of the number of repeating units per micelle versus concentration.

lectrolyte system like this, the micelles tend to reduce their surface charge densities at high concentrations by reducing their aggregation number to minimize the double-layer repulsive energies and at the same time increase the entropy of dispersion. The reason for a reduced R observed at high concentration is related to the penetration of water molecules deeper into the head-group region. The increase of hydration number from 10 at low concentration to 30 at the highest concentration implies that the contrast between the head group and the solvent is gradually lost in this process. The cylinder radius thus appears to be smaller to neutrons. The intermicellar structure factor extracted from the data by dividing it by the micellar form factor (Figure 6) shows an interacting peak occurring at $Q_{max} = 0.05$ Å^{-1} which moves to larger Q as the concentration increases. Another unusual feature is a rising component above unit at the very small Q region. This observation is consistent with SANS data for star-branched polystyrene in a good solvent.[15] In the latter case, when $c > c^*$, an increase in $I(Q)$ is observed at small Q and at the same time the maximum at intermediate Q is shifted to higher Q as the concentration increases. This feature cannot be easily explained without a detailed knowledge of the structure factor of cylindrical micelles, for which some theoretical progress has been made in recent years,[16,17] but a practical method for data analysis has not been proposed.

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Registry No. Neutron, 12586-31-1; (maleic anhydride)(1-octadecene) (alternating copolymer, lithium salt), 113109-85-6.

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Lattice Models for Bulk Polymers at Interfaces

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ABSTRACT: Lattice models for the prediction of conformational characteristics and thermodynamic properties at bulk polymer/solid and bulk polymer/gas interfaces are critically examined. Existing models are shown to fall into two broad categories: bond models, in which the probability of a chain conformation is expressed as a product of bond transition probabilities, and site models, in which the probability of a conformation is proportional to a product of probabilities characteristic of the sites occupied by successive chain segments. A general mathematical formulation is developed for bond models, which includes Dill and Flory's model of liquid bilayer membranes and Helfand's model of a pure homopolymer at an interface as special cases. The key assumptions, leading to closure of the bond model equations in each of these two cases, are elucidated.

Introduction

In this series of papers we discuss some lattice approaches for modeling the microscopic structure and thermodynamic properties of bulk polymers at interfaces. We are mainly concerned with polymer/solid, polymer/gas, and polymer/vacuum interfaces, across which there is a relatively abrupt change in polymer segment density. Immiscible polymer/polymer interfaces, for which several theoretical approaches have been developed,[1] will thus not be an object of our investigation. Our interest will focus

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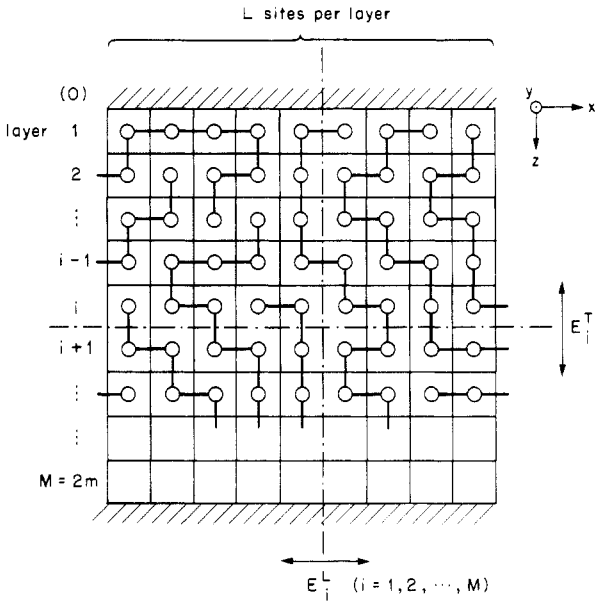

Figure 1. Two-dimensional representation of the lattice model used to study a pure homopolymer in the vicinity of a solid surface.

on bulk multichain systems, as opposed to polymer solutions, which have also been studied rather extensively in the vicinity of an interface.[2,3] We will be concerned with linear, flexible homopolymer chains, or copolymer chains consisting of two types of segments, with different affinities for the surface.

Understanding the properties of bulk polymers at interfaces is important in a variety of technical areas, such as adhesion and the performance of composite materials, as well as the mechanical, electrical, and optical behavior of thin polymer films. The details of molecular structure and conformation in the vicinity of the interface play a critical role in determining these properties. Entropic effects, due to the presence of a solid barrier, or a discontinuity at the surface, as well as adsorption energy effects, due to the dissimilarity of segment–segment and segment–surface interactions, may cause the conformation of chains to deviate significantly from its bulk characteristics. Idiosyncrasies of structure will lead, in turn, to spatially dependent properties within the polymer in the vicinity of the surface.

The concept of spatially dependent mechanical properties at a solid/polymer composite interface has been invoked to explain experimental observations by Theocaris.[4] A third phase, termed the "mesophase", of thickness of the order 2400 Å, is postulated to lie between the polymer matrix and the solid inclusion phases; its modulus is assumed to vary smoothly between the moduli of the two phases, according to an empirical power law. Factors such as surface roughness, the presence of microvoids, and local stresses due to differences in thermal expansivity, may affect local properties at a composite interface. Even in the absence of such imperfections, however, a spatial variation will still exist as a result of the special conformational characteristics of chains at the interface.

To clarify the connection between interfacial structure and local mechanical properties, we consider the highly idealized case of a glassy polymer, occupying a three-dimensional simple cubic lattice, adjacent to a perfectly smooth, flat solid surface. (A two-dimensional representation is sketched in Figure 1.) The interface is pictured as extending infinitely in the x- and y-directions; we concentrate on a portion of it, having L sites on the surface layer. Layers are numbered successively from the surface layer along the z-direction. Without loss of generality it may be assumed that the model system is bounded by a second smooth solid surface, adjacent to layer $M = 2m$.

Let n_{bi}^T be the number of bonds per surface site connecting layers i and $i + 1$, and n_{bi}^L the number of bonds per surface site lying flat in layer i. As a first approximation we assume that, upon imposition of a small deformation, the model interfacial system responds affinely, each intersite space in the lattice behaving as a Hookean element, with spring constant k^s, for a space between a surface segment and the solid; k^b, for an intersite space between two bonded polymer segments; and k^{nb}, for an intersite space between two nonbonded polymer segments.

The spring constants k^s, k^b, and k^{nb} reflect the magnitude of the curvature of the adsorptive (surface–segment), bonded (segment–segment), and nonbonded (segment–segment) interaction potentials, respectively. Normally, one would expect

$$k^b \gg k^{nb} \tag{1}$$

the value of k^s being determined by the nature of polymer and solid.

In a deformation of the system along the z-direction, the region between layers i and $i + 1$ will respond with a local transverse Young's modulus of

$$E_0^T = k^s/l \qquad \text{(solid/polymer contact plane)} \tag{2}$$

and

$$E_i^T = \frac{1}{l}[k^{nb} + n_{bi}^T(k^b - k^{nb})] \qquad \text{(polymer matrix)} \tag{3}$$

In a deformation of the system along the x- or y-directions, intersite spaces on the ith layer will respond with a local longitudinal Young's modulus of

$$E_i^L = \frac{1}{l}\left[k^{nb} + \frac{n_{bi}^L}{2}(k^b - k^{nb})\right] \tag{4}$$

In the unconstrained bulk limit n_{bi}^T and n_{bi}^L will assume asymptotic forms that are layer-number independent. For a monodisperse polymer of chains r segments long, in a simple cubic lattice,

$$\lim_{i\to m} n_{bi}^T = \frac{1}{2}\lim_{i\to m} n_{bi}^L = \frac{1}{3}\,\frac{r-1}{r} \tag{5}$$

The unconstrained bulk will be isotropic, with E_i^T and E_i^L equal and position-independent. In the vicinity of the surface, however, local anisotropy is induced; the profiles $\{n_{bi}^T\}$ and $\{n_{bi}^L\}$ are nonuniform and the local elastic constants spatially dependent.

Very significant improvement of composite interfacial properties is achieved by the use of coupling agents. Silanes,[5,6] for example, are widely employed to enhance adhesion between polymer resins and glass surfaces. According to prevailing views silanes form a chemically bonded monolayer on the glass surface, on top of which lie chemisorbed polysiloxanes and physically adsorbed silane hydrolyzates. Functional groups on the silane coupling agent react with matching groups in the polymer. Within the framework of the lattice model a resin in the presence of coupling agent can then be seen as a copolymer; in each chain of this copolymer there is a small number of segments, capable of reaction with the coupling agent, with much greater affinity for the surface than the majority of segments. Local mechanical properties will be drastically affected by this modification. In the simple picture represented by eq 2–4, the constant k^s, characterizing direct attachment to the surface, will increase. Moreover, the tendency for preferential attachment of

chains through specific segments will give rise to orientation effects, which will persist to much larger distances from the surface than is the case for a pure homopolymer. In other words, the profiles $\{n_{bi}^T\}$ and $\{n_{bi}^L\}$ and, consequently, $\{E_i^T\}$ and $\{E_i^L\}$, will be modified.

Knowledge of the spatial variation of local elastic constants in the vicinity of the interface is very important for predicting the overall mechanical response of the composite in elastic deformation, as well as its ultimate properties. As regards the latter, we note that the local elastic modulus enters the Griffith criterion for failure[7] and thus plays a key role in predicting whether the material will fail cohesively or interfacially at high stresses.

Improving our fundamental knowledge of chain conformation and bond orientation characteristics at the microscopic level will greatly enhance our ability to predict the macroscopic properties of interfacial systems.

Lattice models offer a simple and consistent picture of the structural characteristics at polymer/solid, polymer/gas, or polymer/vacuum interfaces. Unlike early continuum Gaussian random walk models[8,1] they are well suited for cases in which conformational properties vary rapidly within a narrow interfacial region,[9] which are of primary interest here. It should be stressed, of course, that all lattice models examined here are based on a mean-field treatment of configurational statistics in a multichain system and are therefore not expected to be rigorously "correct".

Our discussion of lattice models for interfaces in this paper falls into two sections. The first section consists of a brief examination of previous lattice approaches, developed by Helfand,[9,2] Dill and Flory,[10,11] and Scheutjens and Fleer.[3] These approaches are shown to fall into two general categories, which we call "bond models" and "site models". In the second section the mathematical structure of bond models is examined, employing a generalization of the formulation introduced by Dill and Flory.[10] It is shown that a condition for closure must be introduced in the set of model equations, and the way in which this is done by Helfand for a homopolymer, and by Dill and Flory for a surface-active polymer system, is elucidated.

In subsequent publications we will develop a simple lattice model for the interfacial behavior of bulk homopolymers, as well as copolymers, consisting of two types of segments, which may interact differently with the surface. Methods for the exploration of structural characteristics at the interface will be introduced, and results on structure and interfacial tension will be compared with experimental evidence.

1. Bond Models versus Site Models for Polymer Interfaces

Existing lattice models that can be applied to bulk polymers at interfaces can conceptually be divided into two categories: bond models and site models.

In *bond models* propagation of a chain through the lattice is viewed as a Markov process. The probability of a conformation is set proportional to a product of bond stepping (transition) probabilities, taken over the entire length of the chain. By bond stepping probability we mean the conditional probability that a segment of a chain occupies a certain position in the lattice, given the position of the preceding segment. Symbolically, for a chain of r segments,

$$P_c = p(\mathbf{r}_{1;c}) \prod_{s=1}^{r-1} p(\mathbf{r}_{s+1;c}/\mathbf{r}_{s;c}) = p(\mathbf{r}_{1;c}) \prod_{s=1}^{r-1} p_{b,s;c} \qquad (6)$$

A bond lattice model for chains of infinite length was introduced by Helfand.[9] This model was applied to polymer/polymer and polymer solution/solid interfaces. Brief consideration was also given to the bulk polymer/solid interface.[2] A "conformation" in the Helfand model should be understood as a configuration of the entire lattice, defined by the sequence of lattice sites occupied by all segments in it; the number r stands for the total number of all segments in the lattice. An equation of the form (6) is written for the probability of a configuration in the absence of the restriction of no multiple occupancy of cells by segments. The conditional probabilities $p_{b,s;c}$ are assumed to depend solely on the layer i from which bond s emanates, and on the direction of this bond. For a pure homopolymer,

$$\begin{aligned} (p_{b,s;c})_H &= g_i^+/z, \quad \text{if } k(s,c) = i, \ k(s+1,c) = i+1 \\ &= g_i^0/z, \quad \text{if } k(s,c) = i, \ k(s+1,c) = i \\ &= g_i^-/z, \quad \text{if } k(s,c) = i, \ k(s+1,c) = i-1 \end{aligned} \qquad (7)$$

where z is the lattice coordination number and $k(s,c)$ stands for the layer number on which segment s finds itself under conformation c. The quantities g_i^+, g_i^0, and g_i^- are termed "anisotropy factors".

For a given site in the lattice let λ_1, λ_0, and λ_{-1} be the fractions of nearest-neighbor sites that lie in the layer below (farther from the surface than), in the same layer as, and in the layer above the considered site. All work presented here will concern a simple cubic lattice, for which $\lambda_1 = \lambda_{-1} = 1/z = 1/6$ and $\lambda_0 = 2/3$. The symbol λ_1 will be used in place of λ_{-1} in the following.

Normalization of the bond conditional probabilities in the Helfand model leads to the requirement

$$\lambda_1 g_i^+ + \lambda_0 g_i^0 + \lambda_1 g_i^- = 1 \qquad 1 \le i \le M \qquad (8)$$

As a result of wall impenetrability in the model system of Figure 1,

$$g_1^- = g_M^+ = 0 \qquad (9)$$

Moreover, the requirement of symmetry upon inversion of the order in which segments are numbered leads to the "chain flux" constraint

$$g_i^- = g_{i+1}^+ \qquad 1 \le i \le M \qquad (10)$$

The restriction of no overlap of segments in lattice sites is introduced by Helfand as a multiplying factor, correcting P_c, and estimated by a Flory–Huggins procedure of filling the lattice with polymer segments. An expression for the entropy is written in terms of conformation probabilities and recast in terms of bond conditional probabilities. For half the system depicted in Figure 1 (layers 1 to m of the lattice, adjacent to one surface), the Helmholtz energy relative to the unconstrained polymer bulk is calculated as

$$\frac{1}{LkT} A\{g_i^+, g_i^0, g_i^-\} = \frac{u_s}{kT} + \sum_{i=1}^{m} (\lambda_1 g_i^+ \ln g_i^+ + \lambda_0 g_i^0 \ln g_i^0 + \lambda_1 g_i^- \ln g_i^-) \qquad (11)$$

where u_s stands for the difference between polymer–surface and polymer segment–segment interaction energies. For preferential adsorption on the surface, $u_s < 0$.

The values of bond stepping probabilities at equilibrium are determined by minimizing the Helmholtz energy given by (11) with respect to the anisotropy factors, subject to the constraints in (8)–(10). The minimization requirement leads to relations of the form

$$g_i^+/g_i^0 = g_{i+1}^0/g_{i+1}^- \qquad 1 \le i \le M-1 \qquad (12)$$

The profiles $\{g_i^+\}$, $\{g_i^0\}$, and $\{g_i^-\}$ can be obtained from eq 8–10 and 12.

The value of the Helmholtz energy at the minimum can be written as

$$\frac{A}{LkT} = u_s - \sum_{i=1}^{m} \zeta_i = \frac{\gamma a}{kT} \tag{13}$$

where ζ_i are the Lagrange multipliers associated with the constraints in (8) at the minimum.

Another bond lattice model was introduced by Dill and Flory,[10,11] to explore the seemingly unrelated problem of the packing of short, surface-active molecules in monolayers and lipid bilayer membranes and to provide an explanation for the experimentally observed "bond disorder gradient". We will discuss this approach only briefly here, since a generalized form of it will be developed in detail in section 2. A conformation, according to the Dill–Flory approach, is defined by the sequence of layer numbers on which successive segments lie. All molecules in a lamellar bilayer membrane are pictured as having their polar heads on one of the bilayer surfaces. In the symbolism of eq 6,

$$\begin{aligned} p(\mathbf{r}_{1;c}) &= 1, \quad \text{if} \quad k(1,c) = 1 \\ &= 0, \quad \text{if} \quad k(1,c) \neq 1 \end{aligned} \tag{14}$$

Bond stepping probabilities are taken as

$$\begin{aligned} (p_{\mathrm{b},s;c})_{\mathrm{DF}} &= f_i, \quad \text{if} \quad k(s,c) = i, \quad k(s+1,c) = i+1 \\ &= q_i, \quad \text{if} \quad k(s,c) = i, \quad k(s+1,c) = i \\ &= 0, \quad \text{if} \quad k(s,c) = i, \quad k(s+1,c) = i-1 \end{aligned} \tag{15}$$

and obey the normalization condition

$$f_i + q_i = 1 \qquad 1 \leq i \leq M \tag{16}$$

As seen from eq 15, "back stepping" of molecules toward the surface is not allowed. This assumption is rationalized on the basis of the short length of the chains and the high degree of order prevailing at the interface. A requirement of full occupancy of the lattice by chain segments is introduced. Employing an elegant generator matrix formalism, Dill and Flory arrive at a set of polynomial equations in the conditional probabilities, which they solve numerically, to obtain bond orientation profiles for a given value of the surface density of chain heads.

In *site models* the probability of a chain conformation is equal to a product of site probabilities, characteristic of the positions occupied by chain segments on the lattice. Symbolically,

$$P_c = \omega_c \prod_{s=1}^{r} p(\mathbf{r}_{s;c}) \tag{17}$$

A site model for polymer solutions at interfaces was presented by Scheutjens and Fleer.[3] In this model, as in the Dill and Flory model, a conformation is defined by the sequence of layer numbers in which successive segments lie. The probability of such a conformation is given by an equation of the form (17). The quantity ω_c is a redundancy factor, proportional to the number of actual chain arrangements on the lattice that are consistent with the considered conformation. It is given by

$$\omega_c = \prod_{s=1}^{r-1} (\lambda_{s,s+1})_c \tag{18}$$

with

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

"Free segment probabilities" $p(\mathbf{r}_{s;c})$ depend solely on the layer on which a segment lies:

$$p(\mathbf{r}_{s;c}) = P_{k(s,c)} \tag{19}$$

The structure of the interfacial system is thus completely defined, if the profile $\{P_i\}$ is known for all layers.

The term "probability", coined by Scheutjens and Fleer to denote the quantities P_i, is somewhat misleading. The ratio of P_i to the asymptotic value, P_*, it assumes in the unconstrained bulk polymer has the physical meaning of an equilibrium constant, expressing the likelihood of finding a monomer in layer i of the interfacial system relative to finding it in the unconstrained bulk. This ratio can well exceed 1, although it necessarily approaches unity at large distances from the surface. To establish a connection between site models and the bond models discussed above, we point out that the ratios P_i/P_* are analogous to the exponentials $\exp(-\zeta_i)$ of the Lagrange multipliers ζ_i appearing in expression 13 for Helmholtz energy in the bond model.

In the site model the probability of a conformation is proportional to a product of quantities characteristic of the positions that successive chain segments occupy (eq 17). By definition, the factor ω_c remains unaltered if the order, in which these segments are numbered, is reversed (eq 18). Thus, the probability distribution of conformations in the site model, eq 17, is automatically invariant under reversal of the chain direction. Unlike the corresponding bond model (eq 6), the site model does not involve conditional bond stepping probabilities and thus does not require the additional imposition of a "chain flux" constraint of the type of eq 10.

The Scheutjens–Fleer model is essentially an extension of Flory–Huggins solution theory to systems in which properties can vary along one of the principal lattice directions, as a result of the presence of an interface. Rather than a priori assuming a Markovian expression, such as eq 6, for conformation probabilities, this model starts from a statistical mechanical analysis of the multichain interfacial system, in the mean-field approximation. A partition function is written for the polymer, employing the Bragg–Williams assumption of random mixing within each layer parallel to the adsorbing surface. The requirement of minimum Helmholtz energy leads to the conformation probability distribution described by eq 17–19. The requirement of full occupancy of the lattice by chain segments results in a set of coupled nonlinear equations, from which free segment probabilities can be calculated for each layer. A detailed implementation of the Scheutjens–Fleer approach for bulk homopolymer at an interface will be presented in an accompanying publication. Further comparisons between the premises and predictions of bond and site models will be made there.

2. Generalized Bond Model for Bulk Polymers at Interfaces

The objective of this section is to formulate a generalized Markov lattice model of bulk polymers at interfaces that can cover both the case of a pure bulk homopolymer adsorbed at a surface (considered by Helfand) and the case of a surface-active polymer (considered by Dill and Flory).

Starting, Stepping, and Ending Probabilities. Our model system is a cubic lattice of $M = 2m$ layers between two impenetrable walls (compare Figure 1). The lattice is filled with polymer chains r segments long. If $M \gg r$, then bulk conditions prevail in the middle region between the surfaces, and the domain $1 \leq i \leq m$ constitutes a good model for a semiinfinite polymer adjacent to a solid surface.

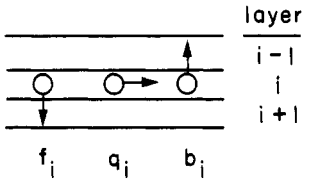

Figure 2. Definition of bond stepping probabilities in the generalized bond model.

We define a "conformation" as an ordered set of r layer numbers, in which the successive segments 1 to r find themselves. Each conformation may thus comprise many chain arrangements (compare treatment in ref 3). Associated with each chain on the lattice is a directionality, defining one of its terminal units as the "start" and the other as the "end".

Let h_i be the probability that a chain starts in layer i. Given that the chain has a segment in layer i, conditional probabilities that it will propagate forward (to layer $i + 1$), sideways (in layer i), or backward (to layer $i - 1$) during its next step are defined as f_i, q_i, and b_i, respectively (see Figure 2). This definition is an immediate extension of that introduced by Dill and Flory (eq 15) and is subject to the normalization condition

$$f_i + q_i + b_i = 1 \qquad 1 \le i \le M \tag{20}$$

The presence of interfaces imposes the restrictions

$$b_1 = 0 \tag{21}$$

$$f_M = 0 \tag{22}$$

In the Markovian formalism employed here the probability of a chain conformation is defined as

$$P_c = h_{k(1,c)} \prod_{i=1}^{M} f_i^{\mu_{i,c}} q_i^{\nu_{i,c}} b_i^{\xi_{i,c}} \tag{23}$$

where $\mu_{i,c}$, $\nu_{i,c}$, and $\xi_{i,c}$ stand for the numbers of forward, sideways, and backward steps taken from layer i by the chain in conformation c (zero values allowed). If $r_{i,c}$ is the number of segments that conformation c has on layer i, then

$$\mu_{i,c} + \nu_{i,c} + \xi_{i,c} + \delta_{i,k(1,c)} = r_{i,c} \tag{24}$$

where the Kronecker δ assumes a value of 1 if $k(1,c) = i$ (chain start of conformation c in layer i) and 0 otherwise. From eq 24 it is obvious that

$$\sum_{i=1}^{M} (\mu_{i,c} + \nu_{i,c} + \xi_{i,c}) = \sum_{i=1}^{M} r_{i,c} - 1 = r - 1 \tag{25}$$

Let

$$\mathbf{H} = \text{col}\ (h_1, h_2, ..., h_M) \tag{26}$$

Let also $\mathbf{G}$ be the stochastic conditional probability matrix

$$\mathbf{G} = \begin{bmatrix} q_1 & f_1 & & & & & \\ b_2 & q_2 & f_2 & & & & \\ & b_3 & q_3 & f_3 & & & \\ & & \cdot & \cdot & \cdot & & \\ & & & b_{M-1} & q_{M-1} & f_{M-1} \\ & & & & b_M & q_M \end{bmatrix} \tag{27}$$

Let

$\mathbf{C}_i =$

$$\text{col}\ (0, 0, 0, ..., 0, 1, 0, ..., 0) \qquad \text{(unity in } i\text{th position)} \tag{28}$$

and

$$\mathbf{B}_i = \sum_{j=1}^{i} \mathbf{C}_j \tag{29}$$

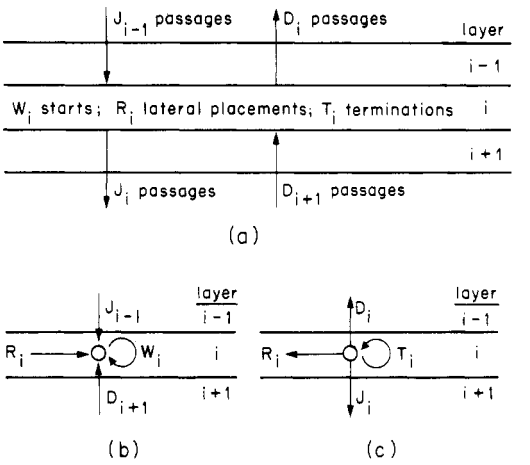

Figure 3. (a) Definition of bond fluxes in the generalized bond model. (b) Balancing all possible origins of a segment, to satisfy the full occupancy requirement. (c) Balancing all possible destinations of a segment, to satisfy the full occupancy requirement.

The requirement of normalization of the starting probabilities can be written as

$$\mathbf{H}^T \mathbf{B}_M = 1 \tag{30}$$

while the stochastic property of $\mathbf{G}$ gives (eq 20–22 and 29)

$$\mathbf{G}\mathbf{B}_M = \mathbf{B}_M \tag{31}$$

Sums of conditional probability products, corresponding to all possible conformations of a chain of r segments, are obtained by raising $\mathbf{G}$ to the power $(r - 1)$. Note that, in this formulation, the possibility of a chain back-folding upon itself is not excluded (patterns of the form $f_i^{\mu_i} b_{i+1}^{\xi_{i+1}} q_i^{\nu_i} q_{i+1}^{\nu_{i+1}}$ with $\mu_i = \xi_{i+1}$ and $\nu_i < \mu_i$ or $\nu_{i+1} < \mu_i$ occur within the elements of $\mathbf{G}^{r-1}$). From eq 23, 30, and 31 one deduces a normalization condition for conformation probabilities:

$$\sum_c P_c = \mathbf{H}^T \mathbf{G}^{r-1} \mathbf{B}_M = \mathbf{H}^T \mathbf{B}_M = 1 \tag{32}$$

The quantity $h_i(\mathbf{G}^k)_{ij}$ is equal to the probability that a chain starts at layer i and finds itself at layer j after k steps. The probability that a chain end is in layer j, irrespective of where it started, will then be

$$e_j = \sum_{i=1}^{M} h_i (\mathbf{G}^{r-1})_{ij} = \mathbf{H}^T \mathbf{G}^{r-1} \mathbf{C}_j \qquad 1 \le i \le M \tag{33}$$

Let

$$\mathbf{E} = \text{col}\ (e_1, e_2, ..., e_M) \tag{34}$$

Ending probabilities are subject to the normalization (compare eq 29 and 32):

$$\mathbf{E}^T \mathbf{B}_M = \sum_{j=1}^{M} e_j = \mathbf{H}^T \mathbf{G}^{r-1} \mathbf{B}_M = \sum_c P_c = 1 \tag{35}$$

Bond Fluxes. Considering a section of the interfacial system with L sites on each surface layer, we define, as shown in Figure 3a, J_i as the number of bonds between layers i and $i + 1$, belonging to chains going from i to $i + 1$; D_i as the number of bonds between layers i and $i - 1$, belonging to chains going from i to $i - 1$; R_i as the number of bonds (lateral placements) lying in layer i; W_i as the number of chain starts in layer i; and T_i as the number of chain ends in layer i.

The numbers of bonds $n_{bi}{}^T$ and $n_{bi}{}^L$ per surface site can be expressed in terms of the above quantities as

$$n_{bi}{}^T = \frac{J_i + D_{i+1}}{L}, \qquad n_{bi}{}^L = R_i/L \tag{36}$$

We now relate the above bond flux quantities to the probabilities of the Markovian model, introduced earlier.

Let n be the total number of chains in the model system. By definition,

$$W_i = nh_i \qquad 1 \le i \le M \tag{37}$$

$$T_i = ne_i \qquad 1 \le i \le M \tag{38}$$

The quantities R_i, J_i, and D_i are given by

$$R_i = n\langle \nu_i \rangle \qquad J_i = n\langle \mu_i \rangle \qquad D_i = n\langle \xi_i \rangle \tag{39}$$

where $\langle \nu_i \rangle$, $\langle \mu_i \rangle$, and $\langle \xi_i \rangle$ are the average numbers of sideways, forward, and back steps per chain in layer i. Now, using the probability distribution of conformations (23),

$$\langle \nu_i \rangle = \sum_c P_c \nu_{i,c} = \sum_c P_c \left[\frac{\partial}{\partial \ln q_i} \ln P_c(\mathbf{H},\mathbf{f},\mathbf{q},\mathbf{b}) \right] = \sum_c \frac{\partial P_c(\mathbf{H},\mathbf{f},\mathbf{q},\mathbf{b})}{\partial \ln q_i} = q_i \frac{\partial}{\partial q_i} [\sum_c P_c(\mathbf{H},\mathbf{f},\mathbf{q},\mathbf{b})]$$

where h_i, f_i, q_i, and b_i are treated as independent variables; i.e., normalizations 20 are *not* taken into account in the differentiations. By eq 32, prior to taking into account the stochastic nature of matrix $\mathbf{G}$,

$$\langle \nu_i \rangle = q_i \frac{\partial}{\partial q_i} \{\mathbf{H}^T \mathbf{G}^{r-1} \mathbf{B}_M\} = q_i \mathbf{H}^T (\mathbf{G}'_{q_i} \mathbf{G}^{r-2} + \mathbf{G}\mathbf{G}'_{q_i} \mathbf{G}^{r-3} + \ldots + \mathbf{G}^{r-2} \mathbf{G}'_{q_i}) \mathbf{B}_M$$

where

$$\mathbf{G}'_{q_i} = \frac{\partial}{\partial q_i} \mathbf{G}(\mathbf{p},\mathbf{q},\mathbf{b})$$

Once the differentiation has been performed, we can use the stochastic property of matrix $\mathbf{G}$ (eq 31) to get

$$\langle \nu_i \rangle = q_i \mathbf{H}^T (\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2})(\mathbf{G}'_{q_i} \mathbf{B}_M) \equiv q_i \mathbf{H}^T (\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2}) \mathbf{C}_i \tag{40}$$

Analogous equations can be deduced for $\langle \mu_i \rangle$ and $\langle \xi_i \rangle$. By combination of (39) and (40),

$$R_i = n\langle \nu_i \rangle = nq_i \mathbf{H}^T (\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2}) \mathbf{C}_i \qquad 1 \le i \le M \tag{41}$$

$$J_i = n\langle \mu_i \rangle = nf_i \mathbf{H}^T (\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2}) \mathbf{C}_i \qquad 1 \le i \le M-1 \tag{42}$$

$$D_i = n\langle \xi_i \rangle = nb_i \mathbf{H}^T (\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2}) \mathbf{C}_i \qquad 2 \le i \le M \tag{43}$$

Impenetrability of the surfaces dictates

$$J_M = 0 \tag{44}$$

$$D_1 = 0 \tag{45}$$

Full Occupancy of Layers. To model a bulk polymer, we demand that the total number of segments in each layer be equal to the number of sites in the layer, L. This we call the "full occupancy" condition. Note that, since the possibility of back stepping of a chain upon itself is not excluded, there is a small but finite probability that there will be void and multiply occupied sites within the layer; the full occupancy condition holds only in an average sense.

The possible origins of a segment in layer i are depicted in Figure 3b. This segment may be the end point of a bond emanating from layer $i-1$, emanating from layer $i+1$, or lying entirely in layer i. It may also be a chain start, in which case it is not preceded by a bond. The full occupancy condition dictates

$$R_1 + W_1 + D_2 = L \qquad \text{(layer 1)}$$

$$J_{i-1} + R_i + W_i + D_{i+1} = L \qquad \text{(layers } 2 \le i \le M-1\text{)}$$

$$J_{M-1} + R_M + W_M = L \qquad \text{(layer } M\text{)} \tag{46}$$

The possible destinations of a segment in layer i are depicted in Figure 3c. A bond may emanate from this segment, leading to layer $i-1$, leading to layer $i+1$, or lying entirely on layer i, or the segment may be a chain end. The full occupancy condition dictates

$$J_1 + R_1 + T_1 + D_1 = L \qquad \text{(layer 1)}$$

$$J_i + R_i + T_i + D_i = L \qquad \text{(layers } 2 \le i \le M-1\text{)}$$

$$J_M + R_M + T_M + D_M = L \qquad \text{(layer } M\text{)} \tag{47}$$

As a result of the full occupancy requirement, the following relation connects the fundamental quantities n, L, M, and r:

$$nr = ML \tag{48}$$

Collecting the System of Model Equations. Not all of the equations introduced above are independent. Equation 46 can be deduced from eq 47, using the normalizations 31, expressions 37, 38, and 41–43, and the definitions 27 and 33. A derivation is given in Appendix A. The last expression of eq 38 can be deduced from the $(M-1)$ first expressions of eq 38, expressions 41–43, 45, 47, and 48, the definition (33), and the normalizations (30) and (31). A derivation is given in Appendix B.

A set of *independent* equations, which comprise a general formulation of the bond lattice model for bulk polymers at interfaces, is given in Table I. The full set of variables appearing in the model is also listed on the same table. There are $(8M+1)$ equations in $(10M-1)$ unknowns. The remaining $2(M-1)$ degrees of freedom must be specified from the physics of the particular situation considered. In the following we apply this general formulation to two limiting cases, studied by previous investigators. The way in which closure of the model is achieved in each of these cases is elucidated.

Bulk Homopolymer at an Interface: Helfand Model. As pointed out by Helfand,[9] for a system of linear chains, composed of a single type of segments, it should make no difference which of the two ends is chosen as the chain start. The probability of a chain conformation should be invariant under reversal of the chain direction. Symbolically,

$$P_c = h_{k(1,c)} \prod_{i=1}^{M} f_i^{\mu_{i,c}} q_i^{\nu_{i,c}} b_i^{\xi_{i,c}} = h_{k(r,c)} \prod_{i=1}^{M} b_{i+1}^{\mu_{i,c}} q_i^{\nu_{i,c}} f_{i-1}^{\xi_{i,c}} \tag{49}$$

for *any* $\{\mu_{i,c}, \nu_{i,c}, \xi_{i,c}\}$ that satisfies requirement (25). This can only happen if

$$h_1 = h_2 = \ldots = h_M \tag{50}$$

and

$$f_i = b_{i+1} \qquad 1 \le i \le M-1 \tag{51}$$

Equation 50 states that the starting probability is equal for all layer numbers. Equation 51 is the Helfand "chain flux" constraint. The correspondence between our notation and the Helfand notation, introduced in section 1, is

$$f_i = \lambda_1 g_i^+ \qquad q_i = \lambda_0 g_i^0 \qquad b_i = \lambda_1 g_i^- \tag{52}$$

The requirement (51) implies that the stochastic matrix $\mathbf{G}$ is symmetric. At first sight, then, one would believe that the $2(M-1)$ conditions (50) and (51) provide the closure needed in the model system. This is not so, however. As proved in Appendix C, once the constraints (50) and (51)

Table I
General Formulation of the Bond Lattice Model for Bulk Polymers at Interfaces

a. Variables

symbol	meaning	no.
q_1, f_1		2
$b_i, q_i, f_i \quad (2 \le i \le M-1)$	bond stepping probabilities	$3M-6$
b_M, q_M		2
$h_i \quad (1 \le i \le M)$	chain-starting probabilities	M
$e_i \quad (1 \le i \le M)$	chain-termination probabilities	M
$W_i \quad (1 \le i \le M)$	no. of chain starts in layer i	M
$T_i \quad (1 \le i \le M)$	no. of chain ends in layer i	M
$R_i \quad (1 \le i \le M)$	no. of bonds in layer i	M
$J_i \quad (1 \le i \le M)$	no. of forward-stepping bonds from layer i	M
$D_i \quad (1 \le i \le M)$	no. of back-stepping bonds from layer i	M
n	no. of chains in model system	1
	total no.	$10M-1$

b. Equations

eq[a]	meaning	no.
30	starting probability normalization	1
31	conditional probability normalization	M
33 $(1 \le i \le M)$	ending probability definition	M
45	surface impenetrability	1
44		1
37 $(1 \le i \le M)$	relation between no. of chain starts and starting probability	M
38 $(1 \le i \le M-1)$	relation between no. of chain ends and ending probability	$M-1$
41 $(1 \le i \le M)$	bond flux–conditional probability relations	M
42 $(1 \le i \le M-1)$		$M-1$
43 $(2 \le i \le M)$		$M-1$
47 $(1 \le i \le M)$	full occupancy requirement in each layer	M
48	full occupancy requirement in all layers	1
	total no.	$8M+1$

[a] See the text for full equation.

are introduced, eq 41–43 and 47 cease being independent. The full occupancy requirement (47) for the first $(M-1)$ layers can actually be *deduced* from (50), (51), and the rest of the model equations in Table I. The system of bond model equations for a bulk homopolymer at an interface thus reduces to eq 30, 31, 33, 37, 38, 41–45, 48, 50, and 51 and eq 47 for $i = M$ only. *An additional $(M-1)$ equations* are needed for closure.

In Helfand's approach these equations are derived by writing a partition function for the lattice polymer, expressing this partition function in terms of bond stepping probabilities, and minimizing the Helmholtz energy subject to the constraints 31 and 51 (see discussion in section 1). The result from this statistical mechanical analysis in an infinite molecular weight system can be expressed as

$$\frac{f_i}{q_i} = \left(\frac{\lambda_1}{\lambda_0}\right)^2 \frac{q_{i+1}}{b_{i+1}} \qquad 1 \le i \le M-1 \tag{53}$$

This is a restatement of eq 12 in our generalized notation. The $(3M-2)$ eq 31, 51, and 53 comprise a set that can conveniently be solved for the $(3M-2)$ conditional probabilities f_i, q_i, and b_i. From the latter, and the known starting probabilities, all quantities of interest can be obtained.

We have shown here that Helfand's model for the bulk homopolymer is a special case of the bond model outlined in Table I. The requirement of equal starting probabilities in all layers (50), the chain flux reciprocity condition (51), and Helfand's partition function analysis, leading to eq 53 for an infinite molecular weight system, are needed to provide closure of the model equations.

Surface-Active Polymer at an Interface: Dill and Flory Model. Dill and Flory consider a system of chains with polar heads. An essentially infinite tendency of polar heads to attach themselves to the surface (i.e., to occupy layer 1) is assumed. To reproduce the Dill and Flory treatment in our model system, we assume that only the upper surface is adsorbing, while the lower constitutes an inert, impenetrable barrier. The starting probabilities become

$$h_i = \delta_{1,i} \qquad 1 \le i \le M-1 \tag{54}$$

All chains have their heads in layer 1. For this to be possible (compare eq 48),

$$n \le L, \quad \text{or} \quad r \ge M \tag{55}$$

In addition to eq 54, another $(M-1)$ equations are needed for closure. Dill and Flory provide these equations by requiring that no back stepping occurs anywhere in the lattice:

$$D_i = 0 \qquad 2 \le i \le M \tag{56}$$

The full set of independent equations thus consists of (54), (56), and the equations in Table Ib.

Requirement (56) implies immediately that $b_i = 0$, $2 \le i \le M$. A set of $(2M-1)$ equations in the remaining $(2M-1)$ bond stepping probabilities is provided by the M normalization conditions (31), together with the following $(M-1)$ polynomial equations, derived from (31), (33), (38), (41)–(43), (47), and (54):

$$\mathbf{C}_1^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})\mathbf{C}_i = 1/\sigma \qquad 1 \le i \le M-1 \tag{57}$$

with $\sigma = n/L$ = surface density of chains. As seen from eq 57, the surface density of chains is the only system parameter required for determining stepping probabilities. In place of eq 57, Dill and Flory give the equation

$$\mathbf{C}_1^{\mathrm{T}}\mathbf{G}^{r-1}(\mathbf{B}_{i-1} + q_i\mathbf{C}_i) = 1 - (f_i/\sigma) \qquad 1 \le i \le M-1 \tag{58}$$

A derivation of (58) from the generalized model equations is given in Appendix D.

The approximation of no back stepping, together with the assumption that all chain heads lie in the surface layer, provides an ingeniously simple closure to the bond lattice

model for the systems examined by Dill and Flory. With this assumption, no explicit consideration of the system partition function is needed.

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Appendix A: Derivation of the Full Occupancy Conditions (46) from Conditions (47)

As stated in section 2, the flux-start conservation conditions (46) can be derived from the flux-termination conditions (47), employing eq 31, 37, 38, and 41–43 and definitions 27 and 33. This is because both eq 46 and 47 express the same physical requirement of full occupancy within each layer. We present the derivation here.

By virtue of (41)–(43) we can write, for $2 \le i \le M-1$,

$$J_{i-1} + R_i + D_{i+1} = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})(f_{i-1}\mathbf{C}_{i-1} + q_i\mathbf{C}_i + b_{i+1}\mathbf{C}_{i+1})$$

From eq 27,

$$f_{i-1}\mathbf{C}_{i-1} + q_i\mathbf{C}_i + b_{i+1}\mathbf{C}_{i+1} = \mathbf{G}\mathbf{C}_i$$

hence

$$J_{i-1} + R_i + D_{i+1} = n\mathbf{H}^T(\mathbf{G} + ... + \mathbf{G}^{r-1})\mathbf{C}_i = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_i + n\mathbf{H}^T\mathbf{G}^{r-1}\mathbf{C}_i - n\mathbf{H}^T\mathbf{C}_i$$

or, from eq 33, 37, and 38,

$$J_{i-1} + R_i + D_{i+1} + nh_i = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_i + ne_i$$

or

$$J_{i-1} + R_i + W_i + D_{i+1} = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_i + T_i \quad (A.1)$$

On the other hand, adding eq 41–43 and using normalization 31, one obtains

$$J_i + R_i + D_i = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_i \quad (A.2)$$

So, by combination of (A.1) and (A.2) and use of (47), which has been assumed true for all i,

$$J_{i-1} + R_i + W_i + D_{i+1} = J_i + R_i + D_i + T_i = L, \quad \text{QED} \quad (A.3)$$

For the special case $i = 1$, eq 41 and 43 give

$$R_1 + D_2 = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})(q_1\mathbf{C}_1 + b_2\mathbf{C}_2)$$

where

$$q_1\mathbf{C}_1 + b_2\mathbf{C}_2 = \mathbf{G}\mathbf{C}_1$$

which can be used exactly as above, to obtain

$$R_1 + W_1 + D_2 = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_1 + T_1 = J_1 + R_1 + T_1 + D_1 = L$$

For the last layer, $i = M$, eq 41 and 42 similarly give

$$J_{M-1} + R_M = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})(f_{M-1}\mathbf{C}_{M-1} + q_M\mathbf{C}_M)$$

where

$$f_{M-1}\mathbf{C}_{M-1} + q_M\mathbf{C}_M = \mathbf{G}\mathbf{C}_M$$

which can be used to obtain

$$J_{M-1} + R_M + W_M = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_M + T_M = J_M + R_M + T_M + D_M = L$$

Appendix B: Derivation of Equation 38 from the Rest of the Bond Model Equations

As stated in section 2, eq 38 for $i = M$ can be derived from eq 38 for $1 \le i \le M-1$, eq 41–43, 47, and 48, definition 33 for $1 \le i \le M$, and the normalizations (30) and (31). We present the derivation here.

Assume eq 38 to be valid for $1 \le i \le M-1$. By eq 33,

$$T_i = n\mathbf{H}^T\mathbf{G}^{r-1}\mathbf{C}_i \qquad 1 \le i \le M-1 \quad (B.1)$$

By adding eq 41 to 43 for each layer, we obtain, exactly as in Appendix A,

$$J_i + R_i + D_i = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\mathbf{C}_i \qquad 1 \le i \le M \quad (A.2)$$

We now form the sum, over all layers:

$$\sum_{i=1}^{M}(J_i + R_i + D_i + T_i) = \sum_{i=1}^{M}(J_i + R_i + D_i) + \sum_{i=1}^{M-1} T_i + T_M \quad (B.2)$$

By combining (B.1), (A.2), and (B.2), we obtain

$$\sum_{i=1}^{M}(J_i + R_i + D_i + T_i) = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2})\sum_{i=1}^{M}\mathbf{C}_i + n\mathbf{H}^T\mathbf{G}^{r-1}\sum_{i=1}^{M-1}\mathbf{C}_i + T_M = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})\sum_{i=1}^{M}\mathbf{C}_i - n\mathbf{H}^T\mathbf{G}^{r-1}\mathbf{C}_M + T_M = n\mathbf{H}^T(\mathbf{I} + \mathbf{G} + ... + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})\mathbf{B}_M + (T_M - ne_M) \quad (B.3)$$

where eq 33 has been used in the last expression. Employing the normalization conditions (30) for the chain starting probability vector and the stochastic matrix $\mathbf{G}$ we obtain from (B.3)

$$\sum_{i=1}^{M}(J_i + R_i + D_i + T_i) = nr + (T_M - ne_M) \quad (B.4)$$

On the other hand, adding eq 47 for all layers, one obtains

$$\sum_{i=1}^{M}(J_i + R_i + D_i + T_i) = LM \quad (B.5)$$

From (B.4) and (B.5), in view of eq 48, one obtains

$$T_M = ne_M, \qquad \text{QED}$$

Appendix C: Derivation of Equation 47 for $1 \le i \le M-1$ from (50), (51), and the Rest of the Bond Model Equations in Table I

We show here that, upon introduction of constraints (50) and (51) for a pure homopolymer at an interface, eq 41–43, 45, and 47 of the bond model outlined in Table I cease being independent. The first $(M-1)$ components of eq 47 are deduced from (50), (51), and the rest of the model equations.

From (50) and (30) we have, for the starting probabilities h_i,

$$\mathbf{H} = (1/M)\mathbf{B}_M \quad (C.1)$$

Moreover, by eq 51, the matrix $\mathbf{G}$ is symmetric:

$$\mathbf{G}^T = \mathbf{G} \quad (C.2)$$

Using (33) in (38), substituting $\mathbf{H}$ from (C.1), summing eq 38, 41–43, and 45 for a particular i $(1 \le i \le M-1)$, and using the normalization condition (31), we obtain

$$J_i + R_i + T_i + D_i = \frac{n}{M}\mathbf{B}_M{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{C}_i + \frac{n}{M}\mathbf{B}_M{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2})\mathbf{C}_i = \frac{n}{M}\mathbf{B}_M{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})\mathbf{C}_i \qquad 1 \le i \le M-1 \tag{C.3}$$

By virtue of the symmetry condition (C.2) and the normalization (31),

$$\mathbf{B}_M{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})\mathbf{C}_i \equiv (\mathbf{B}_M{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})\mathbf{C}_i)^{\mathrm{T}} = \mathbf{C}_i{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2} + \mathbf{G}^{r-1})^{\mathrm{T}}\mathbf{B}_M = \mathbf{C}_i{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G}^{\mathrm{T}} + \ldots + (\mathbf{G}^{r-1})^{\mathrm{T}})\mathbf{B}_M = \mathbf{C}_i{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G}^{\mathrm{T}} + \ldots + (\mathbf{G}^{\mathrm{T}})^{r-1})\mathbf{B}_M = \mathbf{C}_i{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-1})\mathbf{B}_M = \mathbf{C}_i{}^{\mathrm{T}}\mathbf{B}_M + \mathbf{C}_i{}^{\mathrm{T}}\mathbf{G}\mathbf{B}_M + \ldots + \mathbf{C}_i{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{B}_M = r$$

Then, for $1 \le i \le M-1$, eq C.3 and 48 give

$$J_i + R_i + T_i + D_i = \frac{n}{M}r = L$$

which is eq 47, QED.

Appendix D: Derivation of Equation 58 from the Generalized Model Equations for the Case Examined by Dill and Flory

From the model equations presented in Table I we deduce the last expression of eq 38 as shown in Appendix B. We also deduce eq 46 as shown in Appendix A.

For the particular case examined by Dill and Flory, eq 46 assume the form

$$R_1 + W_1 = L \tag{D.1}$$

$$J_{i-1} + R_i + W_i = \mathrm{L} \qquad 2 \le i \le M \tag{D.2}$$

Moreover, eq 47 assumes the form

$$J_i + R_i + T_i = L \qquad 1 \le i \le M \tag{D.3}$$

Equating (D.1) and the first expression of eq D.3 we obtain

$$J_1 = W_1 - T_1 \tag{D.4}$$

Equating (D.2) and (D.3) for all but the first layer, we obtain

$$J_i - J_{i-1} = W_i - T_i \tag{D.5}$$

Adding (D.4) and (D.5) for all layers up to a layer i,

$$J_i = \sum_{j=1}^{i} W_j - \sum_{j=1}^{i} T_j \tag{D.6}$$

Now, from eq 54, 30, and 37, we obtain, in the Dill and Flory case,

$$W_j = n\delta_{1j} \tag{D.7}$$

Hence [(D.6), (D.7), (38)],

$$J_i = n - \sum_{j=1}^{i} T_j = n - n\sum_{j=1}^{i} e_i$$

By use of eq 33 for the ending probabilities,

$$J_i = n - n\mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\sum_{j=1}^{i}\mathbf{C}_j$$

By definition 29

$$J_i = n - n\mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{B}_{i-1} - n\mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{C}_i \tag{D.8}$$

From eq 42 and 57,

$$J_i = nf_i\mathbf{C}_1{}^{\mathrm{T}}(\mathbf{I} + \mathbf{G} + \ldots + \mathbf{G}^{r-2})\mathbf{C}_i = nf_i\left(\frac{1}{\sigma} - \mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{C}_i\right) \tag{D.9}$$

and, by equating (D.8) and (D.9),

$$nf_i\left(\frac{1}{\sigma} - \mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{C}_i\right) = n - n\mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{B}_{i-1} - n\mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{C}_i$$

or

$$(f_i/\sigma) + \mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{C}_i(1 - f_i) = 1 - \mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}\mathbf{B}_{i-1}$$

and, from the normalization condition (31), with $b_i = 0$,

$$\mathbf{C}_1{}^{\mathrm{T}}\mathbf{G}^{r-1}(\mathbf{B}_{i-1} + q_i\mathbf{C}_i) = 1 - (f_i/\sigma), \qquad \mathrm{QED} \tag{58}$$

List of Symbols

a	area per surface lattice site
A	Helmholtz energy
b_i	bond back-stepping probability in layer i
$\mathbf{B}_i$	the vector sum $\sum_{j=1}^{j}\mathbf{C}_j$
c	conformation number
$\mathbf{C}_i$	the M-long vector col (0, 0, ..., 0, 1, 0, ..., 0) with unit in i position
D_i	number of bonds passing from layer i to layer $i-1$
e_i	probability that a chain ends in layer i
E	Young's modulus
$\mathbf{E}$	vector of ending probabilities, col (e_1, e_2, ... e_M)
f_i	forward-stepping probability in layer i
g_i^-, g_i^0, g_i^+	Helfand's anisotropy factors for back, side, and forward stepping
$\mathbf{G}$	bond stepping probability matrix
h_i	probability that a chain starts in layer i
$\mathbf{H}$	vector of chain starting probabilities
i	layer number
J_i	number of bonds passing from layer i to layer $i+1$
k	Boltzmann constant
k^b	spring constant describing mechanical response of the lattice between bonded polymer segments
k^{nb}	spring constant describing mechanical response of the lattice between nonbonded polymer segments
k^s	spring constant describing mechanical response of the lattice between solid surface and adsorbed segments
$k(s,c)$	layer number in which segment s of conformation c finds itself
l	lattice step size
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_b	number of bonds per surface site
$P_{b,s;c}$	transition probability for bond s in conformation c
P_c	probability of conformation c
$p(\mathbf{r}_{s+1;c}/\mathbf{r}_{s;c})$	conditional probability that segment $s+1$ in conformation c lies at position $\mathbf{r}_{s+1}$, given that segment s lies at position $\mathbf{r}_s$
$p(\mathbf{r}_{s;c})$	a priori probability that segment s in conformation c lies at position $\mathbf{r}_s$
q_i	side-stepping probability in layer i
r	number of segments per chain
$\mathbf{r}_{s;c}$	position of segment s in conformation c
R_i	number of chain lateral placements in layer i
s	index for segments and bonds along a chain
T	temperature
T_i	number of chain terminations in layer i
u_s	difference between polymer segment–surface and polymer segment–segment interaction energies
W_i	number of chain starts in layer i
z	lattice coordination number

Greek Symbols

γ	surface tension; interfacial tension
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 the same layer as the considered site
λ_1	fraction of nearest-neighbor sites to a given site lying in the layer above (i.e., nearer the surface) the layer of the considered site

λ_{-1}	fraction of nearest-neighbor sites to a given site lying in the layer below the layer of the considered site
μ_i	number of forward steps of a chain from layer i
ν_i	number of side steps of a chain in layer i
ξ_i	number of backward steps of a chain from layer i
σ	surface density of chains
ω_c	factor proportional to the number of arrangements of conformation c on the lattice in the site model

Superscripts

b	bonded
L	longitudinal (in direction parallel to surface)
nb	nonbonded
s	surface
T	transverse (in direction perpendicular to surface); matrix transpose
–	back stepping
0	side stepping
+	forward stepping

Subscripts

b	bond
c	conformation
i	pertaining to layer i
s	pertaining to bond s or segment s
–1	pertaining to the layer above
0	pertaining to the same layer
1	pertaining to the layer below
*	unconstrained bulk polymer

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Structure and Thermodynamics of Bulk Homopolymer/Solid Interfaces: A Site Lattice Model Approach

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ABSTRACT: A site lattice model for pure homopolymers at interfaces is derived, based on Scheutjens and Fleer's formulation for polymer solutions. Techniques are developed for the exploration of bond orientational characteristics at the interface. The model is implemented for monodisperse homopolymer systems of various molecular weights. Surface free energy is found to increase with chain length, as a result of entropic constraints at the interface. Bond orientation deviates from isotropy only within a narrow interfacial region, approximately six lattice layers (25 Å) thick; it alternates from layer to layer between a parallel and a perpendicular arrangement with respect to the surface. The shape of polymer chains is flattened in the vicinity of the surface, while far from the surface it assumes unperturbed bulk characteristics. Our site model is shown to converge to Helfand's bond model in the limit of infinitely long chains.

Introduction

The details of molecular structure and conformation of bulk polymers at interfaces play a critical role in determining the performance of adhesives, lubricants, composite materials, and thin polymer films. Improving our fundamental understanding of the interface at the molecular level can greatly enhance our ability to efficiently design interfacial systems for specific uses.

In a previous publication[1] we considered lattice models, which provide a simple but adequate theoretical framework for describing the basic features of chain conformation and thermodynamic properties at interfaces in the mean-field approximation. According to their mathematical structure, we distinguished lattice models into bond models and site models. We also presented a general formulation for bond models that contains previous approaches for pure homopolymers and surface-active polymers as special cases.

In this paper we examine bulk homopolymers at interfaces using a site model approach, inspired by Scheutjens and Fleer's formulation for polymer solutions.[2] Our site model employs essentially the same lattice picture as the generalized bond model we discussed earlier.[1] The set of model equations, and some new techniques for the exploration of local structure in the vicinity of the interface, are developed in section 1. In section 2 of the paper, obtained results are discussed and compared with previous approaches.

1. Site Model for a Bulk Polymer at an Interface

Model Formulation. Consider the simple cubic lattice between two smooth solid surfaces of infinite extent, introduced in ref 1. We focus on a portion of the lattice, having L sites on each layer. The total number of layers is $M = 2m$. We will assume m to be large enough, so that conformational characteristics in the neighborhood of layer m are identical with those of the bulk polymer. The lattice is fully occupied by n flexible homopolymer chains, of length r segments each:

$$nr = ML \tag{1}$$

In the simple, constant-volume picture employed here the

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