at lower velocity gradients than for the mean thickness measured with ellipsometry. That work represented the first attempt at measuring the properties of an adsorbed layer beneath a flowing solution whereas this work and previous studies have involved the flow of pure solvent.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Gramain, Ph.; Myard, Ph. *Macromolecules* **1981**, *14*, 180.
(2) Cohen, Y.; Metzner, A. B. *Macromolecules* **1982**, *15*, 1425.
(3) DiMarzio, E. A.; Rubin, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 457.
(4) Fuller, G. G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 151.
(5) Warner, H. R., Jr. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 379.
(6) Hauge, P. S.; Dill, F. D. *IBM J. Res. Dev.* **1973**, *17*, 472.
(7) Azzam, R. M. A.; Bashara, N. M. "Ellipsometry and Polarized Light"; North Holland: Amsterdam, 1979.
(8) Stromberg, R. R.; Tutas, D. J.; Passaglia, E. *J. Phys. Chem.* **1965**, *69*, 3955.
(9) Sparrow, E. M.; Lin, S. H.; Lundgren, T. S. *Phys. Fluids* **1964**, *7*, 338.
(10) Takahashi, A.; Kawaguchi, M.; Hirota, H.; Kato, T. *Macromolecules* **1980**, *13*, 884.
(11) Grant, W. H.; Smith, L. E.; Stromberg, R. R. *Faraday Discuss. Chem. Soc.* **1975**, *No. 59*, 209.
(12) de Gennes, P.-G. *J. Chem. Phys.* **1974**, *60*, 5030.
(13) Hinch, E. J. Proceedings of the Symposium on Polymer Lubrication, Brest, 1974.

Statistical Thermodynamics of Short-Chain Molecule Interphases.
1. Theory

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ABSTRACT: Amphiphilic molecules comprised of a polar head and hydrocarbon tail associate in aqueous environment to form micelles, vesicles, bilayers, or other aggregates, consisting of hydrocarbon domains separated from the water regions by the head groups. Statistical theory for the hydrocarbon "interphase" region of such systems is developed, extending previous work to account for chain bending energies and to allow prediction of thermodynamic as well as structural properties. Expressions for the statistical weights of chain configurations and a configurational partition function are obtained subject to the constraint of approximately constant density within the hydrocarbon core, which is a consequence of strongly attractive isotropic van der Waals forces, balanced by hard-core steric repulsive forces. Expressions for positional and orientational probability distributions are derived.

Amphiphilic molecules comprised of a polar head and hydrocarbon tail associate in aqueous environment to form micelles, vesicles, bilayers, or other aggregates, consisting of hydrocarbon domains separated from the water regions by the head groups. The density within the hydrocarbon core is approximately equal to that within bulk liquid alkane phases, a consequence of strongly attractive isotropic van der Waals forces which are balanced by hard-core, short-range steric repulsive forces.[1] The constraints imposed by the different solubilities of head groups and tails in water and by the balance of intermolecular forces severely restrict the configurations available to the molecules. As a consequence, the degree of structural order within the hydrocarbon domain is not constant; rather, it varies over molecular dimensions along a coordinate axis determined by system geometry.[2,3] For example, in lipid bilayers, the hydrocarbon chains have greater orientational order near the heads than near the terminal methyl groups.[4] Such systems, herein termed "interphases", differ significantly from other condensed polymer phases such as liquids, crystals, and nematic liquid crystals, in which the degree of order is independent of spatial position.

Statistical mechanical theory has previously been developed which accounts for these constraints and which predicts structural properties of interphases, assuming freely jointed hydrocarbon chains.[2,3] In the present work, we extend the theory to take into account chain bending energies and also to allow the prediction of thermodynamic properties of interphases.

The Model

Subject to the continuity of the hydrocarbon chains and the nearly constant density within the interphase, the configurations of the chains may be systematically enumerated through use of a spatial lattice. The volume of space occupied by the interphase hydrocarbons is partitioned into nonoverlapping sites of equal volume, each of which may contain one chain segment. Chains are comprised of $n + 1$ "segments", occupying $n + 1$ contiguous sites, and thus of n "bonds" connecting the segments. In order that all bonds be of equal length, the sites must be isodiametric. Thus, the chain width dictates the segment length; for polymethylenic chains, each segment is comprised of approximately 3.6 CH_2 groups. For a planar monolayer or bilayer, sites may be considered to occur in planar layers, numbered $i = 1, 2, ..., n$ from the interface. For nonplanar interphases, layers are concentric with the interface and labeled in the same manner, and the number of sites per layer, N_i, varies with layer index, i.

Let J_1 be the total number of chains; then $\sigma_1 = J_1/N_1$ is the surface density of chains, where $0 \leqslant \sigma_1 \leqslant 1$. Assuming that the polar head groups are localized at the water/hydrocarbon interface, the first segments of each of the J_1 chains must all be in the first layer. We assume further that there exist only forward and lateral bonds, i.e., that if some segment (i) in a given chain is in layer j, then the next segment ($i + 1$) along that chain is either in layer $j + 1$ (forward bond) or in layer j (lateral bond) but may not backtrack (toward the interface) into layer $j - 1$. We define T_j to be the number of chains whose terminal (n + 1st) segment is in layer j, and J_j to be the chain flux, the number of chains which enter layer j from layer $j - 1$. Chain flux into successive layers decreases solely as a result of terminations; $J_j = J_{j-1} - T_{j-1}$ for each layer j, and

$$J_j = J_1 - \sum_{i=1}^{j-1} T_i \qquad (2.1)$$

We allow for the possibility that for some system geometries, a few layers may not be fully occupied by chain segments. The number of sites occupied by segments in layer j is f_jN_j, $0 \leq f_j \leq 1$, where f_j is the site occupation fraction in layer j, most layers having $f_j = 1$ (see below).

The difference between the number of segments in a layer and the flux into that layer is the number of lateral bonds R

$$R_j = f_jN_j - J_j \qquad (2.2)$$

Combining eq 2.1 and 2.2 and dividing by the total number of chains, we obtain a set of constraint equations

$$\frac{R_j}{J_1} = f_j\sigma_j^{-1} - 1 + \sum_{i=1}^{j-1}\frac{T_i}{J_1} \qquad j = 1, 2, ..., n + 1 \quad (2.3)$$

where $\sigma_j = J_1/N_j$.

Chain Configurational Statistics

We assume that the statistical weight of a chain configuration can be expressed as the product of the weights of its n bonds but that the weights of the bonds along the chain are not independent. There will be two contributions to the weight of a bond: one determined completely by the bond's orientation and the position (layer) in which it occurs, and the other "bond-pair" contribution resulting from intramolecular interactions determined by the relative orientations of the bonds immediately adjacent to it along the chain. In order to avoid double counting of bond-pair contributions to the total chain statistical weight, we take the bond weights to be conditional upon the orientation of only the preceding bond along the chain.

A cubic lattice with one segment per lattice site admits of only two relative orientations of the two consecutive bonds constituting a pair: collinear and bent at 90°. Relative to that of a collinear pair, the energy of a bent pair is defined to be ϵ. The statistical weight of a bent pair relative to a collinear pair is thus $\omega = e^{-\epsilon/kT}$, where kT is the Boltzmann constant multiplied by temperature. The energy differences of the rotational isomeric states are thus taken into account, within the approximation of the lattice model.

Those contributions to a bond's weight which are determined completely by its position and orientation are obtained as follows. We define z to be the lattice coordination number: for a simple cubic lattice, $z = 6$. Then $\gamma = z - 2$ is the lateral coordination number, i.e., the number of sites adjacent to a given site in the same layer. Thus, a lateral bond in layer j may adopt any of γ possible absolute orientations. However, since the total number of sites in each layer is fixed, not all of these possible orientations are available, due to competition among all the chains in that layer. For each layer, the degree of competition depends on both the flux of chains J_j and the total number of available sites f_jN_j. These steric constraints are accounted for by reducing the weight of lateral bonds in layer j by an a priori unknown factor ζ_j, $j = 1, ..., n$, where $0 \leq \zeta \leq 1$. There is no ζ_{n+1}, since there can be no lateral bonds in layer $n + 1$. A forward bond, unlike a lateral one, can have only one absolute orientation.

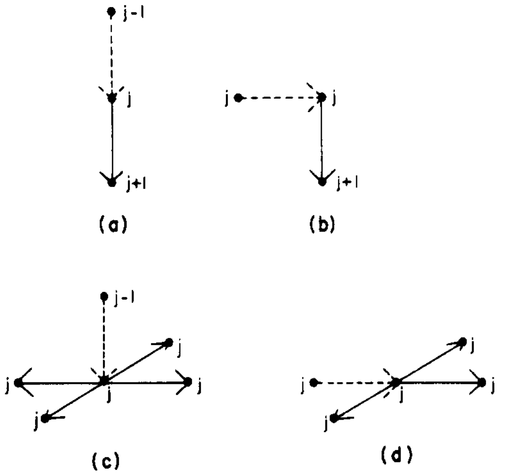

Figure 1. Four bond types a–d corresponding to cases 1–4 in the text, respectively, with $\gamma = 4$ for a cubic lattice. Segments are represented by points at the center of the occupied sites and labeled by layer index. The bond is represented by a solid arrow, and the preceding bond along the chain by a dashed arrow.

We are at liberty to choose the reference chain state consisting of n forward bonds to have weight equal to 1. With this choice, the perfect crystal, which contains all-trans chains, will have chain partition function $\Xi = 1$, and thus its chain configurational free energy will be zero. From the considerations discussed above, we may obtain the statistical weights of all possible bonds. A bond can be of four possible types, in the approximation of this model, determined by whether it is lateral (,L) or forward (,F) and whether the preceding bond is lateral (L,) or forward (F,) as follows (Figure 1):

1. (F,F): The bond is forward (j to $j + 1$) and the previous bond is forward (from layer $j - 1$ to j). There is no bending energy and no lateral reduction, so the weight is independent of layer. With the assignment of 1 for the weight of the all-trans chain, the product of the weights of n such bonds must be 1, and thus the statistical weight of this bond type also equals 1.

2. (L,F): The bond is forward (from layer j to $j + 1$) and the preceding bond is lateral (in layer j). In this case, there is a bending energy contribution giving bond statistical weight ω.

3. (F,L): The bond is lateral (in layer j) and the preceding bond is forward (from layer $j - 1$ to j). There are γ different orientations of the lateral bond, which is reduced by ζ_j to account for packing constraints in the jth layer. The weight is also reduced by ω, since the pair is bent. Its statistical weight is thus $\alpha\zeta_j$, where $\alpha = \omega\gamma$.

4. (L,L): The bond is lateral (layer j) and preceded by a lateral bond (layer j). There are $\gamma - 1$ such configurations; one is linear and $\gamma - 2$ are bent. All weights must be reduced by ζ_j since the bond is lateral. The overall statistical weight is thus $\beta\zeta_j$, where $\beta = (\gamma - 2)\omega + 1$.

This scheme is applicable to all abut the first bond, in which case the preceding ("zeroth") bond is the connection to the head group and thus of a different chemical nature and approximately forward. If the first bond is forward, it is assigned weight equal to 1. If it is lateral, the statistical weight must include a factor ζ_1 and a different bending reduction factor $\omega_h = e^{-\epsilon_h/kT}$, since the bending energy ϵ_h may in the general case differ from ϵ. Thus a lateral first bond has weight $\alpha_h\zeta_1$, where $\alpha_h = \omega_h\gamma$.

There may be some fraction $(1 - f_j)$ of the sites in layer j not occupied by chain segments. The resulting energy of contact between chain segments and the "solvent" molecules occupying those sites may differ from the segment–segment contact energy. For simplicity we only consider here the case of equal contact energies, in which approximation the bond statistical weights obtained above apply. This is most appropriate for bilayers or for monolayers at an oil (good solvent)/water interface and less suitable for monolayers at an air/water interface. For unswollen micelles, $f_j = 1$ for all layers j, and the problem does not arise.

The statistical weight of any chain configuration is specified by the sequence of forward and lateral bonds. Since the bond contributions contain only multiplicative factors, every bond sequence has a statistical weight which can be written in the form

$$W_k = g_k(\alpha_{\mathrm{h}},\alpha,\beta,\omega_{\mathrm{h}},\omega)\prod_{j=1}^{n}\zeta_j^{u_{jk}} \tag{3.1}$$

where the index k labels the bond sequence, u_{jk} is the number of lateral bonds in layer j for the kth sequence, and $g_k(\alpha_{\mathrm{h}},\alpha,\beta,\omega_{\mathrm{h}},\omega)$ is a function of the form $g_k = {\alpha_{\mathrm{h}}}^{k_1}\alpha^{k_2}\beta^{k_3}{\omega_{\mathrm{h}}}^{k_4}\omega^{k_5}$, where $k_1, ..., k_5$ are nonnegative integers, determined by the bond sequence. The sum over all sequences gives the chain partition function $\Xi = \sum_k W_k$.

The chain statistical weights can be enumerated through construction of a generating "supermatrix" **G**:

$$\mathrm{G} = \begin{bmatrix} \mathrm{Q}_1 & \mathrm{P} & 0 & 0 & & & \\ 0 & \mathrm{Q}_2 & \mathrm{P} & 0 & \cdots & \cdots & 0 \\ 0 & 0 & \mathrm{Q}_3 & \mathrm{P} & & & \\ 0 & 0 & 0 & \mathrm{Q}_4 & \ddots & & \\ & & \vdots & & & \ddots & \\ & & & & \mathrm{Q}_{n-1} & \mathrm{P} & 0 \\ & & 0 & & 0 & \mathrm{Q}_n & \mathrm{P} \\ & & & & 0 & 0 & 0 \end{bmatrix}$$

each "element" of which is a 2 × 2 matrix:

$$\mathbf{Q}_1 = \zeta_1\begin{pmatrix} 0 & \alpha_{\mathrm{h}} \\ 0 & \beta \end{pmatrix};\ \mathbf{Q}_j = \zeta_j\begin{pmatrix} 0 & \alpha \\ 0 & \beta \end{pmatrix} \qquad j = 2, 3, ..., n$$

$$\mathrm{P} = \begin{pmatrix} 1 & 0 \\ \omega & 0 \end{pmatrix};\ \mathbf{0} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

G bears close resemblance to the generating matrix used previously.[2,3] We also define the following vectors:

$$\mathbf{A}_0 = (\mathbf{a}_1, \mathbf{0}, \mathbf{0}, ..., \mathbf{0}); \qquad \mathbf{a}_1 = (1, 0), \qquad \mathbf{0} = (0, 0)$$

$$\mathbf{C}_{j\mathrm{F}} = \mathrm{col}\ (\mathbf{0}, \mathbf{0}, ..., \mathbf{0}, \mathbf{c}_{\mathrm{F}}, \mathbf{0}, \mathbf{0}, ..., \mathbf{0}); \quad \mathbf{c}_{\mathrm{F}} = (1, 0)$$

$$\mathbf{C}_{j\mathrm{L}} = \mathrm{col}\ (\mathbf{0}, \mathbf{0}, ..., \mathbf{0}, \mathbf{c}_{\mathrm{L}}, \mathbf{0}, \mathbf{0}, ..., \mathbf{0}); \quad \mathbf{c}_{\mathrm{L}} = (0, 1)$$

$$\mathbf{C}_j = \mathbf{C}_{j\mathrm{F}} + \mathbf{C}_{j\mathrm{L}}; \qquad \mathbf{B}_j = \sum_{i=1}^{j}\mathbf{C}_i$$

where $\mathbf{c}_{\mathrm{F}}$ and $\mathbf{c}_{\mathrm{L}}$ are the jth "elements" in the vectors $\mathbf{C}_{j\mathrm{F}}$ and $\mathbf{C}_{j\mathrm{L}}$, respectively.

Given a system of chains of $n + 1$ segments each, the statistical weight W_{nj} of those chains whose nth (last) bond terminates in layer j (i.e., whose n + 1st segment is in layer j) is

$$W_{nj} = \mathbf{A}_0\mathbf{G}^n\mathbf{C}_j \tag{3.2}$$

This weight can be written as the sum of two terms, $W_{nj} = W_{nj\mathrm{F}} + W_{nj\mathrm{L}}$, where $W_{nj\mathrm{F}}$ and $W_{nj\mathrm{L}}$ are the weights for those chains whose nth bond is forward or lateral, respectively; i.e.

$$W_{nj\mathrm{F}} = \mathbf{A}_0\mathbf{G}^n\mathbf{C}_{j\mathrm{F}}$$

$$W_{nj\mathrm{L}} = \mathbf{A}_0\mathbf{G}^n\mathbf{C}_{j\mathrm{L}} \tag{3.3}$$

Summing W_{nj} over the layer index j gives the chain partition function Ξ:

$$\Xi = \sum_{j=1}^{n+1} W_{nj} = \mathbf{A}_0\mathbf{G}^n\mathbf{B}_{n+1} \tag{3.4}$$

These weights, W_{nj}, represent the orientation and position of the last bond along the chain. We may generalize this to account for any arbitrary bond (i) along the chain, i.e., the statistical weight of those chains whose ith bond is lateral in layer j ($W_{ij\mathrm{L}}$), whose ith bond is forward into layer j ($W_{ij\mathrm{F}}$), or whose i + 1st segment is in layer j ($W_{ij} = W_{ij\mathrm{L}} + W_{ij\mathrm{F}}$). We define three supermatrices $\mathbf{H}_j$, $\mathbf{H}_{j\mathrm{F}}$, and $\mathbf{H}_{j\mathrm{L}}$, each having only its (j, j) "element" ($\mathbf{h}$, $\mathbf{h}_{\mathrm{F}}$, and $\mathbf{h}_{\mathrm{L}}$, respectively) nonzero, where

$$\mathrm{h}_{\mathrm{F}} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \qquad \mathrm{h}_{\mathrm{L}} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

and $\mathbf{h} = \mathbf{h}_{\mathrm{F}} + \mathbf{h}_{\mathrm{L}}$. Then the weights given above can be written as

$$W_{ij\mathrm{F}} = \mathbf{A}_0\mathbf{G}^i\mathbf{H}_{j\mathrm{F}}\mathbf{G}^{n-i}\mathbf{B}_{n+1}$$

$$W_{ij\mathrm{L}} = \mathbf{A}_0\mathbf{G}^i\mathbf{H}_{j\mathrm{L}}\mathbf{G}^{n-i}\mathbf{B}_{n+1}$$

$$W_{ij} = \mathbf{A}_0\mathbf{G}^i\mathbf{H}_j\mathbf{G}^{n-i}\mathbf{B}_{n+1} = W_{ij\mathrm{L}} + W_{ij\mathrm{F}} \tag{3.5}$$

Division of the statistical weights by the partition function gives the probability distribution of the chain configurations. Thus, by summing $W_{ij\mathrm{F}}$ or $W_{ij\mathrm{L}}$ in eq 3.5 over layer index j and dividing by Ξ, we obtain the overall probability that a bond is forward (p_i*) or lateral (q_i*).

$$p_i^* = \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^i[\sum_{j=1}^{n+1}\mathbf{H}_{j\mathrm{F}}]\mathbf{G}^{n-i}\mathbf{B}_{n+1}$$

$$q_i^* = \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^i[\sum_{j=1}^{n+1}\mathbf{H}_{j\mathrm{L}}]\mathbf{G}^{n-i}\mathbf{B}_{n+1} \tag{3.6}$$

The probability that a chain terminates in layer j is

$$\frac{T_j}{J_1} = \frac{W_{nj}}{\Xi} = \frac{\mathbf{A}_0\mathbf{G}^n\mathbf{C}_j}{\mathbf{A}_0\mathbf{G}^n\mathbf{B}_{n+1}} \tag{3.7}$$

using eq 3.2 and 3.4. Combining eq 3.7 and 2.1 gives the chain flux into layer j:

$$\frac{J_j}{J_1} = 1 - \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^n\mathbf{B}_{j-1} \tag{3.8}$$

For any sequence (labeled k) of lateral and forward bonds, the number of lateral bonds in layer j is given by the exponent u_{jk} in eq 3.1. To obtain the number of lateral bonds per chain in layer j, $\langle u_j\rangle$ and thus R_j/J_1, we take the sum over bond sequences k:

$$\langle u_j\rangle = \frac{R_j}{J_1} = \frac{\sum_k u_{jk}W_k}{\sum_k W_k} \tag{3.9}$$

(Note that the single index k labels the bond sequence; multiple indices (W_{ij}) indicate specific bond and layer statistical weights.) Using eq 3.1 and 3.4, we obtain

$$\frac{\partial \Xi}{\partial \zeta_j} = \frac{1}{\zeta_j}\sum_k (u_{jk} W_k) \qquad (3.10)$$

and thus

$$\frac{R_j}{J_1} = \frac{\partial \ln \Xi}{\partial \ln \zeta_j} = \frac{\zeta_j}{\Xi}\mathbf{A}_0\{\mathbf{G}_j'\mathbf{G}^{n-1} + \mathbf{G}\mathbf{G}_j'\mathbf{G}^{n-2} + \ldots + \mathbf{G}^{n-1}\mathbf{G}_j'\}\mathbf{B}_{n+1} \qquad (3.11)$$

where $\mathbf{G}_j' = \partial\mathbf{G}/\partial\zeta_j$. Substituting eq 3.4, 3.7, and 3.11 into eq 2.2 or 2.3, we obtain the n constraint equations, $j = 1, 2, \ldots, n$:

$$\mathbf{A}_0\left(\left[\zeta_j\{\mathbf{G}_j'\mathbf{G}^{n-1} + \ldots + \mathbf{G}^{n-1}\mathbf{G}_j'\} - \left(\frac{f_j}{\sigma_j} - 1\right)\mathbf{G}^n\right]\mathbf{B}_{n+1} - \mathbf{G}^n\mathbf{B}_{j-1}\right) = 0 \qquad (3.12)$$

For the case of cylindrical or spherical micelles, for which each layer is assumed to be completely filled by chain segments, ($f_j = 1$ for all layers j), eq 3.12 are n equations in the n unknowns, ζ_j. We can now consider those systems such as bilayers or monolayers at an oil/water interface, for which some layers may not be completely filled. For those layers $j = 1, \ldots, j_c$ in which there is lateral competition for sites, $\zeta_j < 1$, and we can assume that the solvent is completely excluded, so $f_j = 1$. In the last few layers ($j = j_c + 1, \ldots, n + 1$) where there are few chains occupying many sites, we assume $\zeta_j = 1$, and we let $0 \leqslant f_j \leqslant 1$. The layer index j_c describes the depth to which solvent penetrates within the interphase. This leaves only one unknown, either ζ_j or f_j, for each layer j, and thus we have the n equations (3.12) in n unknowns. For a given system, defined by values of (n, σ_j, γ, ϵ, ϵ_h), there is only one value of j_c for which equations (3.12) can be solved consistently with $0 \leqslant \zeta_j \leqslant 1$, $0 \leqslant f_j \leqslant 1$, for all j. This is done by using the secant method for solving simultaneous nonlinear equations. Having obtained values of ζ, we can evaluate any configurational property of the interphase, such as Ξ, T_j, R_j, J_j, W_{ij}, etc.

The order parameters may be evaluated as follows. The overall probability that a bond, beginning in layer j, independent of its position along the chain, is either forward (p_j) or lateral (q_j), is

$$p_j = J_{j+1}/(R_j + J_{j+1})$$

$$q_j = R_j/(R_j + J_{j+1}) \qquad (3.13)$$

$$j = 1, 2, \ldots, n$$

p_j measures the degree of order in layer j; it can be expressed as an order parameter S_j

$$S_j = {}^3\!/_2 p_j - {}^1\!/_2 \qquad (3.14)$$

which expresses the degree of orientational order along the interfacial normal as a function of depth within the interphase (spatial position). A different parameter, S_i^*, giving the degree of order as a function of segment position along the chain (at the ith bond) can also be defined:

$$S_i^* = {}^3\!/_2 p_i^* - {}^1\!/_2 \qquad (3.15)$$

using the expression for p_i^* from eq 3.6.

We also compute the probability that a given bond pair (i, $i + 1$) is either bent or linear, regardless of position. All of the (L,F) and (F,L) bond pairs and $(\beta-1)/\beta$ of the (L,L) pairs are bent, whereas $1/\beta$ of the (L,L) pairs and all of the (F,F) pairs are linear. It can be shown that the probabilities V_i that the bond pair (i, $i + 1$) is either (F,F), (F,L), (L,F), or (L,L) are

$$V_i(\mathrm{F,F}) = \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^i[\sum_{j=1}^{n}\mathbf{H}_{j\mathrm{F}}\mathbf{G}\mathbf{H}_{(j+1)\mathrm{F}}]\mathbf{G}^{n-i-1}\mathbf{B}_{n+1}$$

$$V_i(\mathrm{F,L}) = \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^i[\sum_{j=1}^{n}\mathbf{H}_{j\mathrm{F}}\mathbf{G}\mathbf{H}_{j\mathrm{L}}]\mathbf{G}^{n-i-1}\mathbf{B}_{n+1}$$

$$V_i(\mathrm{L,F}) = \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^i[\sum_{j=1}^{n-1}\mathbf{H}_{j\mathrm{L}}\mathbf{G}\mathbf{H}_{(j+1)\mathrm{F}}]\mathbf{G}^{n-i-1}\mathbf{B}_{n+1}$$

$$V_i(\mathrm{L,L}) = \frac{1}{\Xi}\mathbf{A}_0\mathbf{G}^i[\sum_{j=1}^{n-1}\mathbf{H}_{j\mathrm{L}}\mathbf{G}\mathbf{H}_{j\mathrm{L}}]\mathbf{G}^{n-i-1}\mathbf{B}_{n+1} \qquad (3.16)$$

Thus the probabilities for the bond pair (i, $i + 1$) are

$$V_i(\mathrm{bent}) = V_i(\mathrm{F,L}) + V_i(\mathrm{L,F}) + \left(\frac{\beta - 1}{\beta}\right)V_i(\mathrm{L,L})$$

$$V_i(\mathrm{linear}) = V_i(\mathrm{F,F}) + \frac{1}{\beta}V_i(\mathrm{L,L}) \qquad (3.17)$$

The expressions obtained herein for the configurational properties of interphases are evaluated in the following paper for a variety of systems.[6] In a subsequent work, the thermodynamic information obtained from the evaluation of the partition function and related quantities will be discussed in detail.

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Appendix. A Simple Approximate Configurational Model

It is possible to approximate the configurational partition function (eq 3.4) as an analytical function of the surface density of chains (σ).

We assume that the distribution of chain ends is sharp enough that the partition function may be approximated by the largest contribution to it (a "maximum term"), i.e., by the statistical weight of those chains terminating in layer $m + 1$, in which the greatest number of ends occurs. A consequence of this assumption is that no chain ends should occur in any layer $l \leqslant m$; thus $\zeta_l \cong \zeta \cong 1 - \sigma$, independent of layer index. Assuming $\omega = 1$, any chain bond may have one forward placement, or $a\zeta$ possible lateral placements, where a is the average lateral bond multiplicity ($\alpha \geqslant a \geqslant \beta$; for a simple cubic lattice, $4 \geqslant a \geqslant 3$); in this approximation the disposition of any bond is considered to be independent of that of the preceding bond along the chain. Since all the chains terminate in layer $m + 1$, each is constrained to have m forward and $n - m$ lateral bonds; therefore the statistical weight of each is $(a\zeta)^{n-m}(1)^m$. Summing over all possible combinations of lateral and forward bonds, subject to these constraints, the partition function, Ξ, becomes

$$\Xi = \frac{n!}{m!(n-m)!}(a\zeta)^{n-m} \qquad (\mathrm{A.1})$$

Use of Stirling's approximation for large n, $n! = (2\pi n)^{1/2}(n/e)^n$, which is accurate to a few percent even for $n = 2$, leads to

$$\Xi \simeq \left(\frac{n}{m}\right)^m\left[\frac{n}{n-m}a\zeta\right]^{n-m}(2\pi)^{-1/2} \qquad (\mathrm{A.2})$$

Assuming complete filling of the layers ($\zeta \leqslant 1$), then $m/n = \sigma$, and

$$\Xi^{1/n} = (\sigma)^{-\sigma}\frac{a^{1-\sigma}}{(2\pi)^{1/2n}} \qquad \text{(A.3)}$$

Upon taking the logarithm, we obtain the configurational free energy, F:

$$\frac{F}{nkT} \simeq \sigma \ln (\sigma) - (1 - \sigma) \ln (a) + \frac{1}{2n} \ln (2\pi) \qquad \text{(A.4)}$$

and thus, relative to the crystal ($\sigma = 1$)

$$\frac{\Delta F}{nkT} = \frac{F - F(\sigma = 1)}{nkT} = \sigma \ln (\sigma) - (1 - \sigma) \ln (a) \qquad \text{(A.5)}$$

References and Notes

(1) Dill, K. A. "Surfactants in Solution"; Mittal, K. L., Lindman, B., Eds.; Plenum Press: in press.
(2) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3115.
(3) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676.
(4) Seelig, J.; Seelig, A. *Q. Rev. Biophys.* **1980**, *13*, 19.
(5) Dill, K. A. *J. Phys. Chem.* **1982**, *86*, 1498.
(6) Cantor, R. S.; Dill, K. A. *Macromolecules*, following paper in this issue.

Statistical Thermodynamics of Short-Chain Molecule Interphases. 2. Configurational Properties of Amphiphilic Aggregates

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ABSTRACT: In the preceding paper, formal expressions for configurational properties of short-chain molecule interphases have been derived. In the present work, expressions giving positional and orientational probability distributions of chain segments and bonds are evaluated for the case of planar systems (representing monolayers at an oil/water interface or bilayers). Configurational properties (e.g., order parameter, chain segment distributions, and probabilities of chain bends) are evaluated as a function of bending energy, length, and surface density of the chains. Results of neutron diffraction experiments on widths of segment position distributions are compared to predictions of the model and are found to be in good agreement. Calculated chain-averaged properties (order parameter and bends/chain averaged over the interphase) are presented as functions of area/chain and are found to fit simple exponential functions remarkably well. For planar systems, chain stiffness is predicted to have relatively little effect on configurational properties, which are determined largely by intermolecular constraints.

In the preceding article,[1] we presented a statistical mechanical formalism which may be used to predict structural and thermodynamic properties of the hydrocarbon regions of amphiphilic chain molecule interphases such as surfactant monolayers, bilayers, and micelles. The lattice model presented therein provides a framework to account for the distribution of the chain configurations in terms, primarily, of three variables: the surface density of the chains relative to that of the crystal (σ), the number, $n + 1$, of flexible segments along the chains, and the energy ϵ, required to convert a bond pair which is collinear to that which is bent at a right angle. Calculations presented here demonstrate the effect which varying these parameters is predicted to have on structural properties such as the distribution of the chain ends, measurable through neutron scattering experiments, and on the order parameter, measurable by NMR methods. The prediction of thermal properties will be described in forthcoming work.

In this work we consider only planar aggregates: monolayers at an oil/water interface or bilayers wherein the area available to the chains is constant with depth. For representative calculations from the model, we have arbitrarily chosen a standard case, for which, in the terminology of the preceding paper,[1] the coordination number of the simple cubic lattice is $z = 6$ and chains have $n + 1 = 11$ segments, are freely flexible ($\epsilon = \epsilon_h = 0$; $\omega = \omega_h = 1$), and have approximately the surface density of dipalmitoyllecithin bilayers at their melt temperature (i.e., $\sigma = 0.64$[4]). Since for n-alkyl chains, each lattice segment represents approximately 3.6 methylene groups along the chain,[1] this standard case corresponds to chains with approximately 40 CH_2 groups. This chain length was chosen to allow reasonable resolution in graphic representations of those properties which depend on depth within the interphase (layer number) or position along the chain (segment or bond number). However, for the purpose of comparison with experimental data, calculations are also performed for systems having chains of shorter length.

1. Properties Which Depend on Distance from the Interface

Chain segments are distributed at various depths within the interphase. The depths are represented as discrete layers in the lattice model.[1] The distribution of the probability of occurrence of a given segment throughout these layers (eq 3.5, ref 1), is shown in Figure 1 for the standard case specified above. Data are presented for three representative segments: one near the head group, one in the middle, and one at the end of the chain. Segments nearer the head group along the chain are predicted to occur in layers nearer the interface and are distributed less broadly along the axis normal to the interface than those nearer the chain ends. This point is made more clearly in Figure 2, which shows a measure of the width of the distribution of each chain segment. The width, δ, is the square root of the second moment of the distribution and is given in units of lattice layers. In Figure 2 (and Figure 3, in which the complete distribution is shown for terminal segments only) three curves are given representing different chain stiffnesses: $\omega = \omega_h = 1, 0.5, 0.2$, corresponding to bending energies $\epsilon = \epsilon_h = 0, 0.69kT$, and $1.61kT$, respectively. Stiffer chains are predicted to have broader segment distributions; this effect is most pronounced near chain ends.

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