

Statistical thermodynamics of amphiphile chains in micelles

(chain conformations/curved micelles and bilayers/maximal entropy/lattice model/order parameters)

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ABSTRACT The probability distribution of amphiphile chain conformations in micelles of different geometries is derived through maximization of their packing entropy. A lattice model, first suggested by Dill and Flory, is used to represent the possible chain conformations in the micellar core. The polar heads of the chains are assumed to be anchored to the micellar surface, with the other chain segments occupying all lattice sites in the interior of the micelle. This "volume-filling" requirement, the connectivity of the chains, and the geometry of the micelle define constraints on the possible probability distributions of chain conformations. The actual distribution is derived by maximizing the chain's entropy subject to these constraints; "reversals" of the chains back towards the micellar surface are explicitly included. Results are presented for amphiphiles organized in planar bilayers and in cylindrical and spherical micelles of different sizes. It is found that, for all three geometries, the bond order parameters decrease as a function of the bond distance from the polar head, in accordance with recent experimental data. The entropy differences associated with geometrical changes are shown to be significant, suggesting thereby the need to include curvature (environmental)-dependent "tail" contributions in statistical thermodynamic treatments of micellization.

Micelles are aggregates of amphiphilic molecules composed of a hydrophilic (polar, ionic, or zwitterionic) "head" and a hydrophobic "tail" that is usually a flexible hydrocarbon chain (1, 2). In aqueous solutions the tails form the interior of the micelle, while the heads are at the hydrocarbon/water interface. The aggregates exist in a variety of sizes, shapes, and phases, depending on their constituent amphiphiles and "external" conditions like concentration, temperature, and ionic strength. Some amphiphiles, like NaDodSO₄, form spherical micelles at low concentrations (just above the cmc, the critical micelle concentration) that grow into rod-shaped micelles as the concentration increases. Further increase in concentration results in a phase transition from an isotropic solution to an ordered, hexagonal phase of long rods. Most phospholipids, on the other hand, aggregate spontaneously into large, nearly planar bilayers arranged as vesicles or lamellae.

Aggregation occurs because $\mu^\circ - \mu_1^\circ < 0$, where μ_1° is the standard chemical potential of a single (monomeric) molecule in solution, while μ° is the standard chemical potential of a molecule in a micelle (3-5). (In NaDodSO₄, for instance, $\mu^\circ - \mu_1^\circ \approx -10kT$.) The value of μ° for a given amphiphile depends on its position in the aggregate (i.e., on the local "geometry" of the micelle). A common assumption in the existing models of amphiphile self-assembly is that the hydrophobic tails forming the micellar core behave like in the corresponding liquid hydrocarbon (e.g., dodecane in the case of NaDodSO₄). According to this "liquid hydrocarbon

droplet" assumption, the statistical-thermodynamic properties of the tails are insensitive to the micellar geometry (3-5). Consequently, the geometry dependence of μ° is usually attributed exclusively to the "opposing forces" that act at the surface of the micelle (3). These are the repulsion between the hydrophilic heads and the hydrophobic effect, which tend, respectively, to maximize and minimize the average area per head group on the micellar surface. But these surface effects give rise to rather small variations in μ° for different micellar geometries ($|\Delta\mu^\circ| \approx kT$), and it is thus not *a priori* reasonable to neglect the effects of the hydrocarbon chains.

In this paper we present a statistical-thermodynamic theory for amphiphile packing in different micellar geometries. A large number of theoretical studies have dealt with the statistical thermodynamics of phospholipids in planar membrane bilayers, particularly within the context of the gel-liquid crystal phase transition (6). On the other hand, very few studies (7-13) have addressed the question of chain packing in nonplanar (e.g., spherical and cylindrical) micelles. Most pertinent to our present paper is the theory of Dill and Flory (11, 12).

In the theory of Dill and Flory, the micellar core is represented by a cubic lattice, appropriately modified for curved surfaces (see Fig. 1). Every chain conformation is regarded as a sequence of steps on the lattice, originating at the surface. To conform to the geometry of the cubic lattice, every chain segment is taken to represent ≈ 3.5 methylene groups of real alkyl chains. Differences in internal energy of different conformations are disregarded, and the only constraints on a chain conformation are due to the presence of other chains and the ("volume-filling") requirement that all lattice sites are occupied. The probabilities of the various chain conformations are generated by a stochastic matrix whose elements describe single-step probabilities on the lattice. The matrix elements are evaluated algebraically through equations representing the volume-filling condition. A key assumption that facilitates the formulation and solution of these equations is the neglect of chain "reversals," (i.e., "backward" steps towards the surface; see Fig. 1). The bond-order parameters predicted by the Dill and Flory model for planar surfaces are in rather good agreement with experimental results, but their predictions for spherical and cylindrical micelles differ qualitatively from recent reported data for these systems (7, 14, 15).

The theory presented below uses, partly for the sake of comparison, the cubic lattice of Dill and Flory. We also impose the volume-filling condition and disregard chain conformation energy. The two major differences between the two theories are: (i) our expressions for chain conformation probabilities are different and are derived by using the maximal entropy principle (the information-theory approach) (16, 17), and (ii) we allow explicitly for chain reversals. We show that incomplete optimization of the conformational entropy can lead to incorrect predictions concerning the chain statistics. In particular, a *simultaneous* maximization of the entropies

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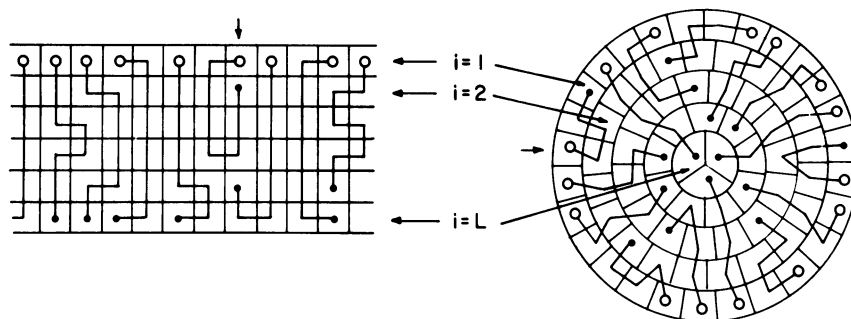


FIG. 1. A two-dimensional representation of the Dill and Flory lattice models (11, 12) describing cylindrical and spherical micelles (Right) and one-half of a planar bilayer (Left). The circles in the surface layer designate the polar heads (or the first chain segment). The arrows point out chains with reversals.

py throughout all layers of the micelle provides bond order-parameter profiles in agreement with experiment; a *sequential* scheme applied successively to one layer at a time, on the other hand, gives the results of Dill and Flory, according to which bond alignment increases from “head” to “tail” for curved aggregates.

THEORY

Lattice Representation. The lattices representing the hydrophobic cores of planar bilayers, cylindrical and spherical micelles (11, 12), and some chain conformations are shown two-dimensionally in Fig. 1. (The theory is for three dimensions.) The cores are divided into L equally thick layers (shells), and every layer i is divided into M_i cells of equal volume. The small circles in the outermost layer represent the hydrophobic heads or the first chain segments connected to the heads if the heads are large or assumed to be surrounded by water. In all geometries the surface layer is denoted as $i = 1$ and the innermost as $i = L$. The length unit in all calculations will be the layer thickness, and the volume unit will be the volume of a cell. Thus, L is the thickness or the radius of the micelle.

Experiments show that the density inside the core is similar to the liquid hydrocarbon density (2, 3) and that water penetration is negligible (15). Accordingly it is assumed here, as in refs. 11 and 12, that all lattice sites are occupied by chain segments. The volume-filling requirement implies $n \geq L$, where n is the number of segments per chain ($n - 1$ bonds); otherwise the chains could not reach the innermost layers. The number of chains, N , that can be accommodated in a micelle of volume $M = \sum M_i$ is bounded by $Nn \leq M$; the equality holds for strict space filling.

The total number of sites in (one-half of) a planar bilayer is $M = \sum M_i = M_1 L$ where M_i is the number of sites per layer. In a cylinder of radius L and length h , $M = \pi L^2 h$, and in a sphere, $M = (4/3)\pi L^3$. (It is assumed that the linear dimensions of the bilayer surface and the cylinder length are much larger than the chain length: $M_1 \gg n^2$, $h \gg n$). In order to deal with integral numbers of sites, we take $M = 4L^3$ and $3L^2 h$ for spheres and cylinders, respectively. (Actually only the ratios M_i/M_1 enter the calculations.) Thus,

$$M_i = M_1 = \text{constant} \quad \text{plane} \quad [1a]$$

$$M_i = 3h[2(L - i) + 1] \quad \text{cylinder} \quad [1b]$$

$$M_i = 4[3(L - i)^2 + 3(L - i) + 1] \quad \text{sphere} \quad [1c]$$

A central parameter in the theories of amphiphile aggregation (3–5) is the average area per head group. In the lattice model this quantity is $m_1 = M_1/N$ ($1/m_1 = \sigma_1$ is the surface

density of head groups). Using the appropriate expressions for $M (=Nn)$ and M_1 , we find

$$m_1 = \frac{n}{L} \quad \text{plane} \quad [2a]$$

$$m_1 = \left(\frac{2n}{L}\right)\left(1 - \frac{1}{2L}\right) \quad \text{cylinder} \quad [2b]$$

$$m_1 = \left(\frac{3n}{L}\right)\left(1 - \frac{1}{L} + \frac{1}{3L^2}\right) \quad \text{sphere} \quad [2c]$$

Eq. 2 shows that for the same L , the average head group areas corresponding to the planar, cylindrical, and spherical geometries relate, approximately, as 1:2:3; these ratios are fundamental in the theories of micelle formation (3–5).

The conformations of n -segment chains can be classified into ordered sequences of $n - 1$ numbers, $a = i_2, i_3, \dots, i_k, \dots, i_n$, where i_k denotes the layer in which the k th segment is located (recall $i_1 \equiv 1$). Thus, for instance, $a = 2, 3, 4, 4, 3$ describes a six-membered chain making three consecutive (“radial”) steps towards the center of the core, then a lateral step in layer 4 and finally a reversal towards the surface (see also Fig. 1). The assignment $a = i_2, \dots, i_n$ does not fully specify the conformation. For instance, $a = 1, 1, 1$ includes 36 conformations all confined to the first layer, of which four describe straight chains while the others involve one, two, or three kinks. In alkyl chains, of course, conformations with different numbers of *gauche* bonds (“kinks”) have different energies. However, within the framework of the Dill and Flory lattice that we adopt here, one cannot simply assign kink energies, mainly due to the various bond angles in the curved lattices (Fig. 1). For this reason, and in the interest of focusing on packing considerations, all conformations will be treated here as energetically degenerate. However, the extension of the theory to include energetic effects is straightforward, as outlined in the last section.

Probability Distribution. According to the maximal entropy principle[‡] the probability distribution function of chain conformations, $P(a)$, is the one that maximizes the entropy function

$$S = -k \sum_s P(a) \ln[P(a)/g(a)] \quad [3]$$

subject to the appropriate constraints on $P(a)$ (16, 17); k is the Boltzmann constant, and $g(a)$ is the degeneracy of a

[‡]The maximal entropy procedure is the basis of the information-theory approach to statistical mechanics (16, 17). This procedure yields the microcanonical distribution $P(a) = g(a)/\sum g(a)$ in the absence of constraints (besides normalization); it leads to the Boltzmann distribution $P(a) \propto g(a)\exp[-E_a/kT]$ when the average energy, $\langle E \rangle = \sum P(a)E_a$, is the only constraint, etc.

[e.g., $g(1, 1, 1) = 36$ as mentioned above]. The normalization condition

$$\sum_a P(a) = 1 \quad [4]$$

is necessarily required. In our system the *additional* (“informative”) constraints on $P(a)$ are the packing constraints implied by the requirement that all sites should be occupied by chain segments.

Let D_i denote the number of times chains reach layer i through (“downward”) transitions from layer $i - 1$. Note that some chains do not reach layer i at all, while others arrive there more than once. For the first layer we set $D_1 = N$, the number of chain heads. Similarly, let U_i be the number of times chains reach layer i through (“upward”) transitions from layer $i + 1$; these transitions involve chain reversals. Finally, we use R_i to denote the number of lateral steps within layer i . (The notation R follows the term “redundancy” used by Dill and Flory for these transitions.)

The M_i sites in layer i must be occupied by chain segments. These sites may be reached through any of the three types of transitions: hence

$$D_i + R_i + U_i = M_i, \quad i = 1, \dots, L, \quad [5]$$

with $D_1 = N$ and $U_L = 0$. The average number of lateral transitions per chain in layer i is $\langle r_i \rangle = R_i/N$. We define similarly $\langle d_i \rangle = D_i/N$ and $\langle u_i \rangle = U_i/N$. If $r_i(a)$ denotes the number of lateral transitions in layer i for the chain conformation a , then $\langle r_i \rangle = \sum P(a)r_i(a)$. Similarly, $\langle d_i \rangle = \sum P(a)d_i(a)$ and $\langle u_i \rangle = \sum P(a)u_i(a)$. [Example: for $a = 2, 3, 3, 3, 2$, we have $d_2(a) = d_3(a) = u_2(a) = 1$ and $r_3(a) = 2$. Note that $d_1(a) = 1$ and $u_L(a) = 0$ for all values of a .] The quantity, $\phi_i(a)$, defined as

$$\phi_i(a) = d_i(a) + r_i(a) + u_i(a), \quad [6]$$

is simply the number of segments in layer i for conformation a . We can now rewrite Eq. 5 in the form

$$\langle \phi_i \rangle = \sum_a P(a)\phi_i(a) = m_i, \quad i = 1, \dots, L, \quad [7]$$

where $m_i = M_i/N$. The L conditions in Eq. 7 are the constraints on $P(a)$ implied by the requirement for volume-filling. In fact only $L - 1$ of these conditions are linearly independent because, by definition, $\sum_i \phi_i(a) = \sum_i \langle \phi_i \rangle = n$, and indeed $\sum_i m_i = M/N = n$.

Entropy Maximization. Finding the distribution that maximizes S subject to Eq. 4 and the $L - 1$ packing constraints in Eq. 7 is a standard procedure (16, 17) that yields

$$P(a) = g(a) \exp \left[- \sum_{i=1}^{L-1} \lambda_i \phi_i(a) \right] / Q = g(a) \prod_{i=1}^{L-1} \alpha_i^{\phi_i(a)} / Q, \quad [8]$$

where $\alpha_i \equiv \exp(-\lambda_i)$. The λ_i s are Lagrange multipliers conjugate to the m_i s. Q is the partition function of a chain in the micelle,

$$Q = \sum_a g(a) \exp \left[- \sum_{i=1}^{L-1} \lambda_i \phi_i(a) \right] = \sum_a g(a) \prod_{i=1}^{L-1} \alpha_i^{\phi_i(a)} \quad [9]$$

The significance of $\phi_i(a)$ as the number of chain segments in layer i implies, through Eq. 8, that every such segment carries a statistical weight factor α_i ($\alpha_L \equiv 1$). Thus, for instance, if $L = 4$ and $n = 6$, the probabilities of $a = 1, 1, 1, 2, 3$ and $a' = 2, 3, 4, 4, 3$ are $[g(a)/Q]\alpha_1^4\alpha_2\alpha_3$ and $[g(a')/Q]\alpha_1\alpha_2\alpha_3^2\alpha_4^2$, respectively.

The Lagrange multipliers are determined through the implicit relations

$$m_i = - \frac{\partial \ln Q}{\partial \lambda_i} = \frac{\alpha_i}{Q} \frac{\partial Q}{\partial \alpha_i}, \quad i = 1, \dots, L - 1, \quad [10]$$

obtained by using Eqs. 7–9, or explicitly:

$$\sum_a g(a) [m_i - \phi_i(a)] \prod_{i=1}^{L-1} \alpha_i^{\phi_i(a)} = 0, \quad i = 1, \dots, L - 1. \quad [11]$$

The general form, Eq. 10, is most useful when simple closed form expressions can be derived for Q . In the present case, this requires some rather drastic approximations. Therefore, we will determine the α_i s by a numerical solution of the $L - 1$ nonlinear algebraic relation, Eqs. 11.

Given $P(a)$ one can calculate all the statistical properties of the chains. For instance, substituting Eq. 8 into Eq. 3, we find that the entropy per chain is given by

$$S = k \left[\ln Q + \sum_{i=1}^{L-1} \lambda_i m_i \right]. \quad [12]$$

More detailed properties reflecting the distribution of chain conformations can also be calculated. For instance, the average number of lateral steps, per chain, in layer i , is $\langle r_i \rangle$. Or, the (“radial”) distribution of chain ends—terminations—among the different layers is easily shown to be given by

$$t_i = \langle d_i \rangle + \langle u_i \rangle - (\langle d_{i+1} \rangle + \langle u_{i-1} \rangle), \quad [13]$$

where it should be noted that $\langle d_1 \rangle \equiv 1$, $\langle d_{L+1} \rangle = \langle u_L \rangle \equiv 0$, and $\sum t_i = 1$.

Other quantities of interest are the bond-order parameters, $S_k = (3/2)(\cos^2 \theta_k) - 1/2$, where θ_k is the angle between the k th bond (connecting segments k and $k + 1$) of the chain and the normal to the micellar surface. On the planar cubic lattice $\theta_k = 0, \pi/2$, or π , corresponding to d, r , and u -type bonds, respectively. (The normal to the surface points into the interior of the micelle.) When all bond directions are possible and equiprobable, $S = 0$, indicating an isotropic (angular) distribution. Note, however, that the first bond of a chain cannot point “upwards,” implying $S_1 \neq 0$, even if all other directions were equally probable. Using $P_k(\parallel)$ and $P_k(\perp) = 1 - P_k(\parallel)$ to denote the probabilities that the k th bond will be parallel and perpendicular to the micellar surface, respectively, we obtain

$$S_k = 1 - (3/2)P_k(\parallel). \quad [14]$$

This equation will be used for all geometries; its applicability for the cylindrical and spherical geometries is discussed in the next section.

RESULTS

In this section we present a set of results for the planar, cylindrical, and spherical geometries for several values of the micellar radius L (corresponding to different head group areas m_1). All the results are for a single chain length, $n = 5$, which represents an alkyl chain of about 15 carbon atoms, according to the construction of the lattice model. First, a few remarks should be made on the calculation of coordination numbers and conformation degeneracies.

Let $Z_{i,i}$ denote the lateral coordination number in layer i (i.e., the number of nearest neighbor sites in the same layer). Similarly, $Z_{i,i-1}$ and $Z_{i,i+1}$ are the number of nearest neighbors in layers $i - 1$ and $i + 1$, respectively. In the regular cubic lattice $Z_{i,i} = 4$, $Z_{i,i+1} = Z_{i,i-1} = 1$. ($Z_{L,L+1} = Z_{1,0} = 0$

for all geometries.) We assume $Z_{i,i} = 4$ also for the curved lattices representing cylindrical and spherical micelles (except that for spheres $Z_{L,L} = 3$ because $M_L = 4$). Clearly, however, $Z_{i,i+1}$ must be modified, and the obvious choice is $Z_{i,i+1} = M_{i+1}/M_i (\leq 1)$ and $Z_{i,i-1} = M_{i-1}/M_i (\geq 1)$. This definition includes the planar lattice as a special case (Z values = 1). It also ensures that the angular distribution of the vectors connecting a given site with all of its nearest neighbors is isotropic (except for sites in the surface layer).

The degeneracy of $a = i_2, \dots, i_n$ can be expressed as

$$g(a) = g(i_2|1) g(i_3|i_2, i_1) \dots g(i_n|i_{n-1}, \dots, 1), \quad [15]$$

where $g(i_k|i_{k-1}, \dots, 1)$ is the number of sites available to the k th segment in layer i_k , given that the previous $k-1$ segments reside in layers $1, \dots, i_{k-1}$. For long chains, approximate calculations of these factors are inevitable. For the short chains considered here, $g(a)$ can be exactly calculated (taking into account "self-avoided walks"). As an illustration consider the following conformations of a four-membered chain: $a_1 = 1, 1, 2, 2$; $a_2 = 1, 2, 3$; and $a_3 = 2, 2, 1$. For a_1 we have $g(a_1) = g(1|1)g(1|1,1)g(2|1,1,1) = Z_{11}(Z_{11}-1)Z_{12} = 4 \times 3 \times Z_{12}$, where the second factor ensures that the third segment does not overlap the first. Similarly, $g(a_2) = Z_{11}Z_{12}Z_{23}$ and $g(a_3) = Z_{12}Z_{22}Z_{21} = Z_{22}(Z_{12} = 1/Z_{21})$.

The probability that a given site in layer i will be occupied via a lateral step is $P_i(r) = \langle r_i \rangle / m_i$. Similarly $P_i(d) = \langle d_i \rangle / m_i$ and $P_i(u) = \langle u_i \rangle / m_i$ are the corresponding probabilities for site occupation via $i-1 \rightarrow i$ and $i+1 \rightarrow i$ steps, respectively. Note, $P_i(d) = \langle d_i \rangle / m_i = 1/m_1$ is the surface density of head groups. Fig. 2 shows $P_i(x)$, $x = d, r, u$ for the three micellar geometries. As noted already in ref. 11, in bilayers the probability of lateral steps is small near the surface and increases towards the midplane due to chain terminations (see Fig. 2). An opposite behavior is observed in the curved geometries, primarily because of the decrease in m_i near the micelle center (Fig. 2, dashed lines). The probabilities of reversals increase with curvature, as expected, but their absolute values are small. The effects of reversals are somewhat more pronounced in other properties, like bond-order parameters, as discussed below.

A "layer-order parameter," $\eta_i = (3\cos^2\theta_i - 1)/2$, may be defined by associating the angles $\theta_i = 0, \pi/2$, and π with d_i, r_i , and u_i bonds. This yields $\eta_i = 1 - (3/2)P_i(r) = (3/2)[P_i(r) + P_i(d)] - 1/2$; from Fig. 2 we see that this type of ordering increases towards the center of spherical and cylindrical micelles and decreases towards the midplane in bilayers.

Fig. 3 shows t_i , the (radial) distribution of chain ends. Also shown, for comparison, are the corresponding distributions of free chains (i.e., chains whose conformations are not disturbed by other chains). For these chains $P(a)$ is the microcanonical distribution, $P(a) = g(a)/\sum g(a)$ (corresponding to all $\lambda_i = 0$ in Eq. 8). The effects of packing constraints are

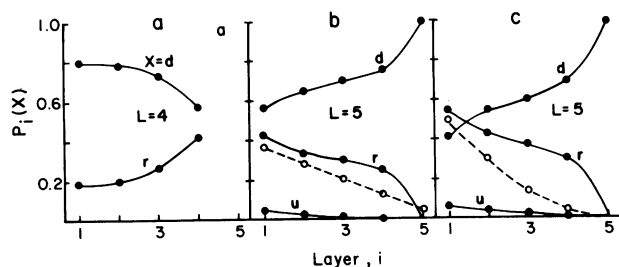


FIG. 2. Fraction of sites in layer i occupied via lateral [$P_i(r) = \langle r_i \rangle / m_i$], downward [$P_i(d)$], and upward [$P_i(u)$] transitions for bilayer (a), cylindrical (b), and spherical (c) geometries. The dashed lines in b and c show the m_i/n . In all cases $n = 5$ and $m_i = m_1 M_i/M_1$. Note the small probability of reversals.

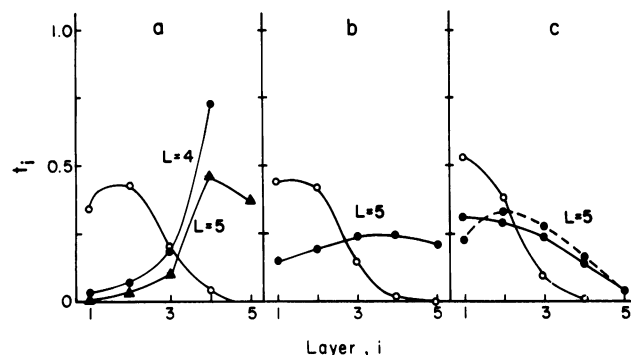


FIG. 3. Probability distribution of chain terminations among the layers in planar (a), cylindrical (b), and spherical (c) micelles. In all cases, $n = 5$ and all sites are strictly occupied (\bullet) (see Fig. 2) except for the case $L = 5$ in a (Δ) where $m_i = m_1 = 1.15$ for $i \leq 4$ and $m_5 = 0.4$. The dashed line in c is obtained when chain reversals are neglected. \circ , t_i of free chains.

most pronounced in bilayers and least pronounced in spheres.

Bond order parameters calculated with the aid of Eq. 14 are shown in Fig. 4. For the planar and cylindrical geometries, this equation is consistent with the requirement that, when all lattice directions are equiprobable, $S = 0$. For spheres this is an approximation. [In a random distribution of bond directions, $P(\parallel) = Z_{ii}/Z = 4/(4 + Z_{i,i+1} + Z_{i,i-1})$. For the planar and cylindrical lattices, $Z_{i,i+1} + Z_{i,i-1} = 2$, implying $P(\parallel) = 2/3$, hence $S = 0$. For spheres this yields a $P(\parallel)$ which is a few percent larger.] The figure shows that for the same L , the degree of chain ordering is highest in bilayers and lowest in spherical micelles and that it decreases with L . Also, for all L and all geometries, the bond-order parameters decrease from the polar head towards the end of the chain. These findings are in accord with experimental results (7, 14, 15) and the calculations of Gruen and de Lacey (13). On the other hand, the Dill and Flory model (11, 12) predicts that S_k increases with k for spheres and cylinders.

Fig. 5 shows chain entropies as a function of the micellar width. Also shown are the entropies of free chains, which can be regarded as a special case of Eq. 12 with $\lambda_i = 0$ and $Q = \sum g(a) \equiv \Omega$ (i.e., $S = k \ln \Omega$). When chain reversals are neglected, the entropies are lower by up to $\approx 10\%$. The main conclusion of this calculation is that, for a given L , the entropies corresponding to the different micellar geometries are substantially different, particularly so for $L \leq n$, which is

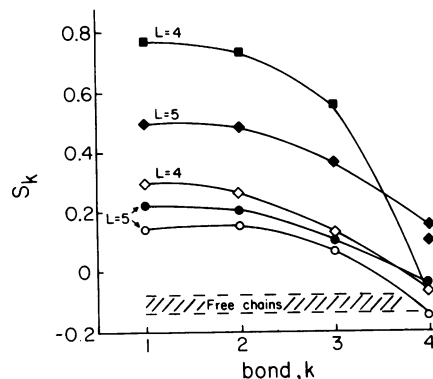


FIG. 4. Bond-order parameters as a function of the bond distance from the head group: bilayers (\blacksquare), cylinders (\diamond , \blacklozenge), and spheres (\circ). Chains without reversals. The cross-hatched region bounds the values of S_k for free chains in all geometries (for $L = 5$). The negative values reflect the effect of the micellar boundary that excludes the upward direction of the first bond.

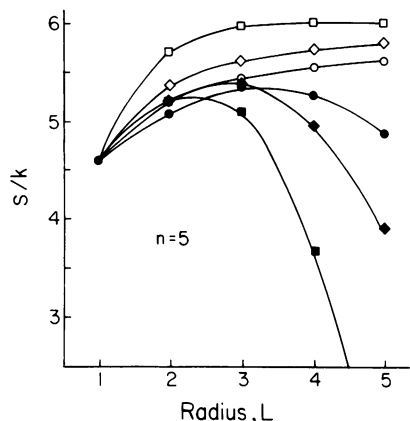


FIG. 5. Chain entropy as a function of micellar radius, for planar (\square , \blacksquare), cylindrical (\diamond , \blacklozenge) and spherical (\circ , \bullet) micelles. Open symbols are the entropies of free chains, $S = k\ln\Sigma g(a)$ (see text).

assumed to be the micellar radius in theories of amphiphile aggregation (3–5).

DISCUSSION AND SUMMARY

The generalized canonical distribution, Eq. 8, corresponds to the thermodynamic state of minimal free energy per chain, subject of course to the assumptions of the model. In our theory, as in the theory of Dill and Flory, the system is regarded as “athermal” because energetic effects are neglected; consequently, the Helmholtz free energy is $-TS$. But our formulation can easily be extended to include conformational energies. To this end the conformations should be classified not only according to their layer sequence, $a = i_2, \dots, i_n$, but also according to their energy E (which is simply proportional to the number of *gauche* bonds). In this case, instead of the probability distribution, Eq. 8, we would have

$$P(b) = g(b) \exp \left[-E(b)/kT - \sum_{i=1}^{L-1} \lambda_i \phi_i(b) \right] / Q, \quad [16]$$

where $g(b)$ is the number of conformations characterized by $b = i_2, \dots, i_n$; $E(b)$. Note that Eq. 16 becomes formally identical to Eq. 15 provided that $g(a) = \Sigma' g(b) \exp(-E(b)/kT)$, where the sum is over all conformations b with the same layer sequence $a = i_2, \dots, i_n$. In other words, energetic effects can be incorporated into the theory without changing the equation determining the λ_i s, Eq. 12, provided the degeneracy factors are properly modified.

Eq. 16 is very similar to the probability distribution used by Gruen and de Lacey (13). From Eq. 12 we see that $k\lambda_i = \partial S / \partial m_i = -(1/T) \partial A / \partial m_i$. But m_i , the number of sites (per chain) in layer i is simply $\langle a_i \rangle$ —the average area per chain in layer i (in lattice units). Thus, $kT\lambda_i = \pi_i = -\partial A / \partial m_i$ is the lateral pressure in this layer. Indeed, in the Gruen and de Lacey model, terms of the type $\pi_i a_i / kT$ appear where the $\lambda_i \phi_i$ terms appear in Eqs. 15 and 16. (To be precise, the analogy is between λ_i and $\pi_i - \pi_L$ because $\lambda_L = 0$.) The major advantage of using the lattice model is the derivation of the algebraic equation, Eq. 11, from which the set of $\alpha_i = \exp(-\lambda_i)$ are evaluated much more easily than by the iterative Monte Carlo approach (13).

One approximation that simplifies considerably Eqs. 8–11 is the neglect of the reversals. This excludes many conformations and implies $\mu_i = 0$ in Eq. 6. In the previous section, we have seen that, at least for short chains, this is a reasonable approximation. In the theory of Dill and Flory, reversals are disregarded entirely. Yet, the bond-order parameters, S_k , predicted by their theory for chains in spherical and cylindrical micelles increase with k rather than decrease as

indicated by our calculations (as well as those of Gruen and de Lacey and experimental data). Thus, the difference between the theory of Dill and Flory and ours must be attributed to the different $P(a)$ s. Indeed, although we used the Dill and Flory lattice and equivalent packing constraints, the derivation of $P(a)$ is similar only if our entropy maximization is carried out differently. Briefly, S may be expressed as a sum of layer entropies, $S = \Sigma S_i$. By maximizing S_1 (subject to $\langle d_1 \rangle + \langle r_1 \rangle = 1 + \langle r_1 \rangle = m_1$), one finds $P_1(r_1)$, the probability of r_1 lateral steps in layer 1. Using this result in S_2 and maximizing S_2 (subject to $\langle r_2 \rangle = m_2 - \langle d_2 \rangle = m_2 - 1 - t_1$) yields $P_2(r_2)$, etc. As noted, however, this *sequential* entropy maximization gives results that differ considerably from those obtained by the *simultaneous* procedure leading to Eq. 11. We conclude accordingly that the increasing order-parameter profile predicted by Dill and Flory is due not to neglect of reversals or chain energies but rather to an incomplete maximization of the packing entropy.

In the framework of the athermal model described in this paper, free-energy changes corresponding to different micellar geometries are given by $\Delta A = -T\Delta S = N\Delta\mu_i^\circ$. Here μ_i° represents the chain (tail) contribution to μ° —the standard chemical potential per amphiphile. In the previous section, for instance, we have seen that, for the chains packed in micelles of the same thickness L but of different shapes, $|\Delta S| \sim k$; hence $|\Delta\mu_i^\circ| \sim kT$. (Similar conclusions were arrived at in ref. 13.) This is of the same order of magnitude as the empirical $\Delta\mu^\circ$, which includes both tail and head contributions. Thus, the assumption commonly made in amphiphile aggregation theories (3–5) that μ_i° (and L) is the same for different micellar shapes is highly questionable. Yet, more careful analyses are required before quantitative conclusions can be drawn.

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