

Chain Packing and the Compressional Elasticity of Surfactant Films

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1. INTRODUCTION

We summarize briefly our work on the effect of excluded volume on the conformational statistics and thermodynamics of semi-flexible chain packing in surfactant layers. Our aim is to establish the important extent to which "tails" compete with "heads" in determining the equilibrium state and compressional properties of mono- and bi-layer amphiphilic films. Using the mean-field theory developed originally for micellar systems [1] we present first some typical results for chain free energies in bilayers as a function of area per molecule. Ensuing estimates for the optimum area per molecule and compression (stretching) force constant are compared with those arising from head-group interactions alone. Then, in order to treat the dependence of these properties on chain contour length (e.g. alkyl carbon number) we discuss a diffusion-equation approach to conformational statistics which takes into account the constraint of uniform segment density. This description provides a natural justification for a scaling of layer thickness which leads to approximately universal compressional behavior. It also allows new insights into the way in which lateral pressure profiles serve to "squeeze" "free" chains into uniformly packed ones. We then treat the important case of mixed-chain systems and derive the corresponding surface-volume relations and their consequences for relative stabilities of planar and curved layers. Finally, we present a simple but accurate model for calculating bending elastic properties of surfactant films in terms of their compressional force constants. In particular we account for how decreasing chain length (carbon number) can lower the curvature energy from 10's of kT to kT.

2. HEADS VS. TAILS: CHAIN ELASTICITY EFFECTS

In the prevailing theories [2] of micellar self-assembly, the surfactant chains are assumed to be "passive." That is, the free energy per molecule, $g(a)$, is taken to depend on head-group area, a , only through the surface contributions. Modeling these latter terms via the notion of opposing forces [3], for example, one writes $g(a) = \gamma a + \frac{C}{a} + g_c$ where γ is an interfacial tension, C characterizes the (steric, electrostatic, or hydration) repulsion between head groups, and g_c is the chain contribution (assumed to be independent of a). The optimum area per molecule is then given by $a = (C/\gamma)^{1/2} = a_0$. At the same time, from surface/volume constraints one has the requirement that $a = kv/\ell$ where v is the chain volume, ℓ the micellar dimension, and $k=1,2,3$ for bilayers, cylinders, and spheres, respectively. It follows that the preferred aggregate geometry will be the highest-curvature (hence smallest size) one which allows $a_0 = kv/\ell$ with $\ell \leq \ell_{\max}$. Here ℓ_{\max} is the maximum micellar dimension, corresponding to the fully stretched "all-trans" chain length.

Using the mean-field theory developed with Szleifer and described elsewhere [1,4], however, it is possible to calculate directly how g_c depends on area per molecule. This simple formulation has been shown to be highly accurate in determining the details of conformational statistics (e.g. bond order-parameter profiles and segment distributions) and thermodynamics, as compared with full

molecular dynamics simulations. In the present context, for say a 12-carbon tail, we find that $g_C(a)$ has a minimum at $a^*=45\text{\AA}^2$ and that stretching the (uniform monomer density) packed chains down to $a=25\text{\AA}^2$ costs as much as $3kT$. Note that, for reasonable values of γ and a_0 , the corresponding change in $g_C(a)$ is only half as large. For this reason, the optimum value of a is no longer $a_0=(C/\gamma)^{1/2}$ but rather something significantly bigger: $a_0 < a_{opt} < a^*$. That is, the a -dependence of g_C can not be neglected--the chains are not "passive" and do not simply "go along for the ride" as the area per molecule is optimized.

A further result of the chain contributions is to enhance dramatically the compressional elasticity of a surfactant layer. Writing $g_C(a) \rightarrow g_C(l) = \kappa(l-l^*)^2$, for example (using $a \rightarrow \gamma$), one can inquire about the contour length (carbon number, n) dependence of both κ and l^* . Suppose g_C depended on the micellar dimension l (bilayer half-thickness) only through the scaled variable $\tilde{l} = l/bn^{1/2}$ where b is the monomer size. Then one would have $l^* \sim n^{1/2}$ and $\kappa \sim n^{-1}$. This indeed turns out to be approximately the case, as discussed in the sections which follow.

3. ARBITRARY CHAIN-LENGTH APPROACH

In recent work with Viovy [5] we have generalized our earlier mean-field theory to the case of arbitrarily large n . This requires that one give up a description which explicitly enumerates chain conformations (whose number increases as 3^n in the usual rotational isomer state model), switching instead to a random walk language. Indeed it is possible to show that the monomer propagator [6] obeys a quasi-one-dimensional diffusion equation in an external field. Unlike in the classic excluded volume problem, however, the external field is not the local segment concentration (to be determined self-consistently in terms of the propagator) but rather the lateral pressure profile which arises from the constraint of uniform monomer density. Again one is able to solve directly for either the chain conformational statistics or thermodynamics with no adjustable parameters.

Plots of g_C vs. l for increasing n show that both the horizontal and vertical positions of the minima can be accounted for in terms of "free" chain properties. (Here and henceforth we speak primarily of bilayer systems.) A "free" chain is one which does not "feel" its neighbors but rather only the constraint due to the impenetrable interfaces. Thus g_C vs. l for a free chain is monotonic decreasing: at small l ($< bn^{1/2}$) the free energy is high because of all the conformations denied by the presence of the interfaces; for larger l , g_C^{free} levels off to a constant. For each n this asymptote turns out to correspond closely with the minimum in g_C vs. l for the packed chain. Indeed, both the horizontal ($l^* \sim n^{1/2}$) and vertical ($g^* \sim \ln n$) positions of the minima in $g_C^{packed}(l)$ are well described by the onsets of the free-chain asymptotes.

The lateral pressure profiles, $\pi(Z)$, which emerge from the diffusion equation approach also serve to point up the crucial role played by free chains in understanding the statistics and thermodynamics of uniformly-packed ones. First we find again (as in our earlier treatments [1,4]) that $\pi(Z)$ is smallest for $l = l^*$, consistent with the fact that the lateral pressures tell us the extent to which "free" chains must be "squeezed" in order to transform them into uniformly packed ones. (Recall that l^* is the optimum bilayer half-thickness, the value which minimizes $g_C(l)$ and allows the packed chains to most closely resemble "free" ones.) Furthermore, the "shape" of $\pi(Z)$ --the dependence of lateral pressure on distance Z from the interfaces--follows closely that of $p^{free}(Z)$, the monomer density of a free chain with the same l : one must squeeze hardest in high-concentration regions in order to achieve uniform segment density.

Our original mean-field theory has also been extended to the important case of mixed- (e.g. short- and long-) chain systems [7]. These are of great interest for understanding microemulsions which are stabilized by addition of short-chain alcohols, say, and biological membranes which have incorporated cholesterol and other "solutes." Before proceeding to a discussion of our results for mixed-chain conformational statistics and thermodynamics, we explain first new features of the surface/volume geometric constraints for these systems.

Recall that, for pure (i.e. single component) micelles, the relation $a = kv/l$ follows trivially from requiring that the aggregate's surface is covered by heads (area per molecule a) and its interior volume filled by chains (v). For mixture of short (s) and long (l) chains with mole fraction X_s , this becomes $a = (k/l)(X_s v_s + (1-X_s)v_l)$ with a the average area per molecule. Now, however, the maximum micellar dimension l_{max} is no longer simply $l_{all-trans,l}$, the fully stretched length of the longest chain. Rather, for a given composition X_s , one must guarantee that l is small enough that there is not too much "interior" volume (i.e. space inaccessible to the shorter chain) for the longer chain to fill at constant segment density. Defining this latter bound by $l_{>}$, we have that l_{max} is equal to the smaller of $l_{all-trans,l}$ and $l_{>}$. Since $l_{>}$ is dependent on X_s (as well as on the different contour lengths), it follows that the minimum value of a ($a = a_{min} \leftrightarrow l = l_{max}$) is a function of composition. That is, instead of $a_{min}^{pure} = kv/l_{all-trans,l}$ as in the pure surfactant case, one has $a_{min} = f^{(k)}(X_s) a_{min}^{pure}$ where $f^{(k)}(X_s) \leq 1$. Note that $a_{min}^{pure} = kv/l_{all-trans,l}$ is independent of n since both chain volume (v) and fully stretched length ($l_{all-trans,l}$) are linear functions of n . Thus, in the limits $X_s \rightarrow 0$ or 1 , $a_{min} \rightarrow a_{min}^{pure} = (22 \text{ \AA}^2)k$, while for intermediate values it is smaller: for spheres ($k=3$), for example, $f^{(3)}(X_s)$ is as small as $\frac{2}{3}$ in the case of $v_l/v_s = 2$.

The fact that mixed spherical micelles can have average areas per molecule which are significantly smaller than in the pure case means that addition of short chains should preferentially stabilize higher curvature. Indeed we find for the $v_l/v_s = 2$ system that the average free energy per chain becomes lower for a sphere (vs. a bilayer) when the molefraction is sufficiently different from 0 or 1. That is, for the pure "long" or "short" chain systems the lamellae are stable, whereas spherical curvature becomes preferable upon the addition of sufficient amounts of the other chain. This phenomenon accounts for the break up of lamellar phases observed by Charvolin and Mely [8] as they move from $X_s=0$ or 1 in aqueous solutions of mixed fatty acids.

We have also used our mean field theory to treat explicitly the conformational statistics in mixed-chain systems. One simply needs to generalize the constraints of constant segment density to include molefraction-weighted contributions from both chains. Minimizing the average free-energy per chain with respect to the probability distribution function for each chain, subject to uniform density, leads to a lateral pressure profile (dependent on area and composition) which again determines the conformational statistics. We find in general that the longer chains occupy smaller areas per molecule at the interface: they are stretched there in order to "save themselves" for filling up the "interiors." Again these predictions are consistent with the order-parameter measurements reported by Charvolin and Mely [9] for mixed fatty acids.

5. COMPRESSION MODEL FOR BENDING ELASTICITY

In this final section we outline briefly work with Roux [10] relating curvature elasticity to the compressional properties of a planar film. Consider the bending at constant area per molecule, of a planar layer of thickness ℓ . For a spherical deformation, for example, $R = \infty \rightarrow R < \infty$ implies $\ell \rightarrow \ell'(a, R)$ in order to maintain the constant head group area a . The bent layer has a higher free energy than the original planar one (assuming, say, a symmetric bilayer) because the constituent molecules have been both stretched and splayed. In the preceding paper [4] we described how this free energy change--and the corresponding bending constants--can be calculated from a full mean-field treatment of chain packing. Here we consider instead an approximation to this approach in which splay contributions are explicitly neglected. That is, we take into account only the free energy change associated with the "compression" $\ell \rightarrow \ell'(R)$: $\delta g_{c, \text{bending}} = \delta g_{c, \text{compression}} = \kappa(\ell'(R) - \ell)^2$. Here κ and ℓ^* are the force constant and optimum thickness for the planar layer. Expanding $\ell'(R)$ in powers of $\frac{1}{R}$ then gives the following result for the bending constant: $k = \kappa \nu^4 / a^5$. Note the $\frac{1}{R}$ strong (and inverse) dependence on area per molecule. Also, from our planar-layer mean-field calculations we find $\kappa \sim n^{-1}$ (to be compared with n^{-1} from scaling), implying $k \sim n^3$ since $\nu \sim n$.

Taking into account the slow variation of a ($= a_{\text{bilayer}}^*$) with n gives rise to a somewhat weaker dependence of k on n ($k \sim n^{2.5}$), in agreement with preliminary experimental data by Roux et al. [11]. Furthermore, we obtain absolute magnitudes for 15-carbon chains (10's of kT) which suggest that indeed the measured bending energies are due predominantly to the chains rather than to the head groups. When the area per molecule is allowed to respond to the bending, i.e. when a is optimized for each R , the values of k estimated from the compression model are more than twice as small, consistent with the full mean field calculations [4]. The variation of k with carbon number remains about the same ($\sim n^{2.5}$), accounting for bending energies as small as kT for $n = 4$ or 5.

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