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Quantitative molecular interpretation of curvature elasticity of saturated surfactant monolayers

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The charge-frustrated model of self assembly is applied to compute the curvature elasticity of saturated surfactant interfaces in bicontinuous microemulsions. Explicit formulas are derived to relate the elastic moduli to molecular properties such as surfactant chain length.

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Much effort has been devoted in recent years to the study of interfaces and membranes [1–3]. The term interface usually refers to the boundary between two phases, as in a binary mixture of a polar species P and a hydrophobic species H (e.g., water and oil). Well below the critical point, the mixture separates into H- and P-rich phases. The finite energy cost per unit interfacial area, or interfacial tension, governs the statistical mechanics and suppresses fluctuations. Amphiphilic surfactants tend to assemble at the P-H interfaces, so that their P- and H-like parts can reside in the preferred component. The resulting surfactant monolayers or thin films have low or vanishing surface tension and exhibit large fluctuations.

The phenomenological description of fluctuating interfaces is provided by Helfrich's Hamiltonian [1–4]

$$\mathscr{H}=\int d^2S[\sigma+\lambda_s H+2\kappa H^2+\bar{\kappa}K]. \tag{1}$$

Here, R_1 and R_2 are the principal radii of curvature of the interface, $H=(1/R_1+1/R_2)/2$ is the mean curvature, $K=1/R_1R_2$ is the Gaussian curvature, and $\lambda_s=-4\kappa/R_0$ is proportional to the spontaneous curvature $1/R_0$. Being geometric in nature, this Hamiltonian describes structureless membranes. It is often a satisfactory approximation for fluid membranes. All chemical and structural information is embodied in the phenomenological constant prefactors: the interfacial tension σ, the bending rigidity κ, the saddle splay modulus $\bar{\kappa}$, and the spontaneous curvature modulus λ_s. Our goal is a molecular theory for these prefactors.

There have been a few theoretical attempts to relate these elasticity parameters to molecular properties such as surfactant chain lengths [5–7]. The usual starting point is an assumed mechanical model of surfactant monolayers. The conformational statistics of the chainlike surfactants are then considered numerically to extract the free energy cost of bending the flat monolayer. These theories, however, lack a direct relation to the general statistical mechanics of amphiphilic mixtures and Landau-Ginzburg models [2]. In contrast, our approach considers independent oil, water and surfactant concentration fields and *derives* the self assembly of interfaces. In particular, we use the charge-frustrated Ising model of oil-water-surfactant mixtures [8,9]. This model provides the minimalist description of the entropy reduction in a P-H mixture caused by the presence of surfactant molecules. Its ingredients are readily measurable quantities: the oil-water interfacial tension in the absence of surfactants, the length of a surfactant molecule, and the surfactant concentration. This charge frustrated extension of the Ising model of binary mixtures was first suggested by Wu *et al.* [8], motivated by the density functional approach of Stillinger [10]. Stillinger's density functional theory was also generalized to study bicontinuous microemulsions [11]. A recent analytical work of ours [9] has shown that a simple mean field treatment of the charge-frustrated Ising Hamiltonian can predict the structure factor of microemulsions with quantitative accuracy. A reduction of the Hamiltonian, followed by a mean field treatment, yields a Landau-Ginzburg free energy functional. With this functional, we may consider the free energy cost of bending the flat oil-water interface. This consideration allows us to derive the elasticity parameters. The approach we take therefore encompasses the whole hierarchy of theories from a microscopic picture to the Helfrich model.

The charge-frustrated Ising model has a Hamiltonian with two fields. These fields label cells on a spatial grid according to whether the cells are occupied by oil-like or waterlike species ($s_i=\pm1$), and whether these species are or are not associated with surfactants ($t_i=1$ or 0). One may, for example, consider a cubic lattice, with intercell spacing a. The specific symmetry of the lattice is irrelevant, but a microscopic length a is a significant number in the theory. It is roughly the diameter of a water molecule or the diameter of a segment of oil [9]. For the oil-water symmetric case appropriate to bicontinuous microemulsions, the Hamiltonian is [8,9]

$$\mathscr{H}[s_i,t_i]=-\frac{1}{2}\sum_{ij} J_{ij}s_is_j+\frac{q^2}{2}\sum_{ij} v_{ij}s_is_jt_it_j-\mu\sum_i t_i. \tag{2}$$

The tendency of oil and water to phase separate is expressed by the nearest-neighbor ferromagnetic interaction,

$$J_{ij}=\begin{cases} J>0, & \text{if } i \text{ and } j \text{ nearest neighbors} \\ 0, & \text{otherwise.}\end{cases}$$

The entropy reduction induced by surfactants is embodied in the Coulombic interaction,

$$v_{ij}=(1/N)\sum_{\mathbf{k}} (4\pi/a^3k^2)\exp(i\mathbf{k}\cdot\mathbf{r}_{ij}), \tag{3}$$

where N is the total number of lattice sites. The frustrating charge is given by Stillinger's formula [10]

$$q=(3/4\pi\beta\rho\Delta^2)^{1/2}, \tag{4}$$

where $\beta=1/k_BT$ and ρ is the number density of surfactants. The characteristic length scale of a surfactant molecule Δ is essentially the root mean square distance between the head and tail groups within the molecule. The chemical potential μ controls the amount of surfactants.

A reduced version of the charge-frustrated Ising model can be obtained from Eq. (2) by integrating out the frustrating charge degrees of freedom t_i. This reduction was done approximately in Ref. [9] with a Debye-Hückel-like approximation. It introduces an additional interaction between oil and water densities besides the hydrophobic interaction J_{ij}. The additional interaction is a screened Coulomb interaction with range of order Δ. Once the charge degrees of freedom are integrated out, standard local mean field theory can be used to obtain the following free energy functional [9]:

$$\beta F[m_i]=-\ln C-Nz+\frac{1}{2}\sum_i [(1+m_i)\ln(1+m_i)+(1-m_i)\ln(1-m_i)]-\frac{1}{2}\sum_{ij}(\beta J_{ij}-G_{ij})m_im_j, \tag{5}$$

where G_{ij} is the inverse Fourier transform of $z/(1+\rho a^3\Delta^2k^2/3z)$ and $z=\exp(\beta\mu)$ is the fugacity of the charged sites.

The minimization of Eq. (5) determines the order parameter for the homogeneous phases, $\bar{m}=\langle s_i\rangle$, given by

$$\bar{m}=\tanh[(6\beta J-z)\bar{m}]. \tag{6}$$

From Eqs. (5) and (6), we get the self-consistent relation between the surfactant density $\bar{\rho}=\rho a^3$ and the fugacity z,

$$2\bar{\rho}=-(1/N)\partial\beta F/\partial\ \ln z\simeq z(1-\bar{m}^2/2), \tag{7}$$

where $\bar{m}$ is determined by (6). In Eq. (7), the contribution from $\ln C$ has been neglected, which can be shown to be a good approximation for large Δ/a [9]. For the oil-water mixed or lamellar phases where $\bar{m}=0$, Eq. (7) reduces to the small density limit of the fugacity series in general grand canonical systems, $z=2\bar{\rho}$. For the case of oil-water phase separation where $\bar{m}^2>0$, the density of surfactants is smaller than in the phase with $\bar{m}=0$ for given values of chemical potential.

The continuum limit of Eq. (5) has the form of a Landau-Ginzburg functional and is derived by taking small-k expansions of the interaction terms [9]:

$$\beta F[m]=\frac{1}{2a^3}\int d\mathbf{r}[-Am^2(\mathbf{r})+g(m)(\nabla m)^2+p(m)\times(\nabla^2m)^2+m^4(\mathbf{r})/6+O(m^6)], \tag{8}$$

where, using Eq. (7) to eliminate ρ,

$$A=6\beta J-1-z, \tag{9a}$$

$$g(m)=c_1+z\Delta^2m^2/12, \tag{9b}$$

$$p(m)=c_2(1-m^2/2)^2, \tag{9c}$$

with

$$c_1=\beta Ja^2-z\Delta^2/6, \tag{10a}$$

$$c_2=z\Delta^4/36. \tag{10b}$$

To derive Eqs. (8) and (9), the local density approximation has been invoked to recast Eq. (7) in the local form

$$2\rho(\mathbf{r})a^3=z[1-m(\mathbf{r})^2/2]. \tag{11}$$

Thus, Eq. (8) is a generalization of the functional used in Ref. [9] to study bicontinuous microemulsions. It is the generalization we need to compute elastic moduli.

A nonlinear field theory is generated by the Landau-Ginzburg free energy functional Eq. (8). Its Euler-Lagrange equation admits classes of localized or solitonlike solutions representing interfaces. To extract the elastic properties of interfaces, specifically the surfactant monolayers, we follow Gompper and Zschocke [12]. In particular, we assume that stationary solutions of the field equation $\delta F/\delta m(\mathbf{r})=0$ that describe a planar oil-water interface with a one dimensional profile $m=m(x)$ exist. This approach neglects long ranged interactions or steric interactions between different monolayers.

Rather than solving the Euler-Lagrange equation numerically, we find it convenient to use the variational method with a trial mean field profile,

$$m=m_0\tanh(x/\xi). \tag{12}$$

The corresponding excess free energy per unit area is minimized with respect to the variational parameter ξ [12]. In Eq. (12), m_0 is the value of the bulk phase order parameter. The boundary condition $\lim_{x\to\pm\infty}dm/dx=0$ together with Eq. (8) gives $m_0=(3A)^{1/2}$. The minimization yields

$$A\xi^2=c_1+z\Delta^2A/20+[(c_1+z\Delta^2A/20)^2+6Ac_2(15A^2-36A+28)/35]^{1/2}. \tag{13}$$

This variational solution becomes the exact solution to $\partial F/\partial m(x)=0$ in the limit $z\to 0$. We can interpret ξ given by Eq. (13) as a measure of the width of the interface. For given βJ and a, ξ increases monotonically with increasing z and Δ. For $\Delta\gg a$, ξ is essentially linear in Δ.

Substitution of Eq. (12) with Eq. (13) into Eq. (8) determines the interfacial tension of the system [13],

$$\beta\sigma=\frac{2A}{3a^3\xi}(2A\xi^2+2c_1+z\Delta^2A/10). \tag{14}$$

For given values of Δ and βJ, σ decreases with increasing chemical potential of surfactant, or with fugacity z. For the values of parameters satisfying

$$c_1+z\Delta^2A/20=-\left[\frac{2Ac_2}{35}(15A^2-36A+28)\right]^{1/2}, \tag{15}$$

the interfacial tension vanishes, and the surfactant monolayer is said to be saturated [2]. Further addition of surfactants simply increases the total area of monolayers, and the elastic

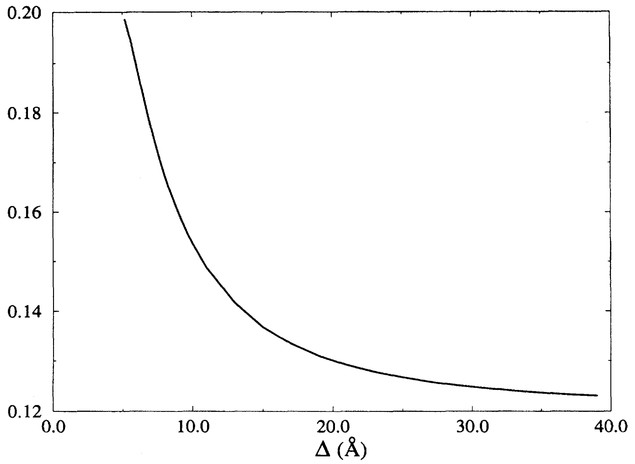

FIG. 1. The minimum of fugacity necessary to saturate the interface z_s as a function of chain length Δ at $\beta J = 0.2$ and $a = 2$ Å.

properties of monolayers are expected to remain approximately constant. Figure 1 shows the saturation points, $z = z_s(\Delta)$, given by Eq. (15) at $a = 2$ Å and $\beta J = 0.2$. These parameter values are those that have been used consistently in Ref. [9] to reproduce experimental scattering data quantitatively. With increasing chain length of surfactant, the fugacity required to saturate the interface decreases to approach the asymptotic value $z_s \simeq 0.12$, reflecting the increase in surfactant amphiphilicity.

In view of the relation between fugacity and density, Eq. (11), it appears that functional (8) overestimates z_s. A larger volume fraction of surfactant ($\sim 10^{-1}$) is required to saturate the interface than typically observed experimentally ($\sim 10^{-3}$). The origin of this discrepancy lies in the approximation, inherent in model (2), which assigns a single constant to characterize all short ranged interactions, irrespective of whether the interacting species involve surfactant or not. Some effects due to the temperature and chain length dependence of the water-surfactant interaction energy are not taken into proper account [9]. One such effect is that surfactant solubility in the bulk phases is overestimated, leading to large values of z_s.

This error could be eliminated by extending the number of energy parameters in the Hamiltonian. But the elastic properties of monolayers, such as the bending moduli, are largely insensitive to this error, as long as the interface is saturated. Indeed, bending moduli are mainly affected by geometric factors like the area per molecule and chain length. These properties are already described correctly by our model, as supported by its success in predicting structure factors quantitatively [9]. As a further support, consider the Gibbs isothermal equation for the area per surfactant at the interface, Σ,

$$\Sigma^{-1} = -(\partial \beta\sigma / \partial \ln z)_T. \tag{16}$$

With this relation and Eqs. (14) and (15), the typical values of Σ at saturation are found to be between 50 and 100 Å^2, in agreement with experiment [14].

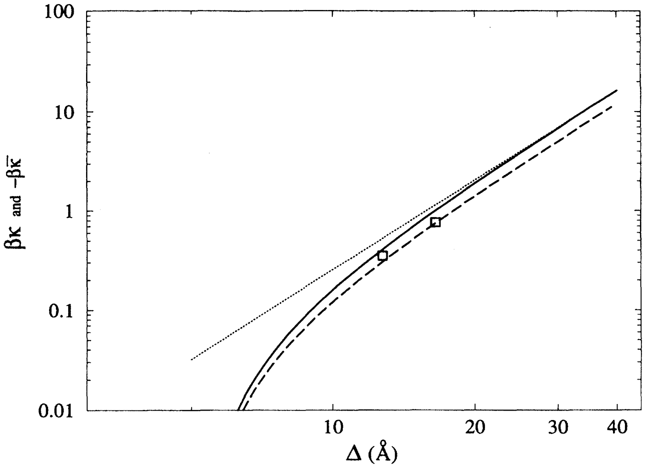

FIG. 2. The bending rigidity κ (solid line) and minus the saddle splay modulus $-\bar{\kappa}$ (dashed line) of saturated monolayers as a function of surfactant chain length Δ at $\beta J = 0.2$ and $a = 2$ Å. The thin dotted line has the slope 3 which represents the asymptotic scaling $\kappa \sim \Delta^3$. The two rectangles represent the data points of bending rigidity from Ref. [16].

The elastic properties of monolayers can be obtained by taking the free energies of the spherical and cylindrical interfaces with radius R, and expanding in $1/R$ [12]. The spontaneous curvature modulus λ_s in Eq. (1) is identically zero since we exclude from consideration any asymmetry between oil and water or surfactant head and tail. The bending rigidity of saturated monolayers κ in units of $k_B T$ is given by

$$\kappa = \frac{z_s \Delta^4 A}{9 a^3 \xi} \left(1 - \tfrac{3}{5} A + \tfrac{27}{140} A^2\right), \tag{17}$$

where $z_s(\Delta)$ is determined by Eq. (15) and A and ξ are given by Eqs. (9a) and (13) with $z = z_s(\Delta)$. Figure 2 shows κ as a function of Δ (solid line). The bending rigidity rapidly increases with increasing chain length of surfactant; for $\Delta \gtrsim 10$ Å, $\kappa \sim \Delta^3$, as would be obtained by regarding the interfacial monolayer as an elastic continuum [15]. Shown together in Fig. 2 are the two data points for C_8E_3 and $C_{10}E_4$ from Ref. [16]. The values of Δ have been taken from the independent fitting of experimental neutron scattering data [9].

The saddle splay modulus $\bar{\kappa}$ is similarly determined as

$$\bar{\kappa} = \frac{c_2 A}{\xi a^3} \left[\frac{2\pi^2}{15} - 4 - \frac{6\pi^2}{35} A + \frac{24}{5} A + \left(\frac{\pi^2}{14} - \frac{197}{105} \right) A^2 \right] + \frac{A\xi}{a^3} \left[(\pi^2/6 - 1) c_1 + \pi^2 z_s \Delta^2 A / 120 \right] + \frac{A^2 \xi^3}{2a^3} (\pi^2/6 - 1), \tag{18}$$

where again z_s is determined by Eq. (15) and A, c_1, c_2, and ξ are given by Eqs. (9a), (10a), (10b), and (13) with $z = z_s$. Figure 2 also shows the plot of $\bar{\kappa}$ as a function of Δ. It obeys the asymptotic scaling $-\bar{\kappa} \sim \Delta^3$.

Our formulas can be extended rather simply to the case of mixtures of surfactants with different chain lengths by using a simple mixing rule

$$\Delta^2=\sum_{\alpha=1}^{M}\Delta_\alpha^2 x_\alpha. \tag{19}$$

Here, M is the number of different surfactant components, and for component α, Δ_α^2 and x_α are the mean square length and the mole fraction, respectively. Equation (19) is motivated by the definition of the length Δ as the mean square root length between the head and tail parts within a surfactant molecule [10]. According to Eq. (19), the bending rigidity of the monolayer is reduced considerably from that of pure long-chain surfactant system upon addition of short-chain surfactants. The short chain molecules act as "spacers" between the long chain molecules, reducing the packing constraint that opposes the bending of monolayers. This reduction has been observed experimentally [17] and noted in numerical calculations [5,7]. It is also consistent with the observation that the addition of alcoholic cosurfactants stabilizes the microemulsion phase of long-chain surfactant systems.

The inequalities $\bar{\kappa}<0$ and $2\kappa+\bar{\kappa}>0$ are always satisfied in our model, suggesting the stability of lamellar phases against the plumber's nightmare and the spherical droplet phases [1–3]. The Hamiltonian (2) is symmetric not only in the oil-water variables (an experimentally realistic situation), but also in the surfactant head and tail groups. This latter symmetry is of course rarely present in reality, except for symmetric diblock copolymers. A consequence of the assumed symmetry is the identically vanishing spontaneous curvature of the interfacial monolayer. This should not be a cause of concern: it simply reflects the fact that in deriving the Hamiltonian (2), one only enforces the stoichiometric constraint that heads and tails of surfactant molecules are connected [8,9], ignoring any asymmetry in the actual length, cross sectional area, or charge state of head and tail groups. Such asymmetries can be accounted for in principle by introducing additional short range couplings in the model. These additional couplings will also improve the quantitative predictions of solubility in the bulk phases. We leave this development for future work.

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