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Bending Moduli and Spontaneous Curvature of the Monolayer in a Surfactant Bilayer

R. A. Kik, J. M. Kleijn, and F. A. M. Leermakers*

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

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We developed a method to evaluate the mechanical properties of the monolayers in symmetric surfactant bilayers using self-consistent field theory. A specific boundary condition is used to impose the same curvature onto the two opposing monolayers at the surfactant chemical potential equal to that of the corresponding homogeneously curved bilayer. Typically, the spontaneous monolayer curvature $J_0^{\rm m} \neq 0$ and its value depend on the surfactant architecture. This is of importance for the thermodynamics and topology of lamellar surfactant phases. Furthermore, it may be relevant in processes involving biological membranes, for example, the fusion and budding of vesicles and the incorporation of proteins in lipid bilayers.

Introduction

Surfactants of appropriate structure self-assemble spontaneously in aqueous media to form lamellar structures. The surfactant tails of two opposing monolayers form the core of the bilayer and the surfactant heads form the coronas such that the core is shielded from the water phase. The biological bilayer composed of lipids is one of the most important structural elements in living cells. As a consequence, it receives attention from many areas of science.

Unconstrained flat bilayers remain tensionless.¹ Helfrich² realized that the physics of tensionless bilayers is controlled by their bending moduli. Introducing the mean $J = 1/R_1 + 1/R_2$ and the Gaussian $K = 1/R_1R_2$ curvature, where R_1 and R_2 are two principle radii of curvature, the surface tension for a weakly curved bilayer is given by

$$\gamma(J, K) = \gamma(0, 0) + \frac{1}{2}k_{c}(J - J_{0})^{2} + \bar{k}K$$
 (1)

Symmetry considerations indicate that the flat bilayer is the lowest in free energy and the spontaneous curvature is $J_0 = 0$. As a result, eq 1 may be simplified for symmetric bilayers. The mean bending modulus (k_c) determines the shape fluctuations, whereas the Gaussian bending modulus (k) is important for the topological stability: closed bilayers (vesicles) are stable when $-2k_c \le k \le 0$. Only the mean bending modulus is (reasonably straightforwardly) experimentally accessible.³ Many mesoscopic descriptions of amphiphilic systems take the bending moduli as input parameters.4 In addition, one is often interested in the mechanical properties of the individual monolayers. Typically, it is assumed that one can apply eq 1 also to the monolayer. As the monolayer is asymmetric, we should anticipate that (in general) there is a finite value for the preferred curvature, $J_0^{\rm m} \neq$ 0, where the superscript index m refers to the monolayer. One may argue that when $J_0^{\rm m}$ deviates much from zero, one has a frustrated bilayer, with subsequent consequences on, for example, the incorporation of proteins into such bilayers.⁴ At present, we do not know a method to directly determine $J_0^{\rm m}$. However, we believe that the value of $J_0^{\rm m}$ can be deduced from experimental results, for example, by fitting these to a detailed model in which the spontaneous curvature has an important contribution. Such procedures will always be delicate, and therefore, it is of extreme importance that there are reliable predictions for this quantity.

To relate the molecular structure of the amphiphiles to the mechanical properties of the resulting monolayer and/or bilayer is the realm of molecular modeling. There are relatively few routes known in the literature for evaluating the mechanical properties of symmetric bilayers. There are predictions for the mechanical properties of densely packed hydrocarbon-like tails end-grafting to a (curved) surface by analyzing the conformational entropy of homogeneously packed cores as a function of imposed curvature.^{5,6} In this approach, headgroups were not included and the strong repulsive interactions with the solvent were omitted. These authors discuss both monolayer and bilayer systems. However, it is clear from the details of their method that the monolayer is not the monolayer in the bilayer configuration. Consequently, they do not find that the mechanical properties of the monolayer could be related to those of the bilayer. This also implies that the spontaneous curvature of the monolayer (next to some oil) may not necessarily be related to that of the monolayer in the bilayer configuration.

In a more complete model, one should account not only for the entropy of densely grafted chains but also for the energetic interactions that drive the self-assembly (hydrophobic effect) and stop the aggregation of the surfactants (headgroup repulsion). Using a molecular realistic self-consistent field (SCF) approach, one can realistically model surfactant self-assembly in systems wherein these aspects are incorporated and where only the curvature of the bilayer as a whole is imposed. Again, it is possible to obtain the partition function with high precision. As a result, the bending moduli of symmetric bilayers are evaluated systematically and accurately. One can identify two major problems that prevented the application to evaluate the

mechanical properties of the constituting monolayers. The first problem is how to embed the apolar side of the monolayer. As argued above, it is not realistic to put the tails next to a vacuum. One may suggest to use an appropriate alkane phase. However, the interdigitation of the alkanes into the monolayer strongly depends on their molecular weight, which renders the mechanical properties of the monolayer to be an undesired function of this choice (explaining the result of Szleifer et al., 6 where the bending modulus of the monolayers was not half that of the bilayer). The second problem is to know the appropriate number of surfactants per unit area corresponding to tensionless layers. This number may depend on the imposed curvature. Small errors in this quantity will imply some stretching or compression of the monolayer, leading to large errors in the predictions. We will suggest solutions for both problems. First, we will go into some more detail about how the mechanical properties of the bilayer can be determined using our SCF theory.

Self-Consistent Field Theory

Oversteegen⁸ showed that one can accurately determine the bending moduli from the fitting of the surface tension $(\gamma(J,K))$ by eq 1 or, alternatively, from the curvature dependence of the lateral pressure profile $(\omega(r))$. It is convenient to introduce the jth moment over the lateral pressure profile $(\omega^0(x))$ of the flat bilayer: $\mathscr{L}_j^0 = \int x^j \omega^0(x) \, \mathrm{d}x$, where x is the coordinate parallel to the membrane normal and x=0 is at the symmetry plane in the bilayer. Unconstrained bilayers have no tension, and thus, $\gamma = \mathscr{L}_0^0 = 0$. The bending moduli are found from

$$-k_{c}J_{0} = \mathcal{L}_{1}^{0} + \left(\frac{\partial \mathcal{L}_{0}}{\partial J}\right)_{T,K}^{0} \tag{2}$$

$$k_{\rm c} = 2 \left(\frac{\partial \mathcal{L}_1}{\partial J} \right)_{TK}^0 + \left(\frac{\partial^2 \mathcal{L}_0}{\partial J^2} \right)_{TK}^0 \tag{3}$$

$$\bar{k} = \mathcal{L}_2^0 + \left(\frac{\partial \mathcal{L}_0}{\partial K}\right)_{TL}^0 \tag{4}$$

These equations show that the mechanical properties cannot be derived from the flat bilayer alone. The fundamental reason for this is that in general the grand potential density $(\omega(r))$ cannot be defined uniquely. One has to make a choice of how to do the bookkeeping for the nonlocal interactions. For example, in the literature, one often finds $\bar{k} = \mathcal{D}_2^0$. The extra term in eq 4 corrects for the ambiguity in how the bookkeeping is implemented. When the binary interactions are split evenly over the coordinates that are involved, one can write the SCF result for the grand potential density as

$$\omega(r) = k_{\rm B}T \sum_{i} \frac{\varphi_{i}(r) - \varphi_{i}^{\rm b}}{N_{i}} - \sum_{\rm A} \varphi_{\rm A}(r) u_{\rm A}(r) - \frac{k_{\rm B}T}{2} \sum_{\rm A} \sum_{\rm B} \chi_{\rm AB}(\varphi_{\rm A}(r)(\langle \varphi_{\rm B}(r) \rangle - \varphi_{\rm B}^{\rm b}) - \varphi_{\rm A}^{\rm b}(\varphi_{\rm B}(r) - \varphi_{\rm B}^{\rm b}))$$
 (5)

Here, $k_{\rm B}T$ is the thermal energy, i is the index to the molecule types, A and B are indices running over all segment types, φ is the volume fraction (superscript index b refers to the homogeneous bulk in equilibrium with the bilayers), u is the self-consistent potential, and $\chi_{\rm AB}$ is the Flory–Huggins exchange energy parameter that quantifies the nearest-neighbor interactions. Finally, the angular brackets give the geometry-dependent local average of the volume fraction (to be specified below),

which comprises the nonlocal contributions to the grand potential density (that depend on the bookkeeping).¹⁰

In this paper, we will use the SCF model with the discretization ansatz of Scheutjens and Fleer. 12 This implies a lattice with layers composed of lattice sites with characteristic length l and surfactant chain molecules of the nonionic type with spherical united atoms and volume that fits on the lattice sites. It is convenient to introduce chain architecture operators $(\delta_{i,s}^{A})$ which obtain the value $\delta_{i,s}^{A} = 1$ when segment s of molecule i is of segment type A and zero otherwise. These operators are fixed because the segments along the chain in the nonionic molecule have known segment types given by the input data. The SCF model comprises a segment potential for each segment type which is a functional of the volume fractions. For uncharged surfactants, only excluded volume and short-range nearest-neighbor contacts are accounted for and $u_A(r) = u'(r)$ $+\sum_{\rm B} \chi_{\rm AB}(\langle \varphi_{\rm B}(r) \rangle - \varphi_{\rm B}^{\rm b})$, where u'(r) is a Lagrange potential coupled to the incompressibility constraint $\sum_{B} \varphi_{B}(r) = 1$. The volume fraction profiles are also a functional of the potentials. Using a Markov approximation, it is possible to formulate an efficient scheme to compute the volume fraction profiles.¹² In short, it is possible to come up with the statistical weights of all possible and allowed conformations and collect them in various Green functions.

$$G_i(r, s|1; N) = G_i(r, s|1) G_i(r, s|N)/G_i(r, s)$$
 (6)

Here, $G_i(r, s|1; N)$ is the statistical weight that segment with ranking number s of molecule i is at coordinate r with the constraint that it is connected by intermediate segments (via all possible walks) to the two terminal segments s = 1 and $s = N_i$. The Green function $G_i(r, s|1)$ gives the statistical weight of all possible conformations of a chain fragment from s' = 1, ..., s, over which all coordinates of the end segment s = 1 are integrated. A comparable definition applies for the complementary Green functions $G_i(r, s|N)$. This set of Green functions is generated by a forward and backward propagator, respectively, which are discrete versions of a diffusion equation:

$$G_{i}(r, s|1) = G_{i}(r, s) \langle G_{i}(r', s-1|1) \rangle = G_{i}(r, s) \sum_{r'} \lambda(r, r') G_{i}(r', s-1|1)$$
(7)

$$G_{i}(r, s|N) = G_{i}(r, s)\langle G_{i}(r'', s+1|N) \rangle = G_{i}(r, s) \sum_{r''} \lambda(r, r'') G_{i}(r'', s+1|N)$$
(8)

which defines the angular brackets also used in eq 5. Here, the sum over r' runs over all possible neighboring coordinates of segment s; that is, the distance r - r' is the lattice length (l). The same applies to summation over r''. The weighting factor ($\lambda(r, r')$) gives the *a priori* statistical weight to step from r' to r and obeys the constraint that $\sum_{r'} \lambda(r, r') = 1$. This weight depends on the local geometry, that is, the curvature of the lattice layers.¹³ as specified below.

In both eqs 6 and 8, the free segment distribution occurs, that is, $G_i(r, s) = \sum_A G_A(r) \delta_{i,s}^A$, where $G_A(r) = \exp(-u_A(r)/k_BT)$ is the Boltzmann weight featuring the segment potential. After normalization of $G_i(r, s|1; N)$, one obtains the volume fraction profiles $(\varphi_i(r, s))$ from which the segment-type-dependent profiles $(\varphi_A(r))$ follow, that is, $\varphi_A(r) = \sum_i \sum_s \varphi_i(r, s) \delta_{i,s}^A$. Below, we will discuss the normalization in more detail. A computer algorithm is used to find the solution for which the segment potentials and segment distributions are consistent with

each other while the incompressibility constraint is obeyed. 12 For more detail, we refer to the literature. 13,12

A slice normally through an infinitely long tubular vesicle leads to a radial distribution function of the (excess) surfactant density. The first moment over this distribution determines the radius of the vesicle (R). Other definitions of the radius can be envisioned; however, for large values of the radius (R), all reasonable definitions give identical results. This means that in the limit of large radii the curvature is uniquely defined. The same applies for a spherically curved bilayer (vesicle). In the inner monolayer, the headgroups are compressed, leading to a relatively high headgroup density. The tails of the inner monolayer have relatively much space. We will choose the curvature for this monolayer to be negative, J = -1/R(cylindrical geometry). The outer monolayer has relatively compressed tails and expanded headgroups, and the curvature is positive, J = 1/R. For sufficiently large R, there is little ambiguity about the assignment of the curvatures to the two monolayers. In the SCF model, we have a radial coordinate counting from the center in units of lattice sites: r = 1, ..., R, ..., M. When $1 \ll R \ll M$, the system boundaries r = 1 and r = M do not influence the curved bilayer and at both boundaries the homogeneous bulk is present. In general, it is expensive (in terms of computer time) to choose the computational volume to be large; instead, we may introduce the new coordinates z =1, ..., M_z , where $r = z + R_l$ and typically $M_z + R_l \le M$ and still have the condition that at $r = R_l < R$ and $r = R_l + M_z >$ R bulk conditions apply.

The boundary conditions are chosen such that between layers z=0 and z=1 as well as between layers $z=M_z$ and $z=M_z+1$ all gradients in u and φ vanish. In more detail, for all segment potentials, we set u(0)=u(1) and $u(M_z+1)=u(M_z)$. In the propagator procedure, the gradients in end-point distribution functions vanish at the system boundaries, that is, G(0, s|1)=G(1, s|1), G(0, s|N)=G(1, s|N), $G(M_z+1, s|1)=G(M_z, s|1)$, $G(M_z+1, s|N)=G(M_z, s|N)$, and also $G_i(0, s|1; N)=G_i(1, s|1; N)$ and $G_i(M_z+1, s|1; N)=G_i(M_z, s|1; N)$. As a result, also, the volume fractions on either side of the boundaries are identical. This symmetry boundary condition in the curved lattice geometry is used below to calculate the mechanical parameters of the monolayers. The boundary condition has minimal consequences for the conformational entropy of the chains, as these can freely cross the boundary.

In the cylindrical coordinate system $L^{c}(z) = \pi(2(z + R_{l}) -$ 1) is the number of lattice sites (per unit length) in layer z and the total grand potential (per unit length of the tubular vesicle) is found by $\epsilon^{c} = \sum_{z} L^{c}(z) \omega^{c}(z) \approx 2\pi R \gamma(J, 0)$ (c = cylindrical geometry and J = 1/R). In spherical geometry, we have $L^{s}(z)$ $=4\pi((z+R_l)^2-(z+R_l)+\frac{1}{3})$ and the grand potential of the spherical vesicle is given by $\epsilon^s = \sum_z L^s(z) \, \omega^s(z) \approx 4\pi R^2 \gamma(J, K)$ (s = spherical geometry and J = 2/R and $K = 1/R^2$). The internal balance for the chain statistics dictates that L(z') $\lambda(z', z) = L(z)$ $\lambda(z, z')$. Using this, we find that the transition probabilities are given by $\lambda(z, z - 1) = A(z)/L(z)/3$, $\lambda(z, z + 1) = A(z + 1)/2$ L(z)/3 and $\lambda(z, z) = 1 - \lambda(z, z - 1) - \lambda(z, z + 1)$, where A(z)is the dimensionless contact area (i.e., the area normalized by l^2) between layers z and z-1. For the cylindrical coordinates, we have the area per unit length $A^{c}(z) = 2\pi(z + R_1)$, whereas, for the spherical coordinate system, the area is given by $A^{s}(z)$ $=4\pi(z+R_1)^2$.

Parameters

Nonionic surfactants (i = 1) of the type $C_n E_m \equiv C_n (OC_2)_m O$ are used where C stands for CH₂ or CH₃ and O is for the oxygen

in the ethylene oxide moiety and also for OH as the terminal segment in the headgroup. Thus, all chain architecture operators for this molecule are fixed, that is, $\delta_{1,1}^{C} = 1, ..., \delta_{1,n+3m+1}^{O} = 1$. Here, we choose to represent the solvent (i = 2) by a (compact) cluster of five W units where there is a central one surrounded by four neighbors so that the solvent (water) is somewhat larger than a C atom. There are three FH interaction parameters which we choose such that the known critical micellization concentration is reproduced: $\chi_{CW} = 1.1$, $\chi_{CO} = 2$, and $\chi_{OW} = -0.6$. These parameters are close to those used in previous studies.¹⁴ Careful comparison of the spherical, cylindrical, and lamellar topologies of various members of the C_nE_m family show that, in agreement with experimental data, 15 C₁₂E₅ forms stable bilayers only at very high surfactant concentrations. The bilayers of C₁₄E₄, however, appear more stable than spherical or cylindrical micelles. This is remarkable because the two surfactants differ just by one O atom. Using this information, we focus below on the subset C_nE_4 of bilayer forming surfactants with $14 \le n \le 18$.

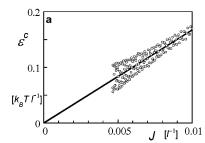
Results and Discussion

Mechanical Properties of Symmetric Bilayers. The determination of the bending moduli of symmetric bilayers starts with the evaluation of the structural properties of the flat bilayer.⁸ The tensionless bilayer is characterized by an area per surfactant molecule (a_0). This quantity increases with increasing tail length (for a given headgroup size). Using a_0 , one can estimate the number of surfactant molecules (n_s) per unit length of a tubular vesicle with radius R, that is, $n_s = 4\pi R/a_0$. In this case, the volume fraction profiles are found from

$$\varphi(z, s) = CG(z, s|1; N) = \frac{n_s}{\sum_{z} L(z) G(z, s|1; N)} G(z, s|1; N)$$
(9)

The normalization constant (C) is also related to the volume fraction of surfactant in the bulk surrounding the bilayer (φ^b) . As in the bulk phase, all Green functions are unity and it follows that $C = \varphi^b/N^{12}$ and thus $\varphi^b = n_s N/(\sum_z L(z) G(z, s|1; N))$. From such an analysis, one obtains the grand potential of the cylindrically curved bilayer $(\epsilon^c(R))$ from which $\gamma^c(R)$ follows by division by $2\pi R$. As J = 1/R and K = 0, we can use eq 1 to evaluate k_c . It is essential to realize that the bulk volume fraction of surfactants is a weak function of the radius of the tubular vesicle as well; that is, $\varphi^{bc}(R)$ is not a constant. We may repeat the procedure for spherical coordinates and find that the grand potential of the spherically curved vesicle is $\epsilon^s = 4\pi(2k_c + \bar{k})$. Using the k_c value from the analysis of the tubular vesicle (cylindrical coordinates), we can thus extract the Gaussian bending modulus (\bar{k}) .

An example of this procedure for the curved bilayer of $C_{14}E_4$ is given in Figure 1, where ϵ^c is plotted as a function of the curvature. In Figure 1a, we have imposed the cylindrical geometry. The data points should ideally fall on the linear trend line. Instead, they scatter around this line where the amplitude of the deviations increases with decreasing J. The fundamental reason for this scatter is the fact that the bilayers feel the underlaying lattice somewhat. Because of this, the SCF solution results in bilayers that have not only curvature energy but also a tiny bit of stretching energy (either negative or positive) caused by the lattice-induced perturbations. These lattice artifacts average out when a large set of vesicles of different sizes is generated, as is easily seen in Figure 1. One can also envisage



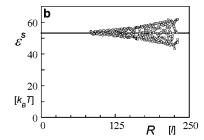
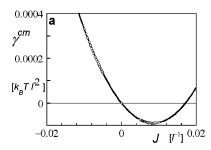


Figure 1. Thermodynamics of $C_{14}E_4$ bilayers cured in (a) cylindrical and (b) spherical geometry. In part a, the grand potential per unit length of the tubular vesicle (ϵ^c) is plotted as a function of the radious of curvature (J = 1/R). The points scatter symmetrically around the linear trend line. In part b, the grand potential of the spherical vesicle (ϵ^s) is plotted as a function of the radius of the vesicle (R). Again, the data points scatter symmetrically around the horizontal trend line.



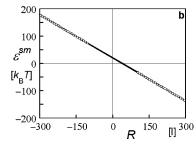


Figure 2. Thermodynamics of $C_{14}E_4$ monolayers (in the bilayer configuration) curved in (a) cylindrical and (b) spherical geometry. In part a, the surface tension (γ^{cm}) of the monolayer in a tubular vesicle is plotted as a function of the radius of curvature (J = 1/R). In part b, the grand potential of a monolayer in spherical geometry (ϵ^{sm}) is plotted as a function of the radius of the vesicle (R).

a numerical procedure to search automatically for vesicles that feel very little of this lattice pressure. We do not show this here. The trend line of Figure 1a crosses the origin convincingly. This shows that the symmetric bilayers do not have a preferential curvature and that the bilayers are tensionless. From the slope, we obtain directly the value of the mean bending modulus (k_c). In Figure 1b, we present similar results for bilayers ($\epsilon^s(R)$) onto which a spherical geometry is imposed. Again, ideally for vesicles that have only curvature energy, the points would fall on the horizontal trend line. The spread of the points increases with increasing radius of the vesicle, showing that the small positive or negative lattice pressure also affects the energetics of spherically curved bilayers. The horizontal line corresponds to the grand potential $\epsilon^s = 4\pi(2k_c + \bar{k})$, and the results convincingly show that for symmetric bilayers $J_0 = 0$.

Mechanical Properties of a Monolayer in the Bilayer **Configuration.** The key ideas for computing the mechanical parameters of the monolayers are (i) to shift the boundary z =1 (i.e., $r = R_l + 1$) to the coordinate r = R + 1 and force the curved bilayer to have its symmetry plane at the lower system boundary and (ii) to normalize the volume fraction profiles with the known $\varphi^{b}(R)$ values. The symmetry boundary condition (i) forces a curved monolayer to interact with a similarly curved monolayer (its mirror image). Again, due to the imposed symmetry, the numbers of chains that (partially) exit and enter the system are identical. As a result, the curved monolayer feels in good approximation the same environment as if it were in the unperturbed bilayer. By imposing the normalization with the known bulk volume fraction (ii), we force the surfactants in the curved monolayer to have the same chemical potential as the surfactant in the homogeneously curved (tubular or spherical) vesicle. The number of surfactants per unit area can adjust so that the monolayer remains unstretched. Hence, we no longer expect to find noise in the data points due to some residual lattice-induced lateral tension. Indeed, now the grand potential of the monolayer only contains bending work. (iii) Next, we shift the symmetry plane of the bilayer to the upper system boundary such that $z = M_z$ is at the center of the bilayer, that is, to r = R. Again, $\varphi^b(R)$ is used to normalize the volume fraction profiles.

For the cylindrical geometry, we thus obtain $\epsilon^{cm}(J)$ (and related to that $\gamma^{cm}(J)$ both for negative and positive values of J, as is shown for an example in Figure 2a. In this graph, we combined the data of the positively and negatively curved monolayers. In the limit of $J \rightarrow 0$, the two branches meet at the value $\gamma^{\rm cm}(0) = 0$; the symmetric uncurved bilayer has no membrane tension. Fitting $\epsilon^{\rm cm}/(2\pi R) = \gamma^{\rm cm}(R)$ to eq 1 gives $k_c^{\rm m}$ and $J_0^{\rm cm}$ straightforwardly. The results obtained following the same procedure for the spherical coordinate system are shown in Figure 2b. In this graph, we show the grand potential of the monolayer $(\epsilon^{sm}(R))$ both for positive and negative R. As expected, a linear dependence of $\epsilon^{\rm sm}(R)$ is found. From the slope, we find the combination $k_{\rm c}^{\rm m}$ and $J_0^{\rm m}$. Using $k_{\rm c}^{\rm m}$ from the cylindrical geometry, we can accurately find $J_0^{\rm sm}$ (here, the superscript index s is added to show that this value of the spontaneous curvature is found from the analysis of spherically curved monolayers). From $\epsilon^{\rm sm}(0)=4\pi(2k_{\rm c}^{\rm m}+\bar{k}^{\rm m})$, we may find \bar{k}^m because $k_{\rm c}^{\rm m}$ is known.

In Figure 3, we show a compilation of the mechanical properties of the bilayer as well as of the monolayers for a series of alkyl ethylene oxide C_nE_4 . The mean bending modulus (k_c) is found to increase linearly with the chain length, and the Gaussian bending modulus is negative and decreases linearly (becomes more negative) with increasing length of the tail of the surfactant. The corresponding quantities for the monolayers are about half of those of the bilayer. This is accurately the case for the Gaussian bending modulus, but there appears to be a small systematic deviation between the mean bending modulus of the bilayer and (twice) that of the monolayer. This difference is close to the numerical noise of our method. The value of $J_0^{\rm m}$ computed from the tubular shaped monolayers are identical to those found from spherically shaped monolayers. This internal consistency of the data inspires confidence in the proposed method. We find that $J_0^{\rm m}$ is positive for n < 16, indicating that for small values of n spherical micelles will become a feasible

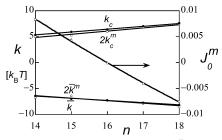


Figure 3. Bending moduli of the bilayer (k_c and \bar{k} , open spheres) and twice that of the constituent monolayers ($2k_c^{\rm m}$ and $2\bar{k}^{\rm m}$, closed spheres) in units of k_BT (left ordinate) and the spontaneous curvature ($J_0^{\rm m}$) (in units of 1/I) as found from cylindrically (triangles) and spherically (open spheres) cured monolayers (right ordinate), as a function of the length (n) of the tail of the C_nE_4 surfactant. The lines are drawn to guide the eyes.

alternative geometry for self-assembly, whereas for $n \ge 16$ the reversed curvature may be considered by the surfactants (and the reversed hexagonal phase is anticipated). This is largely in agreement with expectations based on packing considerations.¹⁶

In the SCF modeling, there are no constraints on the surfactant assemblies other than the curvature of the bilayers or monolayers. The headgroups or tail segments choose positions such that the free energy is optimized; we account not only for conformational entropy in the molecule but also for all relevant interactions in the molecule and with the solvent. As a result, the surfactants partition between the bulk (where the concentration is close to the critical micellization concentration) and the densely packed surfactant layers. In the same way, the solvent is free to partition somewhat into the bilayer, albeit that the tails force most of the solvent (water) out of the bilayer because of the unfavorable interactions. Our curved bilayer and monolayers are free of any lateral tension, as the area per molecule is always optimized. Therefore, the grand potential of our curved bilayers and monolayer can safely be assigned to the curvature energy in the system. Moreover, the tails can and will cross the symmetry plane in the bilayer⁷ such that the free energy is minimized.

Physically, one expects that the bending moduli for the monolayer $(k_{\rm c}^{\rm m}$ and $\bar{k}^{\rm m})$ are just half the values of the full bilayer. The good correspondence observed between the bilayer rigidity and twice that of the monolayer (cf. Figure 3) is in agreement with this expectation. The small deviations observed are attributed to minor details regarding the interdigitation of tails into the opposite monolayer (just a tiny little bit different using the symmetry boundary condition than in the real situation). This directly proves that the correct embedding of the monolayer is of utmost importance.

Our predictions complement corresponding results in the literature. 5,6,11 In the work of Szleifer et al., 5,6 only the tail contribution to the bending moduli is considered. These authors tether short semiflexible hydrocarbon chains to a plane at fixed curvature. They enforce some ad hoc (albeit justifiable) assumptions regarding the homogeneity of the chain packing. It is necessary to mention that these authors discuss both bilayers and monolayers. In the case of the bilayer, they implement a constant density throughout the layer, whereas, in the monolayer system, the packing density may vary. The argument is that a reduced tail density is supplemented by (unspecified) oil molecules. From this, it is clear that their monolayer is not the monolayer in the bilayer configuration. Therefore, it is not surprising that the bending modulus of their bilayers is not twice that of their monolayer at a corresponding area per surfactant molecule. It is difficult to compare our predictions with those

by Szleifer et al.⁶ This is because they keep the area per molecule as a variable in the problem, and it is impossible to extract what area per molecule corresponds to a tensionless bilayer. Such direct comparison would already be complicated because in the Szleifer papers there are no headgroups, there is no positional fluctuation of the grafting point (representing the fluctuation on the headgroup position), there is no solvent penetration, and there are some doubts regarding the way interdigitation is allowed for in their bilayer calculations.

From a statistical mechanical point of view the method of Szleifer et al.5,6 has many aspects in common with our SCF theory. For example, they need a local pressure $(\pi(x))$ (they use the x coordinate in the normal direction of the bilayer), which is linked to the compressibility constraint (constant tail density). This pressure can be compared to our Lagrange field (u'(r)). Subsequently, the profile $(\pi(x))$ is used to evaluate the bending moduli using equations similar to our eqs 2-4. In fact, they can simplify these equations because their lateral pressure $(\pi(x))$ is local; there is no bookkeeping issue because they do not account for nonlocal interactions. In our case, u'(r) is also part of the grand potential density $(\omega(r))$ (which may be interpreted as a lateral pressure), but we have several additional contributions to this pressure profile. We put no constraints on the value of u'(r); however, Szleifer et al. force $\pi(x) \ge 0$. This has important consequences. As they compute $k = -\int x^2 \pi(x) dx$, it is clear that they will always find k < 0. We know that this cannot be generally true, which seriously questions the Szleifer approach. Our predictions of the mechanical parameters of the monolayer in a bilayer configuration are therefore expected to be more accurate that those found in the literature.^{5,6,11}

In the SCF method, there are two operational ways to evaluate the mechanical properties of surfactant mono- and bilayers. The first one is using eqs 2-4. The second one is to evaluate the overall grand potential as a function of J and K and fit the results to the Helfrich equatoin (eq 1). Oversteegen⁸ showed that these two ways give identical results. Computationally, the evaluation of the bending moduli from integrals over moments of the grand potential density profiles (and their derivatives) is tedious and, as it turns out, less accurate. In our case, it is far more easy, and computationally much more efficient, to use the route of fitting the overall grand potential to eq 1, as used above. From this fitting procedure, we can also filter out the effects of, for example, the lattice-induced tension. Our method is computationally extremely efficient, as the mechanical parameters for a particular surfactant mono- or bilayer can be performed in the order of a few seconds CPU on a desktop PC. Consequently, our method may be used also for other more complex systems, for example, block copolymers and mixtures of surfactant. 17 The result that it is possible to accurately evaluate the spontaneous curvature of the monolayer, when it is embedded in the bilayer, is important for obtaining a deeper understanding of selfassembling systems.

Outlook and Conclusions

Using a symmetry boundary condition in curved geometry and placing such a boundary at the midplane of a surfactant bilayer is a useful way to analyze the mechanical properties, including the spontaneous curvature, of the monolayers constituting a symmetric bilayer. This idea is implemented in a molecularly realistic self-consistent field model. It is possible to choose the surfactant architecture such that the spontaneous curvature of the monolayer is close to zero and the bilayer is without frustration. In general, this is not the case and the monolayers have nonzero spontaneous curvatures. We note that

this does not immediately result in the loss of thermodynamic stability of the bilayer. Indeed, it may be thermodynamically stable even when the monolayers have a significant nonzero spontaneous curvature. The method is not limited to nonionic systems, as discussed in this paper. Corresponding results for (models of) phospholipids in biological membranes may be found elsewhere. 18 It is also possible to evaluate the spontaneous curvature in surfactant layers swollen by an apolar compound, that is, a suitable oil. This offers the possibility to smoothly go from a Helfrich-type of analysis of swollen surfactant layers to that of microemulsion systems. The finite $J_0^{\rm m}$ values in the surfactant bilayers are expected to be biologically relevant.¹⁹ More specifically, the spontaneous curvature of the monolayer is expected to be important in processes such as the incorporation of protein molecules in lipid bilayers, 4 fusion and budding of vesicles, nucleation of pores in bilayers, and transport of macromolecules across bilayers.

References and Notes

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