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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:

$$nr = ML \qquad (1)$$

In the simple, constant-volume picture employed here the

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surfaces act purely as entropic barriers for the chains. Assuming only nearest-neighbor interactions, there will be a constant adsorption energy contribution of Lu_s per surface, regardless of the conformation of chains. Also, chain segment–segment interactions will contribute a constant term for any configuration of the system. Average structural and thermodynamic properties will be symmetric with respect to the midplane between m and $m + 1$.

Following the Scheutjens–Fleer treatment, we define a conformation c as r ordered indices, denoting the layers on which successive segments find themselves:

$$\{k(s,c)\}, \qquad 1 \le s \le r \tag{2}$$

With this definition[2] there are a number of different arrangements that correspond to the same conformation.[3] This number is given by

$$Lz^{r-1}\prod_{s=1}^{r-1}(\lambda_{s,s+1})_c = Lz^{r-1}\omega_c \tag{3}$$

where the fractions of nearest-neighbor sites λ and the redundancy factor ω_c have the meaning attributed to them in section 1 of ref 1. We will use the notation

$$\begin{aligned}(\lambda_{s,s+1})_c &= \lambda_0, \quad \text{if} \quad k(s,c) = k(s+1,c)\\ &= \lambda_1, \quad \text{if} \quad |k(s,c) - k(s+1,c)| = 1\end{aligned} \tag{4}$$

Back-folding of the chain upon itself is not excluded, a priori, in the model.

Let n_c be the number of chains belonging to conformation c. A simple population balance dictates

$$n = \sum_c n_c \tag{5}$$

The full occupancy requirement, taken over all lattice layers, dictates

$$L = \sum_c r_{i,c}n_c \qquad 1 \le i \le M \tag{6}$$

Equations 1, 5, and 6 are not independent. By summing (6) over all layers and using the full occupancy condition (1), one recovers (5). Under a set of conformations $\{n_c\}$ the canonical partition function for our interfacial system can be written[2] as

$$Q(M,L,T,\{n_c\}) = \frac{\Omega}{\Omega^*}e^{-U/kT} \tag{7}$$

In this expression, a system of n chains of unconstrained bulk polymer (away from any surface), each r segments long, is used as a reference. Ω is the number of ways of arranging the members of conformations $\{n_c\}$ on the lattice in the interfacial system; Ω^* is the number of ways of arranging the same total number of chains over the same number of sites in the unconstrained bulk polymer. U is the potential energy of the interfacial system, relative to the bulk polymer. As noted above, this is independent of the conformation distribution, and equal to

$$U = 2Lu_s \tag{8}$$

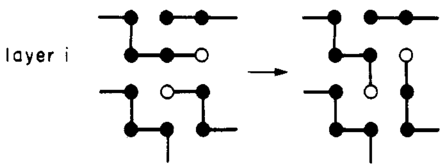

Figure 1. Simple change in the distribution of conformations, which does not violate the requirement of full occupancy.

To obtain Ω we envision a Flory process of filling the lattice with chain segments. Each conformation c is taken successively. For each conformation we place all its n_c members one by one in the lattice, in a segment-by-segment fashion. We make use of the Bragg–Williams approximation of random mixing,[2] according to which, at each step of this filling procedure, all sites in a given layer i have the same vacancy probability, equal to the fraction of unoccupied sites in that layer. Let ρ_i stand for the number of segments occupied in layer i. Also let $\rho_{i,c;j_c}$ be the value of ρ_i after the j_cth chain of conformation c has been placed in the lattice. Then the number of ways in which the j_cth chain of conformation c can be placed is equal to

$$\begin{aligned}\Omega_{j_c} &= L\omega_c z^{r-1} \prod_{\substack{s=1\\ \text{all segments}\\ \text{of chain } j_c}}^{r} \left(1 - \frac{\rho_{k(s,c)}}{L}\right) = \\ &\omega_c\left(\frac{z}{L}\right)^{r-1} \prod_{\substack{s=1\\ \text{all segments}\\ \text{of chain } j_c}}^{r} (L - \rho_{k(s,c)}) = \\ &\omega_c\left(\frac{z}{L}\right)^{r-1} \prod_{i=1}^{M} \prod_{\rho_i=\rho_{i,c;j_c-1}}^{\rho_{i,c;j_c}-1} (L - \rho_i) \quad 1 \le j_c \le n_c\end{aligned}$$

where

$$\rho_{i,c;j_c} = \rho_{i,c;j_c-1} + r_{i,c} \qquad \rho_{i,c;0} = \rho_{i,c-1;n_{c-1}} \qquad \rho_{i,0;n_0} = 0$$

The number of ways in which all members of a given conformation can be placed in the lattice is then

$$\Omega_c = \frac{1}{n_c!}\prod_{j_c=1}^{n_c}\Omega_{j_c} = \frac{1}{n_c!}\omega_c^{n_c}\left(\frac{z}{L}\right)^{n_c(r-1)} \prod_{i=1}^{M} \prod_{\rho_i=\rho_{i,c-1;n_{c-1}}}^{\rho_{i,c;n_c}-1} (L - \rho_i)$$

where the factor $n_c!$ corrects for the indistinguishability of chains in a given conformation.

The number of ways in which the whole set $\{n_c\}$ can be arranged on the lattice will be

$$\begin{aligned}\Omega = \prod_c \Omega_c = \prod_c \left[\frac{1}{n_c!}\omega_c^{n_c}(z/L)^{n_c(r-1)}\right] \prod_{i=1}^{M} \prod_{\rho_i=0}^{\sum_c r_{i,c}n_c-1} (L - \rho_i) = \\ (z/L)^{(r-1)\sum_c n_c} \prod_c \{\omega_c^{n_c}/n_c!\} \prod_{i=1}^{M} (L!)\end{aligned}$$

or

$$\Omega = (L!)^M (z/L)^{n(r-1)} \prod_c \omega_c^{n_c}/n_c! \tag{9}$$

In the unconstrained bulk polymer,[2,4]

$$\Omega^* = \frac{(rn)!}{n!}\left(\frac{z}{rn}\right)^{n(r-1)} \tag{10}$$

From (9) and (10), using Stirling's approximation and the full occupancy condition (1), one arrives at the expression

$$\ln(\Omega/\Omega^*) = n \ln(n/M) - \sum_c n_c \ln(n_c/\omega_c) \tag{11}$$

The partition function (eq 7, 8, 11) then becomes

$$\ln Q(M,L,T,\{n_c\}) = n \ln(n/M) - \sum_c n_c \ln(n_c/\omega_c) - \frac{2Lu_s}{kT} \tag{12}$$

Imagine now a change in the configuration of the interfacial system that takes a chain from a conformational category and puts it in another. This change must involve at least one other chain switching conformation, so as not to violate the requirement of full occupancy of all layers. In the simple change depicted in Figure 1, for example, four conformations switch occupancy by one. For such local changes, that modify the occupancy of some conformational categories, while leaving all other categories unchanged, one has

$$-kT \, \Delta \ln Q = \Delta A = \sum_{c} \mu_{\mathrm{chain},c} \Delta n_c \qquad (13)$$

where A the Helmholtz energy of the system and $\mu_{\mathrm{chain},c}$ the chemical potential of a chain in conformation c.

At equilibrium all conformations must have the same chemical potential, hence

$$\mu_{\mathrm{chain},c} = \mu_{\mathrm{chain}} \qquad \text{for all } c \qquad (14)$$

From (13) and (14) and the conservation of chains,

$$-kT \, \Delta \ln Q = \mu_{\mathrm{chain}} \sum_{c} \Delta n_c = 0 \qquad (15)$$

Therefore, the condition of equilibrium dictates

$$\ln Q(M,L,T,\{n_c\}) = \text{maximum} \qquad (16)$$

under the *constraints*

$$\sum_{c} r_{i,c} n_c = L \qquad 1 \le i \le M \qquad (6)$$

Introducing a Lagrange multiplier for each of the constraints (6), we require that the function

$$F = \ln Q - \sum_{i=1}^{M} \zeta_i \left(\sum_{c} r_{i,c} n_c - L\right) = -\frac{2Lu_s}{kT} + n \ln\left(\frac{n}{M}\right) - \sum_{c} n_c \left(\ln \frac{n_c}{\omega_c} + \sum_{i=1}^{M} \zeta_i r_{i,c} \right) + L \sum_{i=1}^{M} \zeta_i \qquad (17)$$

has a stationary point at equilibrium. This is translated into the conditions

$$\partial F / \partial n_c = -\ln (n_c/\omega_c) - \sum_{i=1}^{M} \zeta_i r_{i,c} - 1 = 0 \qquad \text{all conformations } c \qquad (18)$$

$$\partial F / \partial \zeta_i = -\sum_{c} r_{i,c} n_c + L = 0 \qquad 1 \le i \le M \qquad (6)$$

Equation 18 leads to a conformation distribution of the form

$$n_c = \frac{\omega_c}{e} \prod_{i=1}^{M} [\exp(-\zeta_i)]^{r_{i,c}} \qquad (19)$$

As in ref 1, we symbolize by $\mu_{i,c}$, $\nu_{i,c}$, and $\xi_{i,c}$ the numbers of forward, sideways, and backward steps taken from layer i by a chain in conformation c. These satisfy the balance

$$\mu_{i,c} + \nu_{i,c} + \xi_{i,c} + \delta_{i,k(1,c)} = r_{i,c} \qquad (20)$$

Employing (20) and the fact that, from (3),

$$\omega_c = \prod_{i=1}^{M} \lambda_1^{\mu_{i,c}} \lambda_0^{\nu_{i,c}} \lambda_1^{\xi_{i,c}} \qquad (21)$$

one can further write (19) as

$$\frac{n_c}{n} = \frac{1}{n} \exp[-1 - \zeta_{k(1,c)}] \times \prod_{i=1}^{M} [\lambda_1 \exp(-\zeta_{i+1})]^{\mu_{i,c}} [\lambda_0 \exp(-\zeta_i)]^{\nu_{i,c}} [\lambda_1 \exp(-\zeta_{i-1})]^{\xi_{i,c}} \qquad (22)$$

This expression is reminiscent of the conformation distribution of the generalized bond model (ref 1, eq 23), with the exponentials in the square brackets of (22) playing the role of Helfand's "anisotropy factors".[5] There is no requirement for normalization of the quantities in the brackets, however; this constitutes a noteworthy difference between site and bond models.

In the limit of an unconstrained bulk polymer there is no distinction among layers. All ζ_i become equal, and (19) gives

$$n^*_c = \frac{\omega_c}{e} \exp(-\zeta^* r)$$

From (5),

$$n^*_c = n \frac{\omega_c}{\sum_{c} \omega_c} \qquad (23)$$

This implies that the probability of a conformation in the unconstrained bulk is solely dependent on the geometrical characteristics of this conformation and remains effectively unperturbed by the presence of other chains around the considered one. Thus, eq 23 is in essence a restatement of Flory's "random coil hypothesis".[4]

In the unconstrained bulk the last term in eq 12 is absent. Also, since the unconstrained bulk was used as a reference for constructing $\ln Q$, we necessarily have

$$\ln Q^* = n \ln (n/M) - \sum_{c} n^*_c \ln (n^*_c/\omega_c) = 0 \qquad (24)$$

From eq 23 and 24 one is led to the self-consistency requirement

$$\sum_{c} \omega_c = M \qquad (25)$$

We now recast the distribution (19) into a form that will allow the use of the Scheutjens and Fleer formalism. Let

$$C = 1/Le \qquad (26)$$

and

$$P_i = \exp(-\zeta_i) \qquad (27)$$

The quantity P_i will be called the "free segment probability" corresponding to layer i. Equation 19 becomes

$$n_c/L = C\omega_c \prod_{i=1}^{M} P_i^{r_{i,c}} \qquad (28)$$

The (unnormalized) conformation probability is defined[2] as

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

Expression 29 is of a characteristic "site model" form (ref 1, eq 17). Following ref 2, we define the "chain probability" as a normalization factor,

$$P(r) = \sum_{c} P(r)_c \qquad (30)$$

The probability that the sth segment of a chain in conformation c be in layer i is defined as

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

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

$$P(s,i;r) = \sum_{c} P(s,i;r)_c \qquad (32)$$

By (30) and (31), $P(s,i;r)$ fulfils the normalization

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

We symbolize by

$$P(i,r) \equiv P(r,i;r) \qquad (34)$$

the "end segment probability", which also fulfils the normalization (33). By virtue of the product form of the conformation distribution (28), end segment probabilities obey the recursive relation

$$P(i,s) = \sum_{j} \lambda_{j-i} P_i P(j,s-1) \qquad (35)$$

A proof is given in ref 2. In our bulk model system the full occupancy condition (6) must be satisfied. Using (28) and (29) in (6) we obtain

$$\sum_c r_{i,c}n_c = CL\sum_c r_{i,c}P(r)_c = LC\sum_c \sum_{s=1}^{r} \delta_{i,k(s,c)}P(r)_c = LC\sum_{s=1}^{r}\sum_c \delta_{i,k(s,c)}P(r)_c = L$$

From (31) and (32) the last equation becomes

$$C\sum_{s=1}^{r}\sum_c P(s,i;r)_c = C\sum_{s=1}^{r} P(s,i;r) = 1 \qquad (36)$$

By definition of $P(r)$ (28–30 and 1),

$$P(r) = \frac{\sum_c n_c}{LC} = \frac{n}{LC} = \frac{M}{r}\frac{1}{C} \qquad (37)$$

Eliminating C from (36) and (37), we obtain

$$\frac{1}{M} = \frac{1}{rP(r)}\sum_{s=1}^{r} P(s,i;r) \qquad (38)$$

Equation 38 expresses the simple physical statement that the ratio of chain segments in layer i to total segments in the model is equal to $1/M$; as is obvious from the above derivation, it arises from translating the full occupancy constraint (6) into the Scheutjens and Fleer probability notation.

Following ref 2 we write the probability $P(s,i;r)$ in terms of end segment probabilities as

$$P(s,i;r) = \frac{P(i,s)P(i,r-s+1)}{P_i} \qquad (39)$$

In eq 39 a chain having its sth segment in layer i is considered as consisting of two subchains, of length s and $r - s + 1$, terminating in layer i. The denominator takes care of double counting the common end segment. By combination of (38) and (39)

$$\frac{1}{rP(r)}\frac{1}{P_i}\sum_{s=1}^{r} P(i,s)P(i,r-s+1) = \frac{1}{M} \qquad (40)$$

The recursive relations (35) and the segment balance conditions (40) constitute the basic equations of the site model for a pure homopolymer. It is convenient to express all probabilities appearing in them relative to the unconstrained bulk polymer. Let P_* be the limiting, layer-independent value assumed by P_i in the unconstrained bulk. Equations 28 and 25 give, for this case,

$$n = \sum_c n^*_c = CLP_*^r\sum_c \omega_c = CP_*^rML \qquad (41)$$

The normalization factor $P(r)$ can now be expressed in terms of P_*, by using (37), (41), and (1):

$$P(r) = M\frac{ML}{rn}P_*^r = MP_*^r \qquad (42)$$

We define the reduced free segment probabilities by

$$p_i = P_i/P_* \qquad (43)$$

The quantity p_i can be thought of as an equilibrium constant, expressing the probability of finding a monomer in layer i of the interfacial system, relative to finding it in the unconstrained bulk. Similarly, we define the reduced end segment probabilities by

$$p(i,s) = \frac{P(i,s)}{P_*^s} \qquad (44)$$

The term "probability", used for denoting quantities p_i and $p(i,s)$ is somewhat misleading.[1] These quantities can well assume values larger than 1; they become equal to 1 in the unconstrained bulk. In the following the adjective "reduced" will be dropped, as a formulation involving only lower case p's will be employed. Using eq 42 and the definitions (43) and (44), we cast the model equations (35) and (40) into the form

$$\begin{bmatrix} p(1,s) \\ p(2,s) \\ \cdot \\ \cdot \\ p(i,s) \\ \cdot \\ \cdot \\ p(M-1,s) \\ p(M,s) \end{bmatrix} = \begin{bmatrix} \lambda_0 p_1 & \lambda_1 p_1 & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1 p_2 & \lambda_0 p_2 & \lambda_1 p_2 & \cdot & & & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \lambda_1 p_i & \lambda_0 p_i & \lambda_1 p_i & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & \cdot & \lambda_1 p_{M-1} & \lambda_0 p_{M-1} & \lambda_1 p_{M-1} \\ 0 & \cdot & \cdot & \cdot & 0 & \lambda_1 p_M & \lambda_0 p_M \end{bmatrix} \begin{bmatrix} p(1,s-1) \\ p(2,s-1) \\ \cdot \\ \cdot \\ p(i,s-1) \\ \cdot \\ \cdot \\ \cdot \\ p(M-1,s-1) \\ p(M,s-1) \end{bmatrix}$$

$$2 \le s \le r \qquad (45)$$

where

$$p(i,1) = p_i \qquad 1 \le i \le M \qquad (46)$$

and

$$\frac{1}{r}\frac{1}{p_i}\sum_{s=1}^{r} p(i,s)p(i,r-s+1) = 1 \qquad 1 \le i \le M \qquad (47)$$

Following ref 2, we will symbolize by $\mathbf{w}$ the matrix appearing in eq 45. We will also set

$$\mathbf{p}(s) = \text{col}\,[p(1,s), p(2,s), ..., p(M,s)] \qquad 1 \le s \le r \qquad (48)$$

Equation 45 is then written as

$$\mathbf{p}(s) = \mathbf{w}\mathbf{p}(s-1) \qquad 2 \le s \le r \qquad (49)$$

There is a formal similarity between eq 49 and a Markovian model, such as the one employed in bond lattice approaches (compare ref 1, eq 31). Nevertheless, $\mathbf{w}$ cannot be characterized as a "transition probability matrix", as it is not stochastic. The $M(r-1)$ equations (45), together with the M equations (47), summarize the site model for a bulk homopolymer in our interfacial system. They comprise a set of equations in the Mr unknowns $p(i,s)$, $1 \le i \le M$, and $1 \le s \le r$. By solving this set, all structural and thermodynamic properties of the model can be obtained.

Interfacial Tension. Using the equilibrium distribution of conformations (28) in the partition function eq 12, we arrive at the following expression for the Helmholtz energy at equilibrium:

$$\frac{A}{LkT} = \frac{2u_s}{kT} + \sum_{i=1}^{M} \ln p_i \qquad (50)$$

A derivation is given in Appendix A.

The unconstrained bulk polymer has been used as a reference state in constucting eq 50. Thus, the free energy A is purely interfacial. If γ is the interfacial tension and a the area per surface site, eq 50 can also be written as

$$\frac{\gamma a}{LkT} = \frac{u_s}{kT} + \sum_{i=1}^{m} \ln p_i \qquad (51)$$

The first term in eq 51 is an energy contribution, due to direct interaction of polymer segments with the surface; this is constant in our constant density model. The second term is an entropic contribution, reflecting the distribution of conformations at equilibrium. In the following we will be using the symbol

$$\epsilon = \frac{\gamma a}{LkT} - \frac{u_s}{kT} = \sum_{i=1}^{m} \ln p_i \qquad (52)$$

to denote the entropic (and more interesting) part of the reduced interfacial energy.

Note the analogy between eq 51 and the corresponding equation for interfacial Helmholtz energy in the Helfand bond model (ref 1, eq 13). This analogy becomes clearer in view of eq 27 and 43, which explicitly relate free segment probabilities to Lagrange multiplers, associated with the full occupancy constraint in each layer. The Helfand Lagrange multiplier ζ_i (ref 1) corresponds to the quantity $\zeta_i - \zeta^*$ in the present approach.

Bond Orientation Characteristics. In the case of pure monomer ($r = 1$) the model equations give a free segment probability of 1 in all layers and a uniform density profile up to the interface. Our simple lattice approach cannot predict the subtle structural features inferred from the measurement of interfacial forces[6] and seen in computer simulations[7] of neat liquids between closely spaced walls.

Nevertheless, the model is useful for exploring the effects of chain connectivity on interfacial structure. To quantify bond orientation near the interface, we define bond stepping probabilities by analogy to the bond model.[1]

Consider the sth bond of an r-segment long chain; this connects segments s and $s + 1$. The joint probability that both segments s and $(s + 1)$ lie on layer i will be proportional to

$$P(s,i;s+1,i;r) = \\ \lambda_0 \sum_{\substack{\text{all } c(1,s)\\ \text{such that}\\ k(s,c)=i}} \omega_{c(1,s)} \prod_{t=1}^{s} P_{k(t,c)} \sum_{\substack{\text{all } c(s+1,r)\\ \text{such that}\\ k(s+1,c)=i}} \omega_{c(s+1,r)} \prod_{t=s+1}^{r} P_{k(t,c)} = \\ \lambda_0 P(i,s) P(i,r-s) \qquad (53)$$

The a priori probability for segment s to be in layer i is given by (39). The (conditional) *side-stepping probability* $q_i(s)$ for bond s on layer i is defined by

$$q_i(s) = \frac{P(s,i;s+1,i;r)}{P(s,i;r)}$$

By (39), (44), and (53)

$$q_i(s) = \lambda_0 \frac{p_i p(i,r-s)}{p(i,r-s+1)} = \frac{\lambda_0 p(1,r-s)}{\lambda_0 p(1,r-s) + \lambda_1 p(2,r-s)} \qquad i = 1$$

$$q_i(s) = \lambda_0 \frac{p_i p(i,r-s)}{p(i,r-s+1)} = \\ \frac{\lambda_0 p(i,r-s)}{\lambda_1 p(i-1,r-s) + \lambda_0 p(i,r-s) + \lambda_1 p(i+1,r-s)} \\ 2 \le i \le M - 1$$

$$q_i(s) = \lambda_0 \frac{p_i p(i,r-s)}{p(i,r-s+1)} = \\ \frac{\lambda_0 p(M,r-s)}{\lambda_1 p(M-1,r-s) + \lambda_0 p(M,r-s)} \qquad i = M \qquad (54)$$

Analogously, the *forward-stepping probability* for bond s in layer i is defined as

$$f_i(s) = \frac{P(s,i;s+1,i+1;r)}{P(s,i;r)} = \lambda_1 \frac{p_i p(i+1,r-s)}{p(i,r-s+1)} = \\ = \begin{cases} \dfrac{\lambda_1 p(2,r-s)}{\lambda_0 p(1,r-s) + \lambda_1 p(2,r-s)} & i = 1 \\ \dfrac{\lambda_0 p(i+1,r-s)}{\lambda_1 p(i-1,r-s) + \lambda_0 p(i,r-s) + \lambda_1 p(i+1,r-s)} & 2 \le i \le M - 1 \\ 0 \qquad i = M & \end{cases} \qquad (55)$$

and the back-stepping probability for bond s in layer i is

$$b_i(s) = \frac{P(s,i;s+1,i-1;r)}{P(s,i;r)} = \lambda_1 \frac{p_i p(i-1,r-s)}{p(i,r-s+1)} = \\ = \begin{cases} 0 \qquad i = 1 & \\ \dfrac{\lambda_1 p(i-1,r-s)}{\lambda_1 p(i-1,r-s) + \lambda_0 p(i,r-s) + \lambda_1 p(i+1,r-s)} & 2 \le i \le M - 1 \\ \dfrac{\lambda_1 p(M-1,r-s)}{\lambda_1 p(M-1,r-s) + \lambda_0 p(M,r-s)} & i = M \end{cases} \qquad (56)$$

The stepping probabilities defined by (54)–(56) satisfy the requirement for normalization. Also, they are bond-order-dependent. In this respect, the site model provides a higher degree of realism than most currently existing implementations of the bond model.[1] For a direct comparison with the predictions of the bond model we form global stepping probabilities for all lattice layers, by averaging over all bond orders.

The average side-stepping probability is thus defined as

q_i = (probability of two consecutive segments lying in layer i)/(probability of one of the $(r - 1)$ first segments lying in layer i) =

$$\frac{\sum_{s=1}^{r-1} P(s,i;s+1,i;r)}{\sum_{s=1}^{r-1} P(s,i;r)} = \frac{\lambda_0 p_i \sum_{s=1}^{r-1} p(i,s) p(i,r-s)}{\sum_{s=1}^{r-1} p(i,s) p(i,r-s+1)}$$

and from the normalization condition (47),

$$q_i = \lambda_0 \frac{1}{r - p(i,r)} \sum_{s=1}^{r-1} p(i,s) p(i,r-s) \qquad 1 \le i \le M \qquad (57)$$

Similarly, an average forward-stepping probability is defined as

f_i = (probability of two consecutive segments lying in layers $(i,i + 1)$)/(probability of one of the $(r - 1)$ first segments lying in layer i)

or

$$f_i = \lambda_1 \frac{1}{r - p(i,r)} \sum_{s=1}^{r-1} p(i,s) p(i+1,r-s) \qquad 1 \le i \le M - 1 \qquad (58)$$

$$f_i = 0 \qquad i = M$$

and an average back-stepping probability as

b_i = (probability of two consecutive segments lying in layers $(i,i - 1)$)/(probability of one of the $(r - 1)$ first segments lying in layer i)

or

$$b_i = 0 \qquad i = 1 \qquad (59)$$

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

By virtue of the recursive relations (45) and the full occupancy conditions (47), the stepping probabilities f_i, q_i, and b_i satisfy the normalization requirement

$$f_i + q_i + b_i = 1 \qquad 1 \le i \le M \tag{60}$$

Notice, however, that the reciprocity condition

$$f_i = b_{i+1} \qquad 1 \le i \le M - 1 \tag{61}$$

introduced in the bond model, does *not* have to be fulfilled here. This is because the a priori probability for a chain segment to lie in layer i depends, in general, on the layer number i. In the site model, Helfand's "chain flux" constraint[1] is automatically satisfied by the product form (28) of the conformation probabilities. (Compare the proof of eq 61 for the pure homopolymer bond model in ref 1.)

Let θ be the angle formed between a bond and the direction normal to the surface plane. In the simple cubic lattice model employed here, θ can only assume the values of 0 and $\pi/2$. Using the conditional probabilities f_i, q_i, and b_i, we define an order parameter, characteristic of bond orientation in layer i, as

$$S_i = \frac{1}{2}(3\langle\cos^2\theta\rangle_i - 1) = \frac{1}{2}\left(3\left(f_i \cos 0 + q_i \cos\frac{\pi}{2} + b_i \cos 0\right) - 1\right) = \frac{1}{2}[3(f_i + b_i) - 1] = \frac{1}{2}(2 - 3q_i) \tag{62}$$

Numerical Solution. For solving the problem of a pure homopolymer between the two adsorbing plates with the site model we exploited the symmetry of the lattice about the midplane, separating layers m and $(m + 1)$:

$$p_i = p_{M-i+1} \qquad 1 \le i \le m \tag{63}$$

By virtue of this symmetry, the number of equations and unknowns in the site model formulation (eq 45–47) is reduced by a factor of 2. The system of equations becomes

$$\begin{bmatrix} p(1,s) \\ p(2,s) \\ \cdot \\ \cdot \\ \cdot \\ p(i,s) \\ \cdot \\ \cdot \\ \cdot \\ p(m-1,s) \\ p(m,s) \end{bmatrix} = \begin{bmatrix} \lambda_0 p_1 & \lambda_1 p_1 & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1 p_2 & \lambda_0 p_2 & \lambda_1 p_2 & \cdot & & & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \lambda_1 p_i & \lambda_0 p_i & \lambda_1 p_i & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & & & \cdot & \lambda_1 p_{m-1} & \lambda_0 p_{m-1} & \lambda_1 p_{m-1} \\ 0 & \cdot & \cdot & \cdot & 0 & \lambda_1 p_m & (\lambda_0 + \lambda_1) p_m \end{bmatrix} \begin{bmatrix} p(1,s-1) \\ p(2,s-1) \\ \cdot \\ \cdot \\ \cdot \\ p(i,s-1) \\ \cdot \\ \cdot \\ \cdot \\ p(m-1,s-1) \\ p(m,s-1) \end{bmatrix} \qquad 2 \le s \le r \tag{64}$$

where

$$p(i,1) = p_i \qquad 1 \le i \le m \tag{65}$$

and

$$\frac{1}{r}\frac{1}{p_i}\sum_{s=1}^{r} p(i,s)p(i,r-s+1) = 1 \qquad 1 \le i \le m \tag{66}$$

We will still be using the symbolisms $\mathbf{p}(s)$ and $\mathbf{w}$ to denote the m-long vector and the $m \times m$ tridiagonal matrix appearing on the right-hand side of eq 64 (compare eq 49).

An algorithm was designed for numerically solving the balances (66) as a set of m equations in the m unknowns $\{p_i\}$, by the Newton Raphson method. The quantities $p(i,s)$ were treated as functions of the unknowns $\{p_i\}$, given by the recursive equations (64).

Equation 64 was differentiated analytically with respect to the unknowns, to arrive at recursive relations for the derivatives $\partial\mathbf{p}(s)/\partial p_k$. These are of the general form

$$\frac{\partial \boldsymbol{p}(s)}{\partial p_k} = \mathbf{w}\frac{\partial \boldsymbol{p}(s-1)}{\partial p_k} + \frac{1}{p_k}\begin{bmatrix} 0 \\ \cdot \\ 0 \\ p(k,s) \\ 0 \\ \cdot \\ 0 \end{bmatrix} \tag{67}$$

At each step of the Newton–Raphson solution the recursive equations (64) and (67) are used for the analytical calculation of the Jacobian of the system of equations (66) with respect to the unknown free segment probabilities. This analytical scheme may be somewhat expensive in storage when compared to a method not requiring derivatives (such as Brown's method); nevertheless, it has excellent convergence characteristics, a factor which proved crucial in the copolymer calculations to be described in a subsequent publication.

Convergence in the bulk homopolymer systems studied was always achieved, starting from the initial guess

$$\mathbf{p}(1) = (1.2, 1, 1, ..., 1) \tag{68}$$

The number of iterations required for reducing the maximum norm of the vector of residuals corresponding to eq 66 to less than 10^{-8} was typically 4.

Computation time, with our analytical scheme, scales approximately as $r^{0.9}m^2$ in the range of chain lengths studied. The calculation of the Jacobian and the residuals is the most time consuming part of the numerical solution. The CPU time per iteration for a $m = 100$, $r = 100$ system on a D.E.C. VAXstation II, running ULTRIX 32m (f77 compiler, 64 bit real arithmetic) is 174 s.

2. Pure Homopolymer at an Interface: Results Obtained with the Site Model

Here we apply the site model developed in section 1 to the case of a pure homopolymer at an interface, to obtain information on interfacial tension and bond orientation characteristics for various chain lengths. In all cases the number of layers m is large enough, so that results are representative of a semiinfinite domain of bulk polymer adjacent to a single adsorbing surface.

Interfacial Tension. The system of equations (64)–(66) was solved numerically for several chain lengths, to determine free segment probability profiles $\{p_i\}$. From those the nondimensionalized entropic part of the surface free energy, ϵ, was determined by using eq 52. Results are presented in Table I. The number of layers, m, used in each calculation is also listed in the same table. The solution, and the value of interfacial tension obtained from it, was completely insensitive to increasing m at each value of r.

The entropic part of the surface free energy is zero for the pure monomer (uniform density profile predicted by this simple lattice approach) and increases with increasing chain length, toward an asymptotic value corresponding to the infinite chain limit. The physical reason for the observed increase in interfacial tension is that longer and longer chains are restricted more and more by the wall (entropic barrier) from assuming the random coil conformations they would be comfortable with in the unconstrained bulk.

The dimensionless entropic interfacial free energy is plotted against inverse chain length in Figure 2a. The

Table I
Variation of Interfacial Tension with Chain Length (Site Model, Pure Homopolymer)

r^a	m^b	$\epsilon^c = \frac{\gamma a}{kT} - \frac{u_s}{kT}$	r^a	m^b	$\epsilon^c = \frac{\gamma a}{kT} - \frac{u_s}{kT}$
1	10	0.0	50	20	0.18037
2	10	0.09210	75	50	0.18164
3	10	0.12259	100	50	0.18227
4	10	0.13784	150	50	0.18291
5	10	0.14699	200	50	0.18323
10	20	0.16540	300	50	0.18355
20	20	0.17472	500	50	0.18381
30	20	0.17785	1000	50	0.18400
40	20	0.17942			

[a] Number of segments per chain. [b] Number of layers used in the numerical solution. [c] Dimensionless entropic surface Helmholtz energy.

relationship is linear to an excellent approximation. Results are described very accurately by the equation

$$\epsilon = \frac{\gamma a - u_s}{kT} = 0.1841\left(1 - \frac{1}{r}\right) \tag{69}$$

Our limiting value 0.1841 is in very good agreement with the value $\epsilon = 0.1842$, reported by Weber and Helfand[8] for a bond model of a pure homopolymer of infinite length in a cubic lattice.

Equation 69 calls for comparison against experimental data. Experimental evidence on the variation of surface tension of polymers with molecular weight[9,10] suggests a dependence of the form

$$\gamma = \gamma_\infty - \frac{K}{M^{2/3}} \tag{70}$$

Equation 69, however, concerns not surface tension itself, but the product γa, where a is the area occupied by a segment on the surface. Within a homologous series, the area a should be inversely proportional to the $^2/_3$ power of mass density. As the phenomenon of densification upon polymerization manifests, the density in a homologous series of polymers is an increasing function of molecular weight; the area a, therefore, decreases with molecular weight.

Consistent with our simple, full-occupancy picture, we obtain an estimate of a from the experimental molar volume of the polymer, V, as

$$a = (V/rN_L)^{2/3} \tag{71}$$

where N_L is Avogadro's number and r the number of skeletal segments per chain. Our lattice model (eq 69) predicts that the quantity

$$\frac{\gamma}{kT}\left(\frac{V}{rN_L}\right)^{2/3}$$

should decrease linearly with inverse chain length. This prediction is tested, by using experimental surface tension and density data for the homologous series of normal alkanes (n-hexane to n-hexadecane) at 20 °C, in Table II and Figure 2b. In analyzing experimental data r was taken as the actual number of skeletal carbons (methylene and methyl segments) per chain. Dimensionless surface free energies of n-alkanes indeed fall on the straight line

$$\frac{\gamma a}{kT} = \frac{\gamma}{kT}\left(\frac{V}{rN_L}\right)^{2/3} = 0.756 - \frac{1.568}{r} \tag{72}$$

when plotted against inverse chain length, to an excellent approximation; the scaling predicted by eq 69 is confirmed.

A quantitative comparison of the model eq 69 to the experimental eq 72 may be attempted, after establishing a correspondence between model chain parameters and actual molecular characteristics. By the usual convention[14] one lattice site can be considered as accommodating ap-

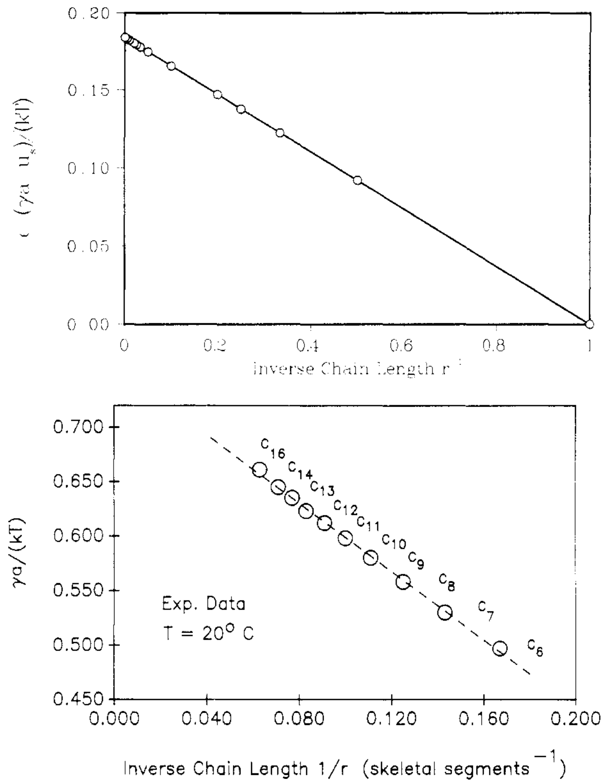

Figure 2. (a, Top) Variation of dimensionless interfacial free energy with inverse chain length, predicted by the site model for a pure homopolymer. (b, Bottom) Experimental values of the dimensionless interfacial free energy for the homologous series of normal alkanes at 20 °C, plotted against inverse chain length. Chain length r is taken here as the number of carbons per molecule. Plotted data are also listed in Table II.

Table II
Surface Tension Data for Linear Aliphatic Hydrocarbons at 20 °C

compound	$1/r$,[a] segms^{-1}	γ,[b] mN/m	V,[c] cm^3/mol	$a^d = [V/(rN_L)]^{2/3}$, Å^2	$\gamma a/(kT)^e$
n-hexane	0.1667	18.40	130.8	10.94	0.4974
n-heptane	0.1429	20.14	146.5	10.65	0.5301
n-octane	0.1250	21.62	162.5	10.44	0.5578
n-nonane	0.1111	22.85	178.6	10.28	0.5805
n-decane	0.1000	23.83	194.9	10.15	0.5977
n-undecane	0.0909	24.66	210.9	10.04	0.6118
n-dodecane	0.0833	25.35	226.8	9.95	0.6233
n-tridecane	0.0769	25.99	243.5	9.89	0.6352
n-tetradecane	0.0714	26.56	259.3	9.82	0.6445
n-hexadecane	0.0625	27.47	292.5	9.73	0.6605

[a] Inverse chain length. [b] Surface tension; experimental values, ref 11. [c] Molar volume; calculated from experimental density and molecular weight, ref 12, 13. [d] Surface area per segment. [e] Dimensionless surface free energy.

proximately 3.5 skeletal segments (i.e., a chain portion of length approximately equal to its diameter.) Comparison of eq 69 and 72 then shows that, although the scaling predicted by eq 69 is correct, the theoretical chain length dependence (i.e., the slope of $\gamma a/kT$ with respect to $1/r$) is too low by a factor of approximately 5.6. The reason for this lies in the exceedingly simplified molecular representation employed in the lattice model. The following comments can be made regarding this representation.

(a) The assumption of a sharp density discontinuity at the surface in the lattice model is clearly an oversimplification. A gradual change of segment density from its unconstrained bulk value down to zero at the free polymer surface would be more consistent with reality. Such a gradual change was in fact observed by Madden[15] in his recent lattice Monte Carlo simulations of bulk polymer surfaces. This density profile, and the associated structural characteristics, should be sensitive to the chemical nature of the polymer (i.e., to segment volume and segment–segment interactions, which determine the cohesive energy density). At a polymer/solid interface, structure would be drastically affected by polymer segment–surface interactions. Such interaction energy effects are overlooked in the present full-occupancy model.

(b) In our simple lattice approach chains are freely jointed. There is no intramolecular (conformational) contribution to the system energy, and the "Kuhn segment length" is effectively taken equal to the lattice cell edge length. In reality intramolecular stiffness is important, particularly in the case of short alkanes, whose conformational characteristics depart significantly from those of freely jointed chains.[16]

(c) The long-range nature of segment–segment and segment–surface interactions, which may significantly affect surface and interfacial tension, is disregarded in any lattice approach.

We are currently developing a more refined lattice model for liquid polymer surfaces, which takes into account density variations at the interface (a), as well as intramolecular chain stiffness (b). In this model the polymer is represented as a lattice occupied by chains and voids, in the spirit of the Sanchez–Lacombe theory.[17] This new model allows for more realistic comparison against experiment, and can separately assess energy and entropic contributions to surface and interfacial tension. Nevertheless, confirmation of the scaling predicted by eq 69 by experiment indicates that the simple, full-occupancy lattice approach described here can capture the salient features of interfacial structure, resulting from entropic constraints on chain conformation.

Bond Orientation at the Interface. Values of the free segment probabilities for the first few segments adjacent to the interface, obtained by numerical solution of the set of equations (64)–(66) for some representative chain lengths, are shown in Table III. Also shown are the bond stepping probabilities b_i, q_i, and f_i and order parameters S_i from eq 57–62 for the layers of interest.

Weber and Helfand[8] report values of the anisotropy factors $g_i^- = b_i/\lambda_1$, $g_i^0 = q_i/\lambda_0$, and $g_i^+ = f_i/\lambda_1$ for the first four layers of a simple cubic lattice, obtained by application of the Helfand bond model to the case of a pure homopolymer; this model assumes chains of infinite molecular weight. We list their reported results at the end of Table III, together with the conditional probabilities and order parameters that one obtains from them, to facilitate comparison with our site model results.

The following conclusions can be drawn on the basis of Table III.

(a) Bond orientation effects, resulting from entropic constraints at the interface, are weak in the case of a pure homopolymer. In all cases studied the absolute value of the order parameter S_i falls below 10^{-5} within six layers from the surface. The deviation of the free segment probability from the asymptotic value of 1, $|p_i - 1|$, falls below 10^{-4} within five to seven layers from the surface. With some degree of arbitrariness, we define the "interfacial layer thickness based on bond orientation" by the layer number at which S_i falls below an absolute value of 10^{-5}. If we follow the usual convention,[14] whereby the edge length of a lattice cell is roughly 4.5 Å, the interfacial layer thickness should be on the order 25 Å.

(b) The extent of the interfacial layer, based on bond orientation, is quite insensitive to chain length. Changes in interfacial tension with chain length are due primarily to changes in p_i values within the first few interfacial layers, rather than to changes in the depth of the $\{p_i\}$ profile. Of these p_i values, p_1 shows the slowest convergence to an asymptotic limit as chain length increases.

(c) Bond orientation *alternates* between a parallel and a perpendicular arrangement with respect to the surface in successive layers. In the first layer there is considerable tendency for bonds to lie flat on the surface, as perpendicular propagation against the surface is inhibited. A weak tendency for perpendicularity is observed for bonds emanating from the second layer, followed by an even weaker tendency for parallelity to the surface in the third layer. The absolute value of the order parameter decreases by practically an order of magnitude as one moves between successive layers.

(d) As chain length increases, bond stepping probabilities $\{b_i\}$ and $\{f_i\}$ conform more and more to the reciprocity condition (61), although, in the site model, there is no a priori requirement for them to do so.

(e) From an examination of numbers on Table III it is obvious that *our site model converges to the Helfand bond model* in the limit of infinitely long chains. This is an interesting conclusion, as the basic philosophy underlying the two models is different, as pointed out in ref 1. In particular, it is seen that the Helfand anisotropy factor g_i^0 is nothing more than the limiting value of the free segment probability p_i. The quantitative relationships between the two models can be expressed as follows, where the limit $r \rightarrow \infty$ is understood to hold for the site model:

$$g_1^- = b_1/\lambda_1 = g_M^+ = f_M/\lambda_1 = 0$$

$$g_i^- = b_i/\lambda_1 = (p_i p_{i-1})^{1/2} \qquad 2 \le i \le M$$

$$g_i^0 = q_i/\lambda_0 = p_i \qquad 1 \le i \le M$$

$$g_i^+ = f_i/\lambda_1 = (p_i p_{i+1})^{1/2} \qquad 1 \le i \le M-1 \tag{73}$$

It is seen that expressions (73) are consistent with the Helfand equations (9)–(12) of ref 1, as well as with the reciprocity relations (61).

Moreover, the normalization conditions (60) give the following interesting relationships between free segment probabilities in the limit $r \rightarrow \infty$:

$$\lambda_0 p_1 + \lambda_1 (p_1 p_2)^{1/2} = 1$$

$$\lambda_1 (p_{i-1} p_i)^{1/2} + \lambda_0 p_i + \lambda_1 (p_i p_{i+1})^{1/2} = 1 \qquad 2 \le i \le M-1$$

$$\lambda_1 (p_{M-1} p_M)^{1/2} + \lambda_0 p_M = 1 \tag{74}$$

Equation 74 was checked against our large r computations. For a system of chains with $r = 500$, for example, a max-

Table III
Variation of the Free Segment Probabilities, Conditional Stepping Probabilities, and Order Parameters with Layer Number for Some Representative Chain Lengths, As Obtained with the Site Model[a]

	r = 10, 30, 50, 200, 500					r = 20, 40, 100, 300, 1000				
i	p_i	b_i	q_i	f_i	S_i	p_i	b_i	q_i	f_i	S_i
			$r = 10$					$r = 20$		
1	1.2043	0.0	0.8166	0.1833	−0.22498	1.2160	0.0	0.8170	0.1830	−0.22545
2	0.9786	0.1821	0.6531	0.1649	0.02037	0.9784	0.1822	0.6528	0.1650	0.02079
3	1.0013	0.1653	0.6679	0.1668	−0.00181	1.0014	0.1652	0.6680	0.1668	−0.00201
4	0.9998	0.1668	0.6665	0.1666	0.00021	0.9996	0.1668	0.6665	0.1666	0.00022
5	1.0000	0.1667	0.6667	0.1667	−0.00002	1.0000	0.1667	0.6667	0.1667	−0.00001
			$r = 30$					$r = 40$		
1	1.2196	0.0	0.8171	0.1829	−0.22566	1.2214	0.0	0.8172	0.1828	−0.22578
2	0.9785	0.1823	0.6527	0.1650	0.02098	0.9785	0.1824	0.6526	0.1650	0.02108
3	1.0016	0.1652	0.6680	0.1668	−0.00207	1.0017	0.1651	0.6681	0.1668	−0.00210
4	0.9996	0.1668	0.6665	0.1666	0.00022	0.9996	0.1668	0.6665	0.1666	0.00022
5	0.9999	0.1667	0.6667	0.1667	−0.00001	0.9999	0.1667	0.6667	0.1667	−0.00002
6	1.0000	0.1667	0.6667	0.1667	0.00000	1.0000	0.1667	0.6667	0.1667	0.00000
			$r = 50$					$r = 100$		
1	1.2224	0.0	0.8172	0.1828	−0.22585	1.2244	0.0	0.8173	0.1827	−0.22599
2	0.9786	0.1823	0.6526	0.1650	0.02114	0.9786	0.1825	0.6525	0.1650	0.02128
3	1.0018	0.1651	0.6681	0.1668	−0.00211	1.0020	0.1651	0.6681	0.1668	−0.00215
4	0.9996	0.1668	0.6665	0.1666	0.00022	0.9997	0.1668	0.6665	0.1666	0.00022
5	0.9999	0.1667	0.6667	0.1667	−0.00002	0.9999	0.1667	0.6667	0.1667	−0.00002
6	0.9999	0.1667	0.6667	0.1667	0.00000	0.9999	0.1667	0.6667	0.1667	0.00000
7	1.0000	0.1667	0.6667	0.1667	0.00000	1.0000	0.1667	0.6667	0.1667	0.00000
			$r = 200$					$r = 300$		
1	1.2253	0.0	0.8174	0.1826	−0.22607	1.2256	0.0	0.8174	0.1826	−0.22610
2	0.9786	0.1825	0.6524	0.1651	0.02135	0.9786	0.1825	0.6524	0.1651	0.02137
3	1.0021	0.1651	0.6681	0.1668	−0.00216	1.0021	0.1651	0.6681	0.1668	−0.00219
4	0.9997	0.1668	0.6665	0.1666	0.00021	0.9997	0.1668	0.6665	0.1666	0.00022
5	1.0000	0.1667	0.6667	0.1667	−0.00002	1.0000	0.1667	0.6667	0.1667	−0.00002
6	1.0000	0.1667	0.6667	0.1667	0.00000	1.0000	0.1667	0.6667	0.1667	0.00000
7	1.0000	0.1667	0.6667	0.1667	0.00000	1.0000	0.1667	0.6667	0.1667	0.00000
			$r = 500$					$r = 1000$		
1	1.2258	0.0	0.8174	0.1826	−0.22612	1.2260	0.0	0.8174	0.1826	−0.22614
2	0.9786	0.1825	0.6524	0.1651	0.02139	0.9786	0.1826	0.6524	0.1651	0.02141
3	1.0021	0.1651	0.6681	0.1668	−0.00217	1.0022	0.1651	0.6681	0.1668	−0.00218
4	0.9998	0.1668	0.6665	0.1667	0.00021	0.9998	0.1668	0.6665	0.1667	0.00022
5	1.0000	0.1667	0.6667	0.1667	−0.00002	1.0000	0.1667	0.6667	0.1667	−0.00002
6	1.0000	0.1667	0.6667	0.1667	0.00000	1.0000	0.1667	0.6667	0.1667	0.00000
7	1.0000	0.1667	0.6667	0.1667	0.00000	1.0000	0.1667	0.6667	0.1667	0.00000

	Helfand ($r = \infty$)						
i	g_i^0	g_i^-	g_i^+	b_i	q_i	f_i	S_i
1	1.2262	0.0	1.0954	0.0	0.8175	0.1826	−0.22615
2	0.9786	1.0954	0.9903	0.1826	0.6524	0.1651	0.02143
3	1.0022	0.9903	1.0010	0.1651	0.6681	0.1668	−0.00218
4	0.9998	1.0010	0.9999	0.1668	0.6665	0.1667	0.00022

[a] The corresponding quantities based on the results of Weber and Helfand[8] from a bond model of chains of infinite length are also shown for comparison.

$$\begin{bmatrix} p_1^{1/2} \\ p_2^{1/2} \\ \cdot \\ \cdot \\ p_i^{1/2} \\ \cdot \\ \cdot \\ p_{M-1}^{1/2} \\ p_M^{1/2} \end{bmatrix} = \begin{bmatrix} \lambda_0 p_1 & \lambda_1 p_1 & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1 p_2 & \lambda_0 p_2 & \lambda_1 p_2 & \cdot & & & \cdot \\ 0 & & & & \cdot & & \cdot \\ \cdot & \cdot & \lambda_1 p_i & \lambda_0 p_i & \lambda_1 p_i & \cdot & \cdot \\ \cdot & & \cdot & & & & 0 \\ \cdot & & & \cdot & \lambda_1 p_{M-1} & \lambda_0 p_{M-1} & \lambda_1 p_{M-1} \\ 0 & \cdot & \cdot & \cdot & 0 & \lambda_1 p_M & \lambda_0 p_M \end{bmatrix} \begin{bmatrix} p_1^{1/2} \\ p_2^{1/2} \\ \cdot \\ p_i^{1/2} \\ \cdot \\ \cdot \\ p_{M-1}^{1/2} \\ p_M^{1/2} \end{bmatrix} \tag{75}$$

imum deviation of 0.02% was observed in the first layer; for $r = 1000$, the deviation dropped to 0.01%. Multiplying eq 74 by $p_i^{1/2}$ we cast them into the form of eq 75 or

$$\mathbf{w}[\mathbf{p}(1)]^{1/2} = [\mathbf{p}(1)]^{1/2}$$

As chains become longer and longer, the end segment probability vector $\mathbf{p}(s)$, for large enough segment orders s, is expected to become independent of s. In this limiting case the recursive relations (64) give

$$\mathbf{w}(\lim_{\substack{s \gg 1 \\ r \to \infty}} \mathbf{p}(s)) = \lim_{\substack{s \gg 1 \\ r \to \infty}} \mathbf{p}(s) \tag{76}$$

From a comparison of eq 75 and 76, we see that the limiting values of the end segment probabilities are equal to

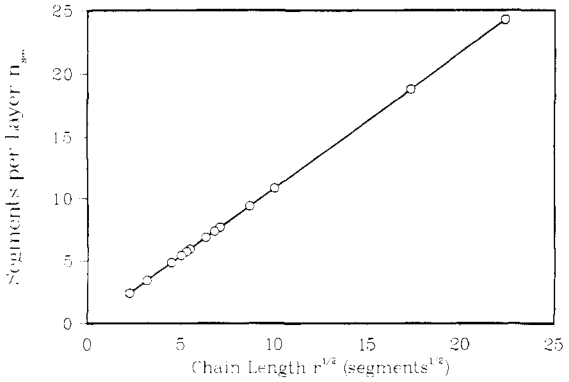

Figure 3. Average number of segments occupied by a chain on a layer through which it passes, $n_{s\infty}$, in the unconstrained bulk limit, as a function of chain length r.

the square roots of the free segment probabilities corresponding to the same layer numbers:

$$\lim_{\substack{s\gg 1\\ r\to\infty}} \mathbf{p}(s) = [\mathbf{p}(1)]^{1/2} \qquad (77)$$

The validity of eq 77 for all segment orders in the limit of infinitely long chains implies that the full-occupancy conditions (47) are automatically satisfied.

Thus, in the limit $r \to \infty$, interfacial structure can be completely determined from solving the simple system of eq 74 in the M free segment probabilities, p_i, instead of the considerably more involved system of eq 64–66. Equation 74 is mathematically equivalent to Helfand's bond model for a bulk homopolymer of infinite molecular weight at an interface (eq 31, 51, and 53 of ref 1). A direct connection between the stochastic transition probability matrix $\mathbf{G}$ of the bond model (ref 1) and the nonstochastic matrix $\mathbf{w}$ of the site model is also established in the limit of infinite chain lengths:

$$G_{ij} = \lim_{r\to\infty} (w_{ij}w_{ji})^{1/2} \qquad 1 \le i \le M, \quad 1 \le j \le M \qquad (78)$$

Chain Shape Characteristics. As will be shown in detail in a companion paper, our site model provides useful information on the conformational characteristics and the overall shape of chains as a function of distance from the surface. For a chain passing through layer i, let n_{si} be the average number of segments that the chain occupies in that layer. Far from the interface n_{si} will assume an asymptotic value, $n_{s\infty}$, characteristic of the unconstrained bulk. The profile n_{si} is a sensitive measure of the perturbations in chain conformation and shape induced by the presence of the surface.

Asymptotic values $n_{s\infty}$ are plotted as a function of chain length in Figure 3. A strictly linear relationship between $n_{s\infty}$ and the square root of the chain length is observed, which simply reflects the fact that our model chains are freely jointed random coils in the unconstrained bulk, away from any interface. Our computed results are correlated almost perfectly with the equation

$$n_{s\infty} = 1.0854r^{1/2} \qquad (79)$$

Equation 79 constitutes, in essence, a computer experimental confirmation of the Flory random coil hypothesis in our model bulk lattice polymer. Our method of calculating n_{si} and $n_{s\infty}$ gives rise to interesting possibilities for exploring the scaling behavior of chain size with chain length in more complicated systems.

The reduced profiles $n_{si}/n_{s\infty}$ for bulk homopolymer interfacial systems, consisting of chains 10–500 segments long, are plotted in Figure 4. These profiles indicate significant flattening of the chains in the vicinity of the interface. In all cases the number of layer sites per chain assumes a maximum in the first layer. The ratio $n_{s1}/n_{s\infty}$ increases with increasing chain length; in other words, adsorbed chains become flatter and flatter as the molecular weight increases. Perturbations of chain conformation from its unconstrained bulk characteristics persist up to a value of i of the order $r^{1/2}$. From a comparison of Figure 4 with the data in Table III one sees that, for systems of appreciable molecular weight, the anisotropy in bond orientation dies out much more rapidly than the flattening effect of the surface on chain shape. An "interfacial thickness" can be defined in terms of bond orientation, as the value of i for which S_i drops practically to zero, or in terms of chain shape, as the value of i for which n_{si} becomes indistinguishable from the asymptotic value $n_{s\infty}$. By the former definition the thickness of the interface is practically molecular weight independent for systems of bulk homopolymers; by the latter definition it grows approximately in proportion to the unperturbed chain radius of gyration.

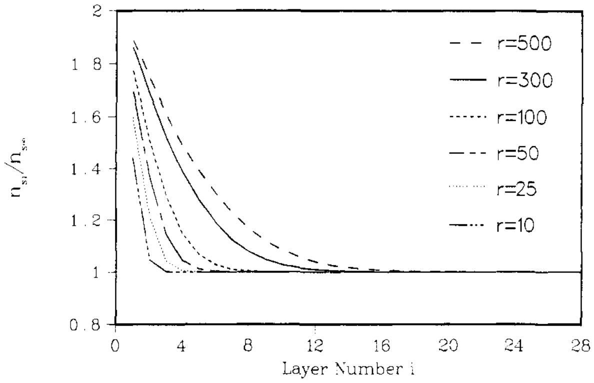

Figure 4. Reduced chain shape profiles for bulk homopolymer systems consisting of chains 10, 25, 50, 100, 300, and 500 segments long.

Our observation of chain flattening at an interface is consistent with Madden's results from a Monte Carlo simulation of a bulk homopolymer melt/vacuum interface.[15]

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Appendix A: Derivation of Equation 50 of the Site Model for the System Helmholtz Energy

Combining eq 28 and 41 one obtains, for the equilibrium distribution of conformations,

$$n_c = n\frac{\omega_c}{M}\frac{1}{P_*{}^r}\prod_{i=1}^{M} P_i{}^{r_{i,c}} = n\frac{\omega_c}{M}\prod_{i=1}^{M}\left(\frac{P_i}{P_*}\right)^{r_{i,c}} = n\frac{\omega_c}{M}\prod_{i=1}^{M} p_i{}^{r_{i,c}} \qquad (A.1)$$

Using (A.1) in (12) we arrive at the value of the partition function at equilibrium:

$$\begin{aligned}\ln Q &= n \ln\left(\frac{n}{M}\right) - \sum_c n_c\left(\ln\left(\frac{n}{M}\right) + \sum_{i=1}^{M} r_{i,c} \ln p_i\right) - \\ &\quad \frac{2Lu_s}{kT} = n \ln\left(\frac{n}{M}\right) - n \ln\left(\frac{n}{M}\right) - \sum_{i=1}^{M}\left(\sum_c n_c r_{i,c}\right) \ln p_i - \\ &\quad \frac{2Lu_s}{kT} = -L\sum_{i=1}^{M} \ln p_i - \frac{2Lu_s}{kT} \qquad (A.2)\end{aligned}$$

Then

$$\frac{A}{LkT} = -\ln Q = \frac{2u_s}{kT} + \sum_{i=1}^{M} \ln p_i$$

which is eq 50.

List of Symbols

a	area per surface lattice site
A	Helmholtz energy
b_i	bond back-stepping probability in layer i
c	conformation number
C	constant, defined by eq 26
f_i	forward-stepping probability in layer i
F	augmented function, incorporating Lagrange multipliers, used for constrained optimization
g_i^-, g_i^0, g_i^+	Helfand's anisotropy factors for back, side, and forward stepping
$\mathbf{G}$	bond stepping (transition) probability matrix in bond lattice model
i	layer number
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_c	number of chains belonging to conformation c
n_s	number of segments
n_{si}	average number of segments that a chain passing through layer i occupies on that layer
N_L	Avogadro's number
p	probability in the site model, reduced by the corresponding value for the unconstrained bulk
$\mathbf{p}(s)$	vector of reduced end segment probabilities $p(i,s)$
P_c	probability of conformation c
P_i	free segment probability in layer i
$P(i,s)$	end segment probability
$P(s,i;r)$	probability that s-th segment of a chain r segments long is in layer i
$P(s,i;r)_c$	probability that s-th 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
q_i	side-stepping probability in layer i
Q	canonical partition function
r	number of segments per chain
$r_{i,c}$	number of segments that conformation c has in layer i
s	index for segments and bonds along a chain
S_i	bond order parameter in layer i
T	temperature
u_s	difference between polymer segment–surface and polymer segment–segment interaction energies
U	potential energy of interfacial system relative to unconstrained bulk
V	molar volume (cm^3/mol chains)
$\mathbf{w}$	matrix in recursive relation (45) or (64)
z	lattice coordination number

Greek Symbols

γ	surface tension; interfacial tension
ϵ	dimensionless entropic contribution to interfacial free energy
ζ_i	Lagrange multiplier, corresponding to the full-occupancy constraint in layer i
θ	angle between a bond and the direction normal to the surface plane
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 than) 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
$\rho_{i,c;j_c}$	number of segments occupied in lattice layer i, after j_c-th chain belonging to conformation c has been placed in the lattice
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

$-$	back stepping
0	side stepping
$+$	forward stepping
$*$	unconstrained bulk

Subscripts

c	conformation
i	pertaining to layer i
s	pertaining to bond s or segment s
-1	pertaining to layer above
0	pertaining to same layer
1	pertaining to layer below
∞	unconstrained bulk polymer, in the absence of interfaces

Registry No. Hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5; undecane, 1120-21-4; dodecane, 112-40-3; tridecane, 629-50-5; tetradecane, 629-59-4; hexadecane, 544-76-3.

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(3) A counting error is in fact introduced by the Scheutjens and Fleer definition of conformations in a system of linear homopolymer chains. As a rule a given chain arrangement is counted twice, as a member of conformations starting at either of its ends. This, however, is not true of arrangements symmetric with respect to the chain midpoint in the sense of eq 20 (e.g., the arrangement 22344322 for a r = 8-segment chain); such symmetric arrangements are counted only once, as members of a single conformation. The error introduced by this discrepancy is not significant in comparison to those due to other approximations involved in the model.

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