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Statistical Mechanics of Chain Molecules at Interfaces

J. Naghizadeh and Ken A. Dill*

Department of Pharmaceutical Chemistry, University of California,
San Francisco, California 94143

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ABSTRACT: In the past few years, several closely related mean-field lattice theories have emerged to predict configurational and thermal properties of polymers at interfaces: in the bulk, adsorbed, in the semicrystalline interphase, in grafted chromatographic interphases, or in surfactant aggregates. In the present work we reformulate these approaches into a single, simpler treatment for bulk homopolymer interphases. We focus on the origin of the constraints and show the relationship to classical conformational theories for chains in the absence of interfaces, with particular attention to intrachain conformational energies and to the nature of the segment insertion process.

Introduction

In a wide variety of situations, polymers interact with interfaces. Bulk polymers may be bounded by surfaces. Polymers in mixtures may adsorb to interfaces, or chains may be anchored at single attachment points to interfaces, by strong adsorption or covalent bonding of a particular chain segment. Phases comprised of anchored chains at high surface densities, which are thus constrained both by the interfacial boundary and by lateral interactions with neighboring chains, have been referred to as "interphases".¹⁻³ Interphases include Langmuir-Blodgett and surfactant monolayer films, bilayer membranes, micelles and other amphiphilic aggregates, interfacial regions in semicrystalline polymers, and the stationary phases used in reversed-phase liquid chromatography, for example, wherein short alkyl chains are covalently grafted onto silica surfaces.

Several statistical thermodynamic theories have arisen during the past few years to predict the configurations and corresponding thermodynamic quantities for chains at interfaces. There are some similarities among these treatments. Helfand and Weber first treated long-chain polymers at solution interfaces.⁴⁻⁶ That approach was extended to account for longer ranged correlations along the chain and applied to problems of the semicrystalline interphase by Marqusee and Dill.⁷

For finite chains, Dill and Flory (DF) developed theory for pure anchored chains at high surface densities in the absence of solvent.^{2,3} Independently, Scheutjens and Fleer and their collaborators have extensively developed theory for polymer adsorption from solution.^{8,9} The packing constraints required in these treatments of finite chains are similar to each other and are similar to those required for long chains at solution interfaces or in semicrystalline polymers, cited above. Gruen¹⁰⁻¹² developed a numerical simulation method for micelles and bilayer membranes which ensures satisfaction of the same packing constraints as in the model of Dill and Flory.

Subsequently, Ben-Shaul, Szleifer, and Gelbart,¹³⁻¹⁸ Theodorou,¹⁹ and Rice et al.²⁰⁻²³ have presented similar models. Ben-Shaul et al. have shown that the relevant Lagrange multipliers are identical with the "lateral pressures" of the Gruen treatment.¹⁰⁻¹² Their method also demonstrates the important result that this class of theories does not require the use of a lattice. The predictions from their treatment of the gradient of chain conformational disorder are in close agreement with those of DF in all cases except for spherical micelles. They concluded that the discrepancy for spherical micelles was

not due to effects of chain stiffness or to effects of reversals of chain direction toward the interface, neglected in the DF model, but was due to "incomplete maximization" of the partition function in DF. However, their conclusion cannot be correct since there is no maximization procedure in the DF model; here we show the origin of this discrepancy. A recent review summarizes the comparison of experimental results with these mean-field theories of chains at interfaces.²³

Here we develop general theory for pure chain phases at interfaces, principally for chains anchored to them at single attachment points. Through consideration of the origins of the constraints and a systematic matrix method for enumeration of the chain configurations, the theory treats either infinitely long chains or short chains of any length and can account for various correlation lengths for the short-ranged interactions along the chains. In order to clarify the origins of intra- and intermolecular interactions, we first describe reference theory for bulk polymers in the absence of interfaces.

Theory

Consider a system comprised of N indistinguishable molecules, each of which is a linear chain of n segments ($n - 1$ bonds). Let $\{R_\alpha\}$ represent the set of vectors specifying the positions of all n segments of the α th chain, $\{R_\alpha\} = \{\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \mathbf{r}_3^\alpha, \dots, \mathbf{r}_n^\alpha\}$, where \mathbf{r}_k^α specifies the position of chain segment k of the α th chain and $\{R_k^\alpha\} = \{\mathbf{r}_1^\alpha, \mathbf{r}_2^\alpha, \mathbf{r}_3^\alpha, \dots, \mathbf{r}_k^\alpha\}$ specifies the chain configuration only up to segment k . Let $\{\mathbf{R}\}$ represent the set of positions of all the chains, $\{\mathbf{R}\} = \{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots, \mathbf{R}_N\}$.

The configurational partition function for the system of chains is

$$Z(N, n, V, \beta) = \frac{1}{N!} \int \dots \int \exp[-\beta U(\{\mathbf{R}\})] d\{\mathbf{R}\} \quad (1)$$

where $U(\{\mathbf{R}\})$ is the total potential energy for all the interactions and $\beta = (kT)^{-1}$, where k is Boltzmann's constant and T is temperature. If the accessible configurations are represented in terms of discrete states rather than a continuum and if we drop the explicit indication of dependence on n , V , and β for convenience, then the partition function becomes a sum over states

$$Z(N) = \frac{1}{N!} \sum_{\{\mathbf{R}\}} W(\{\mathbf{R}\}) \quad (2)$$

where

$$W(\mathbf{R}) = \exp[-\beta U(\mathbf{R})] \quad (3)$$

defines the statistical weight for the given configuration $\{\mathbf{R}\}$ of the system of chains and $\sum_{\{\mathbf{R}\}}$ denotes the sum over all degrees of freedom of all N chains. For a single chain α we denote the partition function by Ξ

$$\Xi = Z(1) = \sum_{\{\mathbf{R}_\alpha\}} W(\{\mathbf{R}_\alpha\}) \quad (4)$$

We assume the potential energy is separable into intermolecular and intrachain contributions^{25,26}

$$U(\mathbf{R}) = U_{\text{interchain}}(\mathbf{R}) + U_{\text{intrachain}}(\mathbf{R}) \quad (5)$$

where "intrachain" refers to only those interactions among connected nearest-neighbor bonds along the chain. Since we consider here only highly concentrated polymer in the absence of solvent, then intrachain interactions are dominated by short-range forces:

$$U_{\text{intrachain}}(\mathbf{R}) = \sum_{\alpha=1}^N U_{sr}(\{\mathbf{R}_\alpha\}) = \sum_{\alpha=1}^N \sum_{k=1}^n \sum_{j=k+1}^{k+m} u_{sr}(\mathbf{r}_k^\alpha, \mathbf{r}_j^\alpha) \quad (6)$$

where $u_{sr}(\mathbf{r}_i^\alpha, \mathbf{r}_j^\alpha)$ is the segment-segment pair interaction potential and m defines the "range" of the potential. In principle, the choice $m \rightarrow n$ permits consideration of all intrachain interactions; however, for dense systems considered here for which long-ranged interactions are screened, we consider only short-ranged contributions, designated sr. We will consider principally two cases here: $m = 1$, referred to below as pair correlations, for which

$$U_{sr}(\{\mathbf{R}_\alpha\}) = \sum_{k=1}^n u_{sr}(\mathbf{r}_k^\alpha, \mathbf{r}_{k+1}^\alpha) \quad (7)$$

and $m = 2$, referred to below as triplet correlations. Similarly, the "intermolecular" forces are those of a chain segment with a segment of another chain or with a solvent molecule. For condensed phases of homopolymeric chains, of interest here, the intermolecular interactions are only among chain segments since there is no solvent. Provided the interchain interactions are pairwise additive, then

$$U_{\text{interchain}}(\mathbf{R}) = \sum_{\alpha=1}^N \sum_{\delta > \alpha}^N U_{\text{inter}}(\mathbf{R}_\alpha, \mathbf{R}_\delta) = \sum_{\alpha=1}^N \sum_{k=1}^n \sum_{\delta > \alpha}^N \sum_{j > k}^n u_{\text{inter}}(\mathbf{r}_k^\alpha, \mathbf{r}_j^\delta) \quad (8)$$

The interchain forces are taken to be further separable into repulsive and attractive contributions

$$u_{\text{inter}}(\mathbf{r}_k^\alpha, \mathbf{r}_j^\delta) = u_{\text{rep}}(\mathbf{r}_k^\alpha, \mathbf{r}_j^\delta) + u_{\text{att}}(\mathbf{r}_k^\alpha, \mathbf{r}_j^\delta) \quad (9)$$

It is common to ascribe repulsions to "excluded volume" and treat them in the mean-field Flory-Huggins approximation.²⁴ The attractive energy is constant for a condensed system of homopolymers at fixed density. For systems of different segment types or of polymer/solvent mixtures, differences in attractions are often treated through the Flory χ parameters.²⁴ Since we consider only pure systems here, only the excluded volume effects are considered in more detail.

Excluded volume for gases or polymers is often treated through use of a fictitious thermodynamic "insertion process". The purpose of the following section is to review theory for insertion processes in polymers, from which we can then also consider anisotropic interfacial systems. Along the way, it is useful to make comparison in the two

sections that follow to well-understood bulk situations: (i) where short-ranged intrachain forces are dominant and (ii) where interchain excluded volume forces are present.

Intrachain Short-Ranged Forces Dominant

When the chain is unperturbed by interchain interactions, i.e., when

$$U_{\text{interchain}}(\mathbf{R}) = 0 \quad (10)$$

then the short-ranged forces among the nearest-neighbor segments determine the configurational properties. This defines the "unperturbed chain",²⁴ denoted by a superscript 0

$$Z^0(N) = \frac{1}{N!} \sum_{\{\mathbf{R}\}} \prod_{\alpha=1}^N w_0(\mathbf{r}_1^\alpha) \prod_{k=1}^{n-1} w_0(\mathbf{r}_{k+1}^\alpha | R_k^\alpha) \quad (11)$$

which follows from eqs 2, 3, and 5-7, provided the conditional statistical weights are defined by

$$w_0(\mathbf{r}_{k+1}^\alpha | R_k^\alpha) = \exp[-\beta u_{sr}(\mathbf{r}_{k+1}^\alpha, R_k^\alpha)]$$

and $w_0(\mathbf{r}_1^\alpha)$ is the statistical weight for the first segment. The subscripts 0 on the w 's indicate the absence of interchain interactions. In this case, inasmuch as the configurations of each chain are independent of the configurations of the other chains, then the product, $\prod_{\alpha=1}^N$, and summation, $\sum_{\{\mathbf{R}\}}$, may be interchanged in eq 11; hence

$$Z^0(N) = (\Xi^0)^N / N! \quad (12)$$

where

$$\Xi^0 = \sum_{\{\mathbf{R}_\alpha\}} w_0(\mathbf{r}_1^\alpha) \prod_{k=1}^{n-1} w_0(\mathbf{r}_{k+1}^\alpha | R_k^\alpha) \quad (13)$$

The sums of products that arise in the calculation of the partition function, Ξ^0 in eq 13, are often readily computed by transfer matrix methods. This approach is the rotational isomeric state theory.²⁷ In those cases, since only relative bond coordinates are important, the partial function is more conveniently represented in terms of bond vectors:

$$\Xi^0 = \sum_{\{\mathbf{R}_\alpha\}} w_0(\mathbf{r}_1^\alpha) \prod_{k=1}^n w_0(\mathbf{r}_{k+1}^\alpha | R_{k,k-1}^\alpha) \quad (14)$$

where

$$\mathbf{r}_{k+1,k}^\alpha = \mathbf{r}_{k+1}^\alpha - \mathbf{r}_k^\alpha$$

$$R_{k,k-1}^\alpha = \{\mathbf{r}_k^\alpha - \mathbf{r}_{k-1}^\alpha, \mathbf{r}_{k-1}^\alpha - \mathbf{r}_{k-2}^\alpha, \dots, \mathbf{r}_2^\alpha - \mathbf{r}_1^\alpha\}$$

The same matrix methods have been useful for chains at interfaces, described below.²⁸

Intermolecular Excluded Volume

Excluded volume in concentrated polymer solutions and melts is usually treated by an insertion process in which molecules are added consecutively into diminishing accessible space within the volume V . The insertion factor for adding a polymer to an interacting assembly of $j-1$ polymer molecules may be defined as F_{j-1}

$$F_{j-1} = \frac{jZ(j)}{Z(j-1)\Xi^0} \quad (15)$$

By successive application of the insertion process, eq 15 can be rearranged to give the partition function in terms

of the insertion factors

$$Z(N) = \frac{(\Xi)^N}{N!} \prod_{\alpha=1}^{N-1} F_{\alpha} \quad (16)$$

The insertion process can also be defined for the individual chain segments:

$$F_{\alpha} = \prod_{k=0}^{n-1} f_{k+1}^{\alpha} \quad (17)$$

If it is assumed, as is done in the so-called "Flory approximation",²⁴ that this depends only on the mean segment density, then

$$f_{k+1}^{\alpha} = 1 - \frac{(\alpha-1)n + (k+1)}{V} \quad (18)$$

Better approximations for the segment insertion factors are also available.²⁹ One limiting case of interest is that in which the molecules fully fill the volume occupied, $V = nN$; then with the use of Stirling's approximation, eq 17 and 18 become

$$\prod_{j=0}^{n(N-1)} \left(1 - \frac{j}{nN}\right) = \left(\frac{1}{nN}\right)^{nN} (nN)! \approx e^{-nN} \quad (19)$$

The effect of excluded volume can alternatively be derived more directly as the ratio H of the partition functions^{25,26}

$$H = \frac{Z(N)}{Z^0(N)} = \frac{\sum_{\{\mathbf{R}\}} \exp[-\beta U_{\text{interchain}}\{\mathbf{R}\}] \exp[-\beta U_{\text{sr}}\{\mathbf{R}\}]}{\sum_{\{\mathbf{R}\}} \exp[-\beta U_{\text{sr}}\{\mathbf{R}\}]} = \langle e^{-\beta U_{\text{interchain}}\{\mathbf{R}\}} \rangle = \left\langle \prod_{\alpha=1}^N \prod_{\delta > \alpha}^N e^{-\beta U_{\text{inter}}(\mathbf{R}_{\alpha}, \mathbf{R}_{\delta})} \right\rangle \quad (20)$$

which equals the mean value of the statistical weights of the interacting polymers averaged over all configurations of the unperturbed chains. Assuming that each chain interacts with the mean field created by others, then the average of the products may be equated with the product of the averages.

$$H = \prod_{\alpha=1}^N \left\langle \prod_{\delta > \alpha}^N e^{-\beta U_{\text{inter}}(\mathbf{R}_{\alpha}, \mathbf{R}_{\delta})} \right\rangle \quad (21)$$

Since all chains are identical, then the expression in brackets in eq 21 can be defined as a single-chain quantity, H_1

$$H = H_1^N = \left(\frac{\Xi}{\Xi^0}\right)^N = \frac{Z(N)}{Z^0(N)} \quad (22)$$

H_1 is the mean statistical weight for the intermolecular interactions of one given test chain with all other chains, averaged over all conformations of the system. Comparing eq 16 with 22 and taking $F_0 = 1$ lead to

$$H_1 = \left[\prod_{\alpha=0}^N F_{\alpha} \right]^{1/N} \quad (23)$$

which is the geometric mean of the chain insertion factors. Likewise H_1 can be further factored into segment contributions, $h(\mathbf{r}_{k+1}|\mathbf{r}_k)$, provided the conformations of each chain segment are independent of all other segments and interact only with the mean-field averaged conformations

$$H_1 = \prod_{k=0}^{n-1} h(\mathbf{r}_{k+1}|\mathbf{r}_k) = \prod_{k=0}^{n-1} \langle e^{-\beta U_{\text{inter}}(\mathbf{r}_{k+1}, \mathbf{r}_k)} \rangle \quad (24)$$

Thus, using eqs 4, 11, and 20–22, Ξ can be expressed as

$$\Xi = \Xi^0 H_1 = \sum_{\{\mathbf{R}_0\}} w(\mathbf{r}_1) \prod_{k=0}^{n-1} w(\mathbf{r}_{k+1}|\mathbf{R}_k^{\alpha}) \quad (25)$$

where

$$w(\mathbf{r}_{k+1}|\mathbf{R}_k^{\alpha}) = w_0(\mathbf{r}_{k+1}|\mathbf{R}_k^{\alpha}) h(\mathbf{r}_{k+1}|\mathbf{r}_k) \quad (26)$$

Hence under these conditions of independence, the chain segment statistical weight can be factored into a short-ranged intrachain contribution and an interchain component. The interchain contribution $-kT \ln h$, is the mean energetic cost of increasing the density of the system by one segment $k+1$ at position \mathbf{r}_{k+1} in fixed volume V . As noted above, the Flory–Huggins theory makes the approximations that (i) $w_0(\mathbf{r}_{k+1}|\mathbf{R}_k^{\alpha}) = 1$ and, (ii) h is only a function of the bulk density, n/V , and is independent of the segment position \mathbf{r}_{k+1} . These excluded volume insertion factors also appear as statistical weights in theories for chains at interfaces. In the following section, our purpose is to consider, in the same mean-field approximation, how the presence of an interface affects the conformations of chains at high densities. This discussion necessarily involves some reiteration of principles described previously.^{2–9,13–17,19,23}

Condensed Chains at Interfaces

The physical properties of chains are altered by the presence of an impenetrable interface. We consider here only interfaces that are simple geometric surfaces, such as planes as models for monolayers, bilayers, and grafted chain phases or spheres or cylinders as models for micelles of those geometries.

The configurations of chains vary with distance normal to the plane of the interface. This characteristic feature of interfacial systems can be represented by using a lattice of layers, numbered $l = 1, 2, 3, \dots, L$ from the interface. If the interface is planar, the layers are constructed to be parallel with it; if the interface is curved, then the layers are concentric with it. For planar interfaces, the number of lattice sites per layer is $M_l = M_0$, a constant independent of l ; for other interfaces, M_l is given by simple geometric considerations.³

The configurations of the chains near an interface are characterized by the relative orientations of the bonds along each chain. Consider a system of chains all of the same length n . Let $\nu_{l,\alpha}^+$ represent the number of segments per chain of forward bonds (directed away from the interface, from layer l to layer $l+1$) in the configuration α , and $\nu_{l,\alpha}^0$ and $\nu_{l,\alpha}^-$ are defined likewise for the number of lateral bonds (parallel to the interface, from one site to another in layer l) and reverse bonds (toward the interface from layer l to $l-1$), respectively. For a chain segment, k , in a given lattice site (where segment 1 is taken as the end chain segment nearest the interface), "forward" and "reverse" uniquely specify a single lattice site into which the next segment, $k+1$, will step. However, a lateral bond in a simple cubic lattice has $(z-2)$ possible orientations, where z is the coordination number of the lattice. Inasmuch as the constraints to be described below do not depend on which of the $(z-2)$ directions is taken by any sidestep, but depend only on the total number of sidesteps and their positions along the chain, then it is more convenient to collect configurations in terms of the

numbers of steps of each type. Accordingly, we let $c = \{\nu_{1,c}^+, \nu_{1,c}^0, \nu_{1,c}^-, \nu_{2,c}^+, \nu_{2,c}^0, \nu_{2,c}^-, \dots, \nu_{L,c}^+, \nu_{L,c}^0, \nu_{L,c}^-\}$ represent a single configuration of the chain. Let N_c be the number of chains in configuration c . The total number of chains is the sum over all these configurations

$$N = \sum_c N_c \quad (27)$$

The multiplicity of configurations of the chains is

$$W = \frac{N!}{\prod_c N_c!} = N! \prod_c \left(\frac{g_c^{N_c}}{N_c!} \right) \quad (28)$$

where g_c is the number of distinguishable configurations of a chain represented by the sequence, c

$$g_c = \prod_{l=1}^L (z - 2)^{\nu_{l,c}^0} \quad (29)$$

The probability of a configuration, c , is

$$P_c = N_c / N \quad (30)$$

The use of Stirling's approximation and the Boltzmann equation lead to the entropy, $S = k \ln W$

$$\frac{S}{k} = -N \sum_c P_c \ln \left(\frac{P_c}{g_c} \right) \quad (31)$$

The number of steps of each type per layer is

$$\langle \nu_l^+ \rangle = \sum_c \nu_{l,c}^+ P_c \quad (32a)$$

$$\langle \nu_l^0 \rangle = \sum_c \nu_{l,c}^0 P_c \quad (32b)$$

$$\langle \nu_l^- \rangle = \sum_c \nu_{l,c}^- P_c \quad (32c)$$

Constraints on Long Chains Anchored at an Interface

One example of a long-chain interphase is that of the interfacial region in semicrystalline polymer materials. Each chain is considered to be anchored, i.e., to "originate", from a point on the interface corresponding to the exit location of a chain stem in the crystalline in layer $l = 0$. The chain conformations at the interface are constrained by the presence of the interface (the boundary condition) and by the lateral packing with neighboring chains.^{6,7} We consider here the case of long chains, for which the incidence of chain ends is small. We aim to calculate the quantities $\langle \nu_l^+ \rangle$, $\langle \nu_l^0 \rangle$, and $\langle \nu_l^- \rangle$ for each layer $l = 1, 2, \dots, L$. To do so, we find the equilibrium distribution, P_c , which is identified as the state of maximum entropy subject to the two constraints on the system. (I) In the absence of solvent or excess volume, lateral packing is constrained by the requirement that each layer be fully occupied by chain segments

$$\langle \nu_{l-1}^+ \rangle + \langle \nu_l^0 \rangle + \langle \nu_{l+1}^- \rangle = M_l / N \quad (33)$$

(II) Since there are no chain ends (sources or sinks) within any layer, the flux of chains into any layer, l , must equal the flux leaving the layer

$$\sum_c (\nu_{l-1,c}^+ + \nu_{l+1,c}^-) = \sum_c (\nu_{l,c}^+ + \nu_{l,c}^-) \quad (34)$$

and on the average

$$\langle \nu_{l-1}^+ \rangle + \langle \nu_{l+1}^- \rangle = \langle \nu_l^+ \rangle + \langle \nu_l^- \rangle \quad (35)$$

Combining eqs 32a-c with eqs 33 and 35, constraints I and II are expressed, respectively, as

$$\sum_c (\nu_{l-1,c}^+ + \nu_{l,c}^0 + \nu_{l+1,c}^-) dP_c = 0 \quad (36)$$

and

$$\sum_c (\nu_{l,c}^+ + \nu_{l,c}^- - \nu_{l-1,c}^+ - \nu_{l+1,c}^-) dP_c = 0 \quad (37)$$

Subject to constraints I and II and the normalization inherent in eqs 27 and 30, maximization of the entropy, eq 31, using the standard method of Lagrange multipliers, leads to

$$dS = \sum_c \left\{ \ln \left(\frac{P_c}{g_c} \right) + 1 + \gamma + \sum_{l=1}^L [\lambda_l (\nu_{l-1,c}^+ + \nu_{l,c}^0 + \nu_{l+1,c}^-) + \xi_l (\nu_{l,c}^+ + \nu_{l,c}^- - \nu_{l-1,c}^+ - \nu_{l+1,c}^-)] \right\} dP_c = 0 \quad (38)$$

where λ_l , ξ_l , and γ are the undetermined multipliers (γ corresponds to the constraint $\sum_c P_c = 1$). In this method, each variation is taken to be independent; hence eq 38 is solved by

$$P_c = \left(\frac{g_c}{e^{1+\gamma}} \right) \prod_{l=1}^L p_l^{\nu_{l,c}^+} q_l^{\nu_{l,c}^0} u_l^{\nu_{l,c}^-} \quad (39)$$

where the quantities p_l , q_l , and u_l are given by

$$p_l = \exp(-\lambda_{l+1} - \xi_l + \xi_{l+1}) \quad (40a)$$

$$q_l = \exp(-\lambda_l) \quad (40b)$$

$$u_l = \exp(-\lambda_{l-1} + \xi_{l-1} - \xi_l) \quad (40c)$$

Combinations of eqs 40a-c lead to a set of L equations:

$$\frac{p_l}{q_l} = \frac{q_{l+1}}{u_{l+1}} \quad (41)$$

For the planar interphase ($M_l = M_0$), eqs 33 and 35 may be rewritten as (see Appendix)

$$p_l + (z - 2)q_l + u_l = 1 \quad (42)$$

and

$$p_{l-1} + u_{l+1} = p_l + u_l \quad (43)$$

These give three equations per layer which may be solved to determine the $3L$ unknowns, p_l , q_l , and u_l .

In some circumstances it is justified to use a more restricted condition in place of the full constraint, eqs 34 and 35.^{5,7,23}

$$w(\mathbf{r}_{k+1}, \mathbf{r}_k; k) = w(\mathbf{r}_k, \mathbf{r}_{k+1}; k) \quad (44)$$

i.e., the directionality of the chain is indistinguishable; then the general flux constraint can be replaced by a "symmetry constraint" (see Appendix).

$$\langle \nu_l^+ \rangle = \langle \nu_{l+1}^- \rangle \quad (45)$$

When symmetry applies, then eq 43 can be replaced by

$$p_l = u_{l+1} \quad (46)$$

and a simple recursion equation may be obtained

$$(z - 2)^2 u_l^2 = (1 - u_l - u_{l+1})(1 - u_l - u_{l-1}) \quad (47)$$

Equations 47 are then solved simultaneously subject to the appropriate boundary conditions.⁷

The partition function for the long-chain interphase with chains anchored at layer 1 is

$$\Xi = \sum_c \left(\frac{g_c}{e^{1+\gamma}} \right) \prod_{l=1}^L e^{-\lambda_l [\nu_{l-1,c}^+ + \nu_{l,c}^0 + \nu_{l+1,c}^-] - \xi_l [\nu_{l,c}^+ - \nu_{l+1,c}^-]} \quad (48)$$

Using eqs 32 and 48, it is easy to verify that

$$\frac{\partial \ln \Xi}{\partial \lambda_l} = \langle \nu_{l-1}^+ \rangle + \langle \nu_l^0 \rangle + \langle \nu_{l+1}^- \rangle = \frac{M_l}{N} \quad (49)$$

Equation 49 indicates that $-kT \ln \Xi$ plays the role of a Gibbs free energy per chain, and since, in the lattice system considered here, M_l/N is the volume per chain in layer l , λ_l may be taken to be the pressure conjugate to this volume. Accordingly λ_l has been referred to as a lateral pressure (see Ben-Shaul et al.¹⁴). The physical meaning of p , q , and u is shown by comparison of eq 39 with eqs 24–26. They represent the three types of statistical weight factors for increasing the density by one segment in layers $l-1$, l , and $l+1$, respectively, averaged over the chain configurations, given that the preceding segment is in layer l . For these interfacial systems, h is dependent not on the mean density of the system as in Flory–Huggins theory, but on the mean density of each layer, and hence depends on one spatial coordinate, the distance from the interface; i.e.

$$h(\mathbf{r}_{k+1}|\mathbf{r}_k) = h(l'|l) = \begin{cases} p_1 & \text{for } l' = l+1 \\ q_l & \text{for } l' = l \\ u_l & \text{for } l' = l-1 \end{cases} \quad (50)$$

Triplet Correlations

Now we consider a better approximation for the short-ranged correlations along the chain.⁷ Rather than a single-bond correlation (two segments), we consider bond pairs (three segments). In this case, we approximate

$$w(\mathbf{r}_{k+1}|\mathbf{R}_k) \approx w(\mathbf{r}_{k+1}|\mathbf{r}_k, \mathbf{r}_{k-1}) \quad (51)$$

and

$$W(\{\mathbf{R}_\alpha\}) = w(\mathbf{r}_1^\alpha) \prod_{k=1}^{n-1} w(\mathbf{r}_{k+1}^\alpha|\mathbf{r}_k^\alpha, \mathbf{r}_{k-1}^\alpha) \quad (52)$$

These statistical weights depend on three segment positions \mathbf{r}_{k+1} , \mathbf{r}_k , and \mathbf{r}_{k-1} . It is equivalent to express them in terms of a set of possible bond directions $w_l(\delta|\beta)$

$$w(\mathbf{r}_{k+1}|\mathbf{r}_k, \mathbf{r}_{k-1}) = \begin{bmatrix} w_l(+|+) & w_l(+|0) & w_l(+|-) \\ w_l(0|+) & w_l(0|0) & w_l(0|-) \\ w_l(-|+) & w_l(-|0) & w_l(-|-) \end{bmatrix} \quad (53)$$

where $w_l(\delta|\beta)$ is the three-segment conditional statistical weight for segment $k+1$ in layer $l+\delta$ given that segment k is in layer l and segment $k-1$ is in layer $l+\beta$. δ and β represent $+1$, 0 , or -1 as indicated in eq 53. This weight can be factored into intramolecular and intermolecular components as in eq 26:

$$w(\mathbf{r}_{k+1}|\mathbf{r}_k, \mathbf{r}_{k-1}) = w_0(\delta|\beta) h(\mathbf{r}_{k+1}|\mathbf{r}_k) \quad (54)$$

The quantities h are again given by eq 50 characterizing the layer dependence of the intermolecular interactions, and the quantities $w_0(\delta|\beta)$ represent the intrinsic conformational statistical weights for chains in the absence of

constraints and are thus independent of the layer number, l . For example, if the inherent bending energy is ϵ , then

$$\begin{aligned} w_0(+|0) &= w_0(-|0) = \omega = e^{-\epsilon/kT} \\ w_0(+|-) &= w_0(-|+) = 1 \\ w_0(+|+) &= w_0(-|-) = 0 \\ w_0^s(0|0) &= 1 \\ w_0^b(0|0) &= \omega \\ w_0^i(0|0) &= 0 \end{aligned} \quad (55)$$

where the superscripts s , b , and i represent the straight, bent, and self-intersecting configurations of the two bonds in layer l , respectively. This approach has been applied to symmetric semicrystalline interphases.⁷ A more general treatment is given in the Appendix.

Constraints on Short Chains Anchored at an Interface

The interphases considered above are those comprised of long chains, wherein the incidence of chain ends is small. In those cases, the factor responsible for the increased configurational freedom of the chains with distance from the interface is the formation of loops, or foldbacks, whereby the chains exit and reenter the crystallite. Foldbacks lead to diminished “flux” of the chains with distance from the interface and greater configurational freedom. The flux, the number of forward or reverse bonds crossing from layer l to $l+1$, will also be affected by geometric factors, such as curvature of the interface, wherein M_l depends on l .

For short chains, an additional mechanism leads to diminished flux from the interface: the terminations of the chains. As in the case above, the equilibrium configurations of the chains are given by that distribution which maximizes the configurational entropy, eq 31, subject only to the “packing” requirement, eq 33. The flux conservation condition eq 35 does not apply here, since the chain terminations act as flux sinks. The more general flux conservation condition which applies here, and which includes sources and sinks, is given in the Appendix eq A15. In what follows, we consider a system of chains of equal length

$$\sum_{l=1}^L (\nu_{l,c}^+ + \nu_{l,c}^0 + \nu_{l,c}^-) = n-1 \quad (56)$$

The configurations of the system may be enumerated through the use of a matrix method.^{2,3,8,9,28} We define the generating matrix

$$\mathbf{G} = \begin{bmatrix} (z-2)q_1 & p_1 & 0 & 0 & 0 & 0 \\ u_2 & (z-2)q_2 & p_2 & 0 & 0 & 0 \\ 0 & u_3 & (z-2)q_3 & p_3 & 0 & 0 \\ 0 & & \dots & & u_L & (z-2)q_L \end{bmatrix} \quad (57)$$

The connectivity constraint, eq A1, defines the recursion relation for the number, $\nu_l(k)$, of segments k in layer l . The recursion relation, eq A6, can be expressed in terms of these generating matrices by

$$\nu(k) = [\nu_1(k), \nu_2(k), \dots, \nu_L(k)] = \nu(k-1)\mathbf{G} \quad (58)$$

By consecutive application, this becomes

$$\nu(k) = \nu(1)G^{k-1} \quad (59)$$

The single-chain partition function is

$$\Xi_k = A_k G^{n-1} B \quad (60)$$

where $B = \text{col } [1 \ 1 \ 1 \dots 1]$ and $A_k = [0 \ 0 \dots 0 \ 1 \ 0 \dots 0]$ which contains 1 in column k , indicating that all chains begin in layer k . For grafted or anchored chains at an interface, $A_k = A_1 = [1 \ 0 \ 0 \dots 0 \ 0]$; all chains begin in the first layer. Other cases are of interest, however, for interphases containing solute chains that are not anchored. This partition function enumerates exclusively all conformations that satisfy eq 56 and constraint eq A15.

The mean number of segments in layer l due to a chain that started in layer k (per chain) is given by

$$\langle \nu_l^+ \rangle = \frac{\partial \ln \Xi_k}{\partial \ln p_l} = \frac{p_l}{\Xi_k} [A_k \{G'_{p_l} G^{n-2} + G G'_{p_l} G^{n-3} + \dots + G^{n-2} G'_{p_l}\} B] \quad (61a)$$

$$\langle \nu_l^0 \rangle = \frac{\partial \ln \Xi_k}{\partial \ln q_l} = \frac{q_l}{\Xi_k} [A_k \{G'_{q_l} G^{n-2} + G G'_{q_l} G^{n-3} + \dots + G^{n-2} G'_{q_l}\} B] \quad (61b)$$

$$\langle \nu_l^- \rangle = \frac{\partial \ln \Xi_k}{\partial \ln u_l} = \frac{\mu_l}{\Xi_k} [A_k \{G'_{u_l} G^{n-2} + G G'_{u_l} G^{n-3} + \dots + G^{n-2} G'_{u_l}\} B] \quad (61c)$$

where G'_{p_l} , G'_{q_l} , and G'_{u_l} are the derivatives of the generating matrix with respect to the step weights (i.e. $G'_{p_l} = \partial G / \partial p_l$). For an interphase in which N_1 chains begin in layer 1, the number of chains, T_l , which terminate in layer l is given by

$$T_l = \frac{N_1}{\Xi_1} [A_l G^{n-1} C_l] \quad (62)$$

where C_l is a column vector with the l th element equal to one and all other elements equal to zero.

For short-chain interphases, the $3L$ unknowns, $\langle \nu_l^+ \rangle$, $\langle \nu_l^0 \rangle$, and $\langle \nu_l^- \rangle$, are calculated as follows. Maximization of the entropy, subject to the packing constraint leads to eq 38 with $\xi_l = 0$; hence there are $2L$ equations

$$p_{l-1} = q_l = u_{l+1} \quad (63)$$

These values are substituted into the generating matrix, eq 57, now the function of a single variable per layer, for example, q_l

$$G = \begin{bmatrix} (z-2)q_1 & q_2 & 0 & 0 & 0 & 0 \\ q_1 & (z-2)q_2 & q_3 & 0 & 0 & 0 \\ 0 & q_2 & (z-2)q_3 & q_4 & 0 & 0 \\ 0 & & \dots & q_{L-1} & (z-2)q_L & \end{bmatrix} \quad (64)$$

This generating matrix is substituted into eqs 61a-c. The q_l 's are then determined from the solution of the packing constraint equations, which for a system of N anchored or grafted chains in layer 1 are

$$\langle \nu_{l-1}^+ \rangle + \langle \nu_l^0 \rangle + \langle \nu_{l+1}^- \rangle + \delta_{l,1} = M_l / N \quad (65)$$

The Kronecker delta, $\delta_{l,1}$, accounts for the first starting segments of the chains in layer 1. The latter is a source term which is treated in more detail in the Appendix. These values, with eqs 63 in 61 then give the bond configuration averages, and the partition function, eq 60.

In the more general case the first segment of a chain may occur in any layer of the interphase, rather than being anchored exclusively in the k th layer. Let there be N_1, N_2, \dots, N_k chains starting in layers 1, 2, ..., k , respectively. The distribution of chain ends in this system is given by the sum of the contributions from various layers (see eq 62)

$$T_l = \sum_{k=1}^L \frac{N_k}{\Xi_k} [A_k G^{n-1} C_l] \quad (66)$$

with C_l defined as in eq 62. As before, the entropy is maximized subject to the packing constraint; hence again G is of the form given by eq 64. Now, however, the packing condition for layer l is a sum of the contributions from chains that start in different layers, namely

$$\sum_{k=1}^L \frac{N_k}{M_l} \left[\frac{\partial \ln \Xi_k}{\partial \ln p_{l-1}} + \frac{\partial \ln \Xi_k}{\partial \ln q_l} + \frac{\partial \ln \Xi_k}{\partial \ln u_{l+1}} + \delta_{k,l} \right] = 1 \quad (67)$$

For the purpose of comparison with the model of Scheutjens and Fleer in the following section, we define a vector

$$J = [j_1, j_2, \dots, j_L] \quad (68)$$

where

$$j_k = \frac{q_k N_k}{\Xi_k M_0} \quad (69)$$

is defined for a planar interphase with M_0 sites per layer. Combining eqs 63 and 67 leads to the expression

$$J \left[\frac{\partial}{\partial p_{l-1}} + \frac{\partial}{\partial q_l} + \frac{\partial}{\partial u_{l+1}} \right] G^{n-1} B + \frac{N_l}{M_0} = 1 \quad (70)$$

In the model of Dill and Flory,² the configurational properties were calculated by a simpler approximate procedure. The incidence of reverse steps was assumed to be negligible, $\langle \nu_l^- \rangle = 0$. Hence only $2L$ equations are required for the $2L$ unknowns, $\langle \nu_l^+ \rangle$ and $\langle \nu_l^0 \rangle$. L equations were provided by the packing constraint, eq 34, as is done here (in the DF notation, $R_l = N \langle \nu_l^0 \rangle$ and $J_l = N \langle \nu_l^+ \rangle$, $J_l + R_l = M_l$). An additional L equations were provided, in the present notation, by the assumption that

$$p_l + (z-2)q_l = 1 \quad (71)$$

Hence that model is fully constrained and there is no need for the maximization of the entropy. Although the DF assumption is correct for long chains at planar interfaces, it becomes a weaker approximation for regions of high densities of chain ends or in regions of high curvature, inasmuch as it approximates $p_l(k) + (z-2)q_l(k)$ as $p_l + (z-2)q_l$ for any k , which is inappropriate for $k = n$. Pursuant to that approximation, in their notation, the DF theory leads to a flux condition, $J_l = J_{l-1} - T_{l-1}$ (by substitution of eq 57 into A11 with $u_{l+1} = 0$). We have compared the configurational properties of the present model with those of the Dill and Flory model and have found that both models give nearly identical results except for spherical micelles, for which the earlier treatment predicted increasing chain order toward the chain ends, whereas the present treatment predicts greater disorder at the chain ends (see Comparison with Experiments). Note that both models and molecular dynamics simulations^{38,39} show that chain order does increase at the micellar center. Ben-Shaul et al.¹³ incorrectly attributed the discrepancy to incomplete maximization of the entropy, which is not possible since no maximization step is involved in the DF model.

The Model of Scheutjens and Fler

Scheutjens and Fler and their collaborators have independently developed theory for the adsorption of chains at interfaces.^{8,9} We show here that their theory, although derived from a different viewpoint, is identical with the treatment above in the case of pure chains with no solvent. Solvent is then readily taken into account through addition of a term using contact interactions implemented with χ parameters. Scheutjens and Fler consider the insertion of chains through use of a Flory insertion process. The degeneracy of states is W

$$W = \prod_c \left(\frac{g_c^{N_c}}{N_c!} \prod_{j=1}^{N_c} f_{jc} \right) \quad (72)$$

where f_{jc} is the insertion factor for the j th chain in configuration c . This is further factored into a product of terms describing the insertion of each chain segment

$$\prod_c \prod_{j=1}^{N_c} f_{jc} = M_0^{-N(n-1)} \prod_{l=1}^L \prod_{\rho_l=0}^{M_0} (M_0 - \rho_l) \quad (73)$$

where, for simplicity, we consider a planar interface, $M_l = M_0$. ρ_l is a counting parameter for the insertion process. Although they have considered the more general case for solvent inclusion at the planar interface, we compare here only the case of pure homopolymers at the interface. In this case, the product of insertion factors is given by

$$W = [M_0!]^L M_0^{-N(n-1)} \prod_c \frac{g_c^{N_c}}{N_c!} \quad (74)$$

Subject to the packing constraint, eq 65, Scheutjens and Fler predict the equilibrium as the state of minimum free energy; the result, for pure homopolymers, is identical with eq 63. They define the matrix

$$\mathbf{G}_{\text{SF}} = \begin{bmatrix} \lambda_0 p'_1 & \lambda_1 p'_1 & 0 & 0 & 0 & 0 \\ \lambda_1 p'_2 & \lambda_0 p'_2 & \lambda_1 p'_2 & 0 & 0 & 0 \\ 0 & \lambda_1 p'_3 & \lambda_0 p'_3 & \lambda_1 p'_3 & 0 & 0 \\ 0 & 0 & 0 & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \lambda_1 p'_L & \lambda_0 p'_L \end{bmatrix} \quad (75)$$

which is the transpose of the matrix \mathbf{G} , eq 64, provided that

$$p'_l = z q_l \quad (76a)$$

$$\lambda_0 = (z - 2)/z \quad (76b)$$

$$\lambda_1 = 1/z \quad (76c)$$

They define the statistical weight that a chain of s segments ends in layer l as $P(l, s)$. Then the chain conformations satisfy the recursion relation

$$P(l, s) = [\lambda_1 P(l-1, s-1) + \lambda_0 P(l, s-1) + \lambda_1 P(l+1, s-1)] p'_l \quad (77)$$

where p'_l is the a priori probability for placing an end segment in layer l . This is expressed more succinctly as

$$\begin{bmatrix} P(1, n) \\ P(2, n) \\ \vdots \\ P(L, n) \end{bmatrix} = \mathbf{G}_{\text{SF}}^{n-1} \begin{bmatrix} p'_1 \\ p'_2 \\ \vdots \\ p'_L \end{bmatrix}$$

Scheutjens and Fler define a quantity

$$P(s, l; n) = \frac{P(l, s) P(l, n-s+1)}{p'_l} \quad (78)$$

where $P(s, l; n)$ is the probability (per site) that segment s of any n -mer (ending at any layer) is located in layer l . The closure (full occupancy condition) is now expressed in terms of the latter quantity as

$$\sum_{s=1}^n P(s, l; n) = 1 \quad (79)$$

We show that eqs 78 and 79 of the Scheutjens and Fler condition are identical with the full occupancy condition of the present treatment given by eq 70. Consider one representative term in eq 70

$$[j_1, j_2, \dots, j_L] \frac{\partial}{\partial u_{l+1}} \mathbf{G}^{n-1} \mathbf{B} \quad (80)$$

The derivative of \mathbf{G}^{n-1} is a sum of terms as in eqs 61. Now consider an individual term, for example, the k th, in this sum on the right-hand side of eq 80

$$[j_1, j_2, \dots, j_L] \mathbf{G}^{k-1} \mathbf{G}'_{u_{l+1}} \mathbf{G}^{n-1-k} \mathbf{B} \quad (81)$$

The derivative matrix, $\mathbf{G}'_{u_{l+1}}$ (represented by eq 57 with all elements zero except the term corresponding to $u_{l+1} = 1$), can alternatively be written as a product of a column vector, $[0, 0, 0, \dots, 0, 1, 0, \dots, 0]$, and a row vector, $[0, 0, \dots, 0, 1, 0, 0, \dots, 0]$, where the 1's are in positions $l+1$ and l , respectively. From this it is clear that the term above represents a product of the probabilities of conformations of two subchains, the first of which begins in any layer and ends with its k th segment in the l th layer, and the second of which is connected to the first in layer l through a reverse bond from its first segment which is layer $l+1$. The terms with derivatives with respect to p_{l-1} and q_l are those whose second subchains begin in layers $l-1$ and l , respectively. Hence the sum, eq 67, describes all the possible connectors for subchains 1 and 2 which meet with segment k in layer l . Thus eqs 78 and 79 of Scheutjens and Fler are identical with eq 70 (hence also eq 67), the packing condition. The quantities " j " thus represent the incidence of chain starts in various layers.

Curved Systems

For curved systems, the number of available sites, M_l , is layer dependent. For cylindrical micelles of radius R_0 and length h this dependence is given by

$$M_l = \pi h [2(R_0 - l) + 1] \quad (82)$$

and for spherical micelles of radius R_0

$$M_l = \frac{4\pi}{3} [3(R_0 - l + 1)(R_0 - l) + 1] \quad (83)$$

These M_l 's are to be used in conjunction with full occupancy condition (33) and flux condition (35) where appropriate. For long-chain systems, the full occupancy and flux conditions may be rewritten in terms of p_l , q_l , and u_l as (using eq A14)

$$M_{l-1} p_{l-1} + M_l (z - 2) q_l + M_{l+1} u_{l+1} = M_l \quad (84)$$

and

$$M_{l-1} p_{l-1} + M_{l+1} u_{l+1} = M_l p_l + M_l u_l \quad (85)$$

For systems with intrinsic curvature, Ben-Shaul et al.¹³ have noted that because the configurations of bonds are more restricted by smaller angular freedom in the direction

toward the center of curvature, then the coordination will depend on the directionality and layer. They defined $z_{l,l}$, $z_{l,l-1}$, and $z_{l,l+1}$ for lateral, downward, and upward bonds, respectively. The quantities must satisfy the relation

$$z_{l,l-1} + z_{l,l} + z_{l,l+1} = z \quad (86a)$$

$$z_{l,l} = z - 2 \quad (86b)$$

Ben-Shaul et al. defined these quantities as

$$z_{l,l-1} = M_{l-1}/M_l \quad (87a)$$

$$z_{l,l+1} = M_{l+1}/M_l \quad (87b)$$

which satisfy eq 86 for cylindrical geometries since M_l is linear with l in these cases. By this definition, however, eq 86 is not satisfied for spherical geometries. For large spheres, eq 86 will be satisfied by

$$z_{l,l} = z - 2 \quad (88)$$

$$z_{l,l-1} = (M_{l-1}/M_l)^{1/2} \quad (88a)$$

$$z_{l,l+1} = (M_{l+1}/M_l)^{1/2} \quad (88b)$$

for layers not near the center of the micelle. Because the coordination number appears as a multiplicative constant in the partition function, it does not contribute to the values of average quantities which appear in the flux or full occupancy relations, eqs 65 and 67. Curved systems have also been treated by Leermakers et al.⁴⁶

Triplet Correlations for Short Chains

A better approximation for the short-ranged interactions than segment pairs is segment triplets. As with long-chain interphases, this permits inclusion of bending energies and exclusion of immediate chain reversals, which are prohibited by excluded volume.

The generating function, G , now becomes a supermatrix:

$$G(\omega) = \begin{bmatrix} H_1 & D_1 & 0 & 0 & 0 & 0 & 0 \\ U_2 & H_2 & D_2 & 0 & 0 & 0 & 0 \\ 0 & U_3 & H_3 & D_3 & 0 & 0 & 0 \\ 0 & 0 & U_4 & H_4 & D_4 & \dots & 0 \\ & & & & & & H_L & D_L \end{bmatrix} \quad (89)$$

where D_l , H_l , and U_l are themselves matrices defined as

$$U_l = u_l \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \omega \\ 0 & 0 & 1 \end{bmatrix} \quad (90a)$$

$$D_l = p_l \begin{bmatrix} 1 & 0 & 0 \\ \omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (90b)$$

$$H_l = q_l \begin{bmatrix} 0 & (z-2)\omega & 0 \\ 0 & (z-4)\omega + 1 & 0 \\ 0 & (z-2)\omega & 0 \end{bmatrix} \quad (90c)$$

where ω has been defined in eq 55.

The generating matrix may be further refined by taking into account correlations of the third, fourth, etc. neighbors along the chain. In such a development, it is possible to account for intrachain correlations to any (finite) number of neighbors while the interchain interactions are treated in the mean-field approximation. Consideration of second-neighbor interactions improves the approximation, by

excluding immediate backtracking and taking into account the chain stiffness. A four-segment treatment should not be expected to produce significant improvement in the cubic lattice model. However, in the five-segment correlation, the single possibility of chain crossing by forming a square (the lattice representation of the pentane effect) may be excluded.

The partition function for a chain of n bonds all with the same flexibility parameter ω may be written in the supermatrix form as

$$\Xi_1 = A_1 G_1 [G(\omega)]^{n-2} B \quad (91)$$

where the supermatrix G_1 corresponds to the first bond.

$$U_1 = u_1 \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 0 & 0 & 1 \end{bmatrix} \quad (92a)$$

$$D_1 = p_1 \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad (92b)$$

$$H_1 = q_1 \begin{bmatrix} 0 & (z-2) & 0 \\ 0 & (z-2) & 0 \\ 0 & (z-2) & 0 \end{bmatrix} \quad (92c)$$

For these supermatrix expressions $A = [1 \ 0 \ 0 \dots 0]$ and $B = \text{col } [1 \ 1 \ 1 \dots 1]$, both vectors being of length $3n$.

If different bonds in the chain have different stiffness, or different preferred orientation, represented by

$$\omega_k = e^{c_k/kT} \quad (93)$$

then the partition function may be written as

$$\Xi_1 = A_1 \left[\prod_{k=1}^{n-1} G(\omega_k) \right] B \quad (94)$$

where $G(\omega_k)$ is the same as $G(\omega)$ except that in its local matrices, ω is replaced by ω_k . The introduction of local correlations does not change the full occupancy relations, which are governed only by the placement of individual segments. This supermatrix method is also useful in more general circumstances for taking into account correlations for short-ranged interactions in polymers not confined to interphases. A version of this formalism for a system of nonreversing chains was given by Cantor and Dill.^{44,45} Triplet correlations in the cubic lattice and its extension to the rotational isomeric state were treated by Leermakers et al.^{47,48}

Comparison with Experiments

The general theory presented here aims to predict configurational and thermodynamic properties of chain molecule interphases. Inasmuch as this theory is general, it reduces in several cases to earlier treatments, with which experimental comparison has already been made.^{23,30-32} However, for short chains, the present theory offers improvement over the theory of Dill and Flory;^{2,3} we compare these differences below.

We have tested the present theory against previously made comparisons of (i) the ¹³C NMR experiments of Cabane,^{30,33} (ii) the small-angle neutron scattering experiments of Chen et al.^{32,34} of the radical distribution function, (iii) the ¹⁹F NMR experiments of Muller and Simsohn,^{31,35} and (iv) the bond disorder gradients in planar² and curved

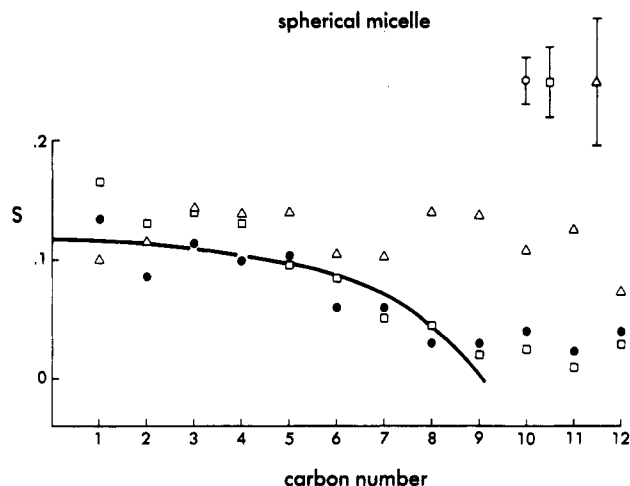


Figure 1. Disorder gradient for spherical micelles. Bond order parameter predictions are compared with molecular dynamics simulations (\square , \bullet)^{38,39} and experimental data on dodecyl sulfate spherical micelles (Δ);³⁷ see also ref 23 for further details.

interphases³ and find that it differs only insignificantly from that of DF. A sensitive test of theory, however, is provided by the order parameter in spherical micelles; hence that comparison is shown in Figure 1.

It has been noted before^{2,3,11} that two order parameters

$$S = \frac{3}{2} \langle \cos^2 \theta_k \rangle - \frac{1}{2} \quad (95)$$

can be defined for interphases. One is the "layer" order parameter for each layer, l , of the lattice

$$S_l^{\text{layer}} = \frac{3}{2} p_l - \frac{1}{2} \quad (96)$$

where θ_k is the angle of each bond in layer l relative to the interfacial normal. The second, which is experimentally measurable, is the "bond" order parameter, where the angle θ_k in eq 95 represents the angle of each bond k relative to the interfacial normal.

$$S_k^{\text{bond}} = \frac{3}{2} [A_1 G^{k-1} Q G^{n-k-2} B] - \frac{1}{2} \quad (97)$$

Q is a matrix identical with G , eq 64, but with the diagonal elements set equal to zero. The two order parameters differ because any given bond may be distributed throughout more than one layer. A detailed comparison of calculated and experimental order parameters for micelles and bilayers has been published.²³

Summary

The purpose of this work has been simply to summarize existing mean-field statistical mechanical theory for chain molecules at high densities at interfaces. We have done so in a physically transparent framework that we believe is simpler and more general than existing treatments of pure polymer interfaces. Although it reduces to the treatment of Scheutjens and Fleer^{3,9} in the appropriate circumstances, we find the present treatment conceptually simpler insofar as the constraints are separated from the statistics and all quantities are obtained as appropriate derivatives of the partition function. It shows the origins of the chain segment statistical weights as insertion factors. It shows the relationship between long-chain theories of the type originated by Helfand and short-chain theories, widely applied to surfactant aggregates and polymer adsorption. Finally, it provides a method for considering the bond correlation effects, of the type that have been treated by using rotational isomeric theory.

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Appendix: Constraints

The conformations of the interphase chains are constrained by their intramolecular connectivity and by the requirement that the interphase volume is filled exclusively by chain segments. These constraints are described in terms of the laws of inference as applied to the conditional statistical weights.

The first constraint is the connectivity condition

$$w(\mathbf{r}_{k+1}) = \sum_{\mathbf{r}_k} w(\mathbf{r}_k, \mathbf{r}_{k+1}) = \sum_{\mathbf{r}_k} w(\mathbf{r}_k) w(\mathbf{r}_{k+1} | \mathbf{r}_k) \quad (A1)$$

i.e., the number of all segments of type $k+1$ that occupy position \mathbf{r}_{k+1} is the sum over all the accessible routes of segment k from all positions \mathbf{r}_k .

In interphases, the position \mathbf{r}_k is specified only by the layer number, l . Thus the conditional statistical weights are defined by

$$w(\mathbf{r}_{k+1} | \mathbf{r}_k) = w(l' | l) \quad (A2a)$$

$$w(l' | l) = \begin{Bmatrix} p_l(k) \\ q_l(k) \\ u_l(k) \end{Bmatrix} = \begin{Bmatrix} p_l \\ q_l \\ u_l \end{Bmatrix} \text{ for } k < n \quad (A2b)$$

and

$$w(l' | l) = \begin{Bmatrix} 0 \\ 0 \\ 0 \end{Bmatrix} \text{ for } k \geq n \quad (A2c)$$

where p , q , and u represent forward ($l' = l + 1$), side ($l' = l$), and reverse steps ($l' = l - 1$), respectively. The number of segments of type k per chain in layer l is defined by

$$w(\mathbf{r}_k) = \nu_l(k) = n_l(k) / N \quad (A3)$$

where $n_l(k)$ is the total number of segments k (from all chains) in layer l . The number of chain ends (terminations) in layer l is given by substitution of $k = n$ into eq A3

$$T_l = N \nu_l(n) \quad (A4)$$

The requirement that layer l be fully occupied by chain segments is given by

$$\sum_{k=1}^n N \nu_l(k) = \sum_{k=1}^n n_l(k) = M_l \quad (A5)$$

Certain averages can be computed in terms of these statistical weights, of the number of forward or reverse steps from layer l and the number of sidesteps within layer l

$$\langle n_l^+ \rangle = \sum_{k=1}^n p_l(k) n_l(k) = p_l \sum_{k=1}^{n-1} n_l(k) \quad (A6a)$$

$$\langle n_l^0 \rangle = \sum_{k=1}^n q_l(k) n_l(k) = q_l \sum_{k=1}^{n-1} n_l(k) \quad (A6b)$$

$$\langle n_l^- \rangle = \sum_{k=1}^n u_l(k) n_l(k) = u_l \sum_{k=1}^{n-1} n_l(k) \quad (A6c)$$

Combination of eqs A4, A5, and A6 leads to

$$p_l = \langle n_l^+ \rangle / (M_l - T_l) \quad (\text{A7a})$$

$$(z-2)q_l = \langle n_l^0 \rangle / (M_l - T_l) \quad (\text{A7b})$$

$$u_l = \langle n_l^- \rangle / (M_l - T_l) \quad (\text{A7c})$$

The two conditions of chain connectivity (A1) and the volume-filling requirement (A5) can be expressed in more useful terms as constraints on certain averages of the system. Substitution of definitions (A2) and (A3) into eq A1 leads to the chain connectivity condition

$$p_{l-1}(k)n_{l-1}(k) + (z-2)q_l(k)n_l(k) + u_{l+1}(k)n_{l+1}(k) = n_l(k+1) \quad (\text{A8})$$

Summing this over k leads to the connectivity constraint on the mean values

$$\langle n_{l-1}^+ \rangle + \langle n_l^0 \rangle + \langle n_{l+1}^- \rangle = \sum_{k=1}^n n_l(k+1) \quad (\text{A9})$$

Equation A8 is identical with the Scheutjens-Fleer expression eq 77 for the statistical weight of a chain with s segments ending in layer l , $P(l,s)$. The full occupancy conditions may be derived from this via eq 78 or the matrix equations (61) and eq (65). However, if p , q , and u are normalized as defined in eqs A7, the full occupancy condition may be obtained by combining eqs A8 and A9 as follows:

$$\langle n_{l-1}^+ \rangle + \langle n_l^0 \rangle + \langle n_{l+1}^- \rangle = M_l \quad (\text{A10})$$

or, using eqs A7

$$p_{l-1}(M_{l-1} - T_{l-1}) + (z-2)q_l(M_l - T_l) + u_{l+1}(M_{l+1} - T_{l+1}) = M_l \quad (\text{A11})$$

More generally, there may be source terms within a layer l defined by

$$S_l = N\nu_l(1) \quad (\text{A12})$$

Equation A11 may then be generalized to

$$p_{l-1}(M_{l-1} + S_{l-1} - T_{l-1}) + (z-2)q_l(M_l + S_l - T_l) + u_{l+1}(M_{l+1} + S_{l+1} - T_{l+1}) = M_l \quad (\text{A13})$$

For long chains, the number of ends per layer is negligible, $T_l \ll M_l$ for any l , and eqs A7 become

$$p_l = \langle n_l^+ \rangle / M_l \quad (\text{A14a})$$

$$(z-2)q_l = \langle n_l^0 \rangle / M_l \quad (\text{A14b})$$

$$u_l = \langle n_l^- \rangle / M_l \quad (\text{A14c})$$

Equations A14 are also valid for a system containing loops in which the number of sources equals the number of sinks in layer l .

The Flux Constraint

In general one may write for any layer l

$$n_{l-1}^+ + n_{l+1}^- = n_l^+ + n_l^- + S_l - T_l \quad (\text{A15})$$

This relation is a way of expressing the full occupancy condition at layer l . When there are no chain ends (long chains) or when the number of sources and sinks within layer l cancel (loops), eq A15 simplifies to (per chain)

$$\langle \nu_{l-1}^+ \rangle + \langle \nu_{l+1}^- \rangle = \langle \nu_l^+ \rangle + \langle \nu_l^- \rangle \quad (\text{A16})$$

which may also be written as

$$M_{l-1}p_{l-1} + M_{l+1}u_{l+1} = M_l p_l + M_l u_l \quad (\text{A17})$$

When the chains are symmetric with respect to the two ends, one may replace the above flux condition with a simpler symmetry condition. Symmetry applies when the following conditions hold. If a chain of n segments begins and ends in the same layer, l , its partition function is given by

$$Z = \mathbf{A}_l \mathbf{G}^{n-1} \mathbf{C}_l \quad (\text{A18})$$

where \mathbf{A}_l is a row vector and \mathbf{C}_l is a column vector with elements $\delta_{li,k}$. Since the transpose of \mathbf{A}_l is equal to \mathbf{C}_l and vice versa, then \mathbf{G} must equal its transpose; therefore

$$u_{l+1} = p_l \quad (\text{A19})$$

and

$$\langle \nu_{l+1}^- \rangle = \langle \nu_{l-1}^+ \rangle$$

Symmetry also applies to any system for which the chain segment distributions are indistinguishable in layers L and L' by virtue of geometric symmetry. Such is the case for a "tie" chain in semicrystalline systems where the chain begins at one crystal boundary and ends at another. The partition function for a tie chain that starts at layer 1 and ends in layer L is given by

$$Z = \mathbf{A}_1 \mathbf{G}^{n-1} \mathbf{C}_L \quad (\text{A20})$$

If the system is symmetric with respect to the exchange of layers 1 and L , then one may write

$$Z = \mathbf{A}_L \mathbf{G}^{n-1} \mathbf{C}_1 \quad (\text{A21})$$

Transpose of the latter equation again will give the symmetry relations of eq A19. Whenever these symmetry relations are valid, they can replace eqs 34 and 35. At planar interfaces the number of sites is independent of l ; thus the packing constraint eq A10 together with eqs A14 and A19 reduces to

$$p_l + (z-2)q_l + u_l = 1 \quad (\text{A22})$$

Triplet Correlation Constraints

For semicrystalline polymers where symmetry relations hold, one may write

$$w(\mathbf{r}_{k+1}, \mathbf{r}_k, \mathbf{r}_{k-1}) = w(\mathbf{r}'_{k+1}, \mathbf{r}_k, \mathbf{r}'_{k-1}) \quad (\text{A23})$$

for $\mathbf{r}_{k+1} = \mathbf{r}'_{k-1}$ and $\mathbf{r}_{k-1} = \mathbf{r}'_{k+1}$. This condition can alternatively be expressed as the requirement for the following matrix to be symmetric about its diagonal:

$$w(\mathbf{r}_{k+1}, \mathbf{r}_k, \mathbf{r}_{k-1}) = \begin{bmatrix} 0 & w_l(+|0)q_l & w_l(+|-)p_{l-1} \\ w_l(0|+)u_{l+1} & w_l(0|0)q_l & w_l(0|-)p_{l-1} \\ w_l(-|+)u_{l+1} & w_l(-|0)q_l & 0 \end{bmatrix} \quad (\text{A24})$$

Three equations arise from symmetry:

$$w_l(+|0)q_l = w_l(0|+)u_{l+1} \quad (\text{A25a})$$

$$2_l(+|-)p_{l-1} = w_l(-|+)u_{l+1} \quad (\text{A25b})$$

$$w_l(0|-)p_{l-1} = w_l(-|0)q_l \quad (\text{A25c})$$

In addition, an alternative more convenient form of the condition (A1) is given in this case by

$$\sum_{\mathbf{r}_{k+1}} w(\mathbf{r}_{k+1}, \mathbf{r}_k, \mathbf{r}_{k-1}) = 1 \quad (\text{A26})$$

which leads to three additional equations:⁷

$$(z-2)w_l(0|+) + w_l(-|+) = 1 \quad (\text{A27a})$$

$$w_l(+|0) + (z-3)w_l(0|0) + w_l(-|0) = 1 \quad (\text{A27b})$$

$$w_l(+|-) + (z-2)w_l(0|-) = 1 \quad (\text{A27c})$$

In general, there is no need to assume symmetry relations. The three segment correlations may be expressed in terms of the two segment correlations via the relations (54) and (55) which result in the unnormalized values of the three segment probabilities

$$\begin{aligned} w_l(+|-) &= p_l \\ w_l(+|0) &= \omega p_l \\ w_l(0|+) &= \omega q_l \\ w_l^s(0|0) &= q_l \\ w_l^b(0|0) &= \omega q_l \\ w_l^i(0|0) &= 0 \\ w_l(0|-) &= \omega q_l \\ w_l(-|+) &= u_l \\ w_l(-|0) &= \omega u_l \end{aligned} \quad (\text{A28})$$

The superscripts s, b, and i represent straight, bent, and self-intersecting conformations of the two bonds in layer l , respectively. With a nonvanishing bending energy ϵ/kT , the chain has an internal energy $\langle E \rangle$ given by

$$\langle E \rangle = \sum_k \sum_{\mathbf{r}_{k+1}, \mathbf{r}_k, \mathbf{r}_{k-1}} w(\mathbf{r}_{k+1}, \mathbf{r}_k, \mathbf{r}_{k-1}) E(\mathbf{r}_{k+1}, \mathbf{r}_k, \mathbf{r}_{k-1}) \quad (\text{A29})$$

Using eqs 53–55, eq A29 becomes

$$\begin{aligned} \langle E \rangle &= \epsilon M_0 \sum_l \{ (z-2)w_l(+|0)q_l + (z-2)w_l(0|+)u_{l+1} + (z- \\ &2)(z-4)w_l^b(0|0)q_l + (z-2)w_l(0|-)p_{l-1} + (z-2)w_l(-|0)q_l \} \end{aligned} \quad (\text{A30})$$

The relevant quantity to be minimized is now the free energy given by

$$F = \langle E \rangle - TS \quad (\text{A31})$$

In terms of the single-bond probabilities, this is given by

$$\begin{aligned} F &= M_0 kT \sum_l \{ p_l [(z-2)\omega q_l + p_{l-1}] \ln p_l + \\ &(z-2)q_l [\omega u_{l+1} + q_l + (z-4)\omega q_l + \omega p_{l-1}] \ln q_l + \\ &u_l [(z-2)\omega q_l + u_{l+1}] \ln u_l \} \end{aligned} \quad (\text{A32})$$

The solution is given by minimizing eq A32 subject to the flux conditions (A17) and the packing condition (A20). A version of this formalism for symmetric systems has been presented by Marqusee.⁴³ The system of equations (A25), (A27), and (A32) with appropriate boundary conditions has been used to solve for the triplet correlations $w_l(\alpha|\beta)$ for the case of $\omega = 1$ and $\epsilon = 0$.⁷

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