

Thermodynamic Analysis of Phase Coexistence and Stability in Textured Amphiphilic Monolayers at the Air/Water Interface

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Starting from an expression for the Gibbs energy derived previously for a monolayer consisting of a single amphiphilic component present in the (LE/LC) coexistence region, the general thermodynamic criteria for internal equilibrium are derived. It is assumed that the solid phase is present as a dispersion of equally sized circular islands. The assumption of isodispersity is justified by the results of an earlier study. The necessary and sufficient conditions for stability of the equilibria are formulated within the constraints imposed by the model. All of these are stated in a general form, independent of the specific analytical expressions for the various thermodynamic quantities. It is pointed out that a more or less complete analysis will only be possible once an explicit expression for the line tension and an equation of state for a 2D fluid of rigid disks with smeared-out dipole moment become available. The latter would allow the calculation of the free energy of mixing, G_{mix} , as well as the formulation of a 2D equation of state for the film within the coexistence region of the phase diagram. A generic functional form of these functions is given that is consistent with the requirements set by dimensional analysis. Finally, generalizations of the thermodynamic formalism to mixed monolayers and noncircular domain shapes are suggested.

1. Introduction

In a previous paper,¹ hereafter referred to as part 1, the system that will also be the subject of the present study was defined as a monolayer composed of a single amphiphilic species (either polar or ionic) sandwiched between two immiscible bulk phases for which we will now choose water, as the subphase, and air.

Systems of this type have been known to exhibit rich phase behavior within the 2D coexistence regions, especially when the surfactant is chiral, e.g., in the case of lipids.^{2,3} The fact that the surface pressure (Π) versus surface area (A) isotherms are curved inside the two-phase region already testifies to this.

In the simplest case a hexagonal pattern of dots consisting of “liquid-condensed” (LC, actually solid) phase against a “liquid-expanded” (LE) background is observed using microscopic techniques such as epifluorescence microscopy⁴ or Brewster angle microscopy (BAM).⁵ Solid lipid domains are known to change their shape upon compression of the monolayer to ellipses, stripes, spirals, triskelions, etc., which have been explained as being the result of an interplay between lateral electrostatic repulsion between surfactant head groups and (anisotropic) line tension in a growing domain.^{6–8}

Here, we will limit our attention to the case of purely dipolar forces between the molecules that will not lead to chiral domain shapes.

The literature on this subject has been mainly concerned with the equilibrium shapes of individual domains in relation to molecular properties, whereas treatments that aim at a more comprehensive description of island films are still relatively scarce.^{8,9}

It was found in part 1, which deals entirely with dotted superstructures at moderately high LC:LE surface coverage ratios ($=\phi/(1-\phi)$, with ϕ the fraction of the film area occupied by solid domains), so that islands can be considered as being effectively immobilized as a result of both their size (on the

order of 10 μm) and electrostatic trapping, that the typical size distribution that minimizes the monolayer free energy, G_{mono} , is fairly narrow, with polydispersity $\leq 10\%$, and approximately Gaussian.

The analysis was based on an explicit expression for G_{mono} that contains a contribution to the free energy of mixing due to the entropy generated by the polydispersity itself, denoted as $-TS_{\text{poly}}$.

In the subsequent sections the narrowness of the size distributions will be taken as a justification for neglecting polydispersity altogether, i.e., taking $S_{\text{poly}} = 0$. On the other hand, the mobility of the islands, which may become important at the onset of condensation (ϕ low), will no longer be neglected a priori.

The resulting simplified expression for G_{mono} , which essentially contains all the information that is needed for predicting the thermodynamic behavior of the two-phase film, will be minimized, leading to the conditions for stationarity and stability, among other things. Obviously, these necessarily pertain to a constrained minimum of G_{mono} as a result of assuming the domains to be isodisperse and maintaining a circular shape for all values of ϕ .

That this is not necessarily a purely academic exercise is demonstrated by the case of films composed of, e.g., dimyristoylphosphatidic acid (DMPA),¹⁰ where the domains have been observed to remain circular throughout the coexistence region. The present model, limited in scope as it may seem, will be developed in the most general possible way so that the treatment may serve as a paradigm for more complex cases, such as those involving anisotropic line tension and mixed monolayers, with their potentially important applications to biological systems, e.g., lung surfactant.¹¹

This would then merely amount to introducing extra parameters or thermodynamic variables in G_{mono} without changing the basic structure of the formalism.

2. Monolayer Free Energy

The expression for the Gibbs (or Helmholtz) energy of a one-component surfactant monolayer can be written in phenomenological form as¹

$$G_{\text{mono}} = G - G_0 = \mu_s N_s - \Pi A \quad (2.1)$$

where G and G_0 are the total Gibbs energies of the system in the presence and absence of the film, respectively, μ_s is the molecular chemical potential, N_s is the number of surfactant (s) molecules, $\Pi = \gamma_0 - \gamma$ is the surface pressure exerted by the film (γ , γ_0 the surface tension with and without surfactant), and A is the surface area.

In the coexistence region, for a dotted hexagonal superstructure of N_d identical LC islands of radii R , the free energy can be written in the more elaborate form¹

$$G_{\text{mono}} = N'_m \lambda_{s,m}^* + j' N_d \lambda_{s,d}^* + 2\pi R N_d (\Gamma_d \lambda_{s,d}^* + \Gamma_m \Lambda_{s,m}^*) - \Pi_m A_m - N_d \pi R^2 \Pi_c + N_d 2\pi R \Lambda + N_d f_{\text{el}}^{\text{edge}} + G_{\text{mix}} \quad (2.2)$$

The meaning of the symbols is as follows: N'_m is the number of surfactant molecules in the contiguous (LE) phase (the “medium”), and j' the number present in each island. Here, we have introduced the “line excesses” Γ_d and Γ_m on each side of the boundary, so that $N_s = N'_m + j' N_d + 2\pi R N_d (\Gamma_m + \Gamma_d)$.

$\lambda_{s,m}^*$ and $\lambda_{s,d}^*$ represent the molecular (electro-) chemical potentials inside uniform films of the corresponding phases with an average area per surfactant molecule that is the same as that in the medium and domains, a_m and a_d , respectively; Π_m and Π_c are the local surface pressures in the interior of each phase for the same imaginary system; $A_m = A - N_d \pi R^2$ is the area of the LE phase; Λ is the line tension; $f_{\text{el}}^{\text{edge}}$ is the electrostatic edge energy of a domain that is associated with the fringe field due to its excess dipole moment density μ . It should be emphasized that instead of the net electrostatic self-energy $f_{\text{el}}^{\text{self}}$ used in part 1 in the expression for G_{mono} we have now sequestered only the edge term and assume the area term to be incorporated in the other domain contributions, which as a result acquire a slightly different meaning in the present context, hence the change in notation from Π^{od} to Π_c , where the latter is now understood to include the electrostatic spreading pressure (Maxwell pressure) of a uniform condensed film.

Finally, G_{mix} is the free energy of mixing, which was discussed in part 1 and is written as

$$G_{\text{mix}} = F_{\text{el}}^{\text{int}}(\text{c.p.}) - \int_{A_{\text{c.p.}}}^A \Pi_d dA \quad (2.3)$$

Here, $F_{\text{el}}^{\text{int}}(\text{c.p.})$ is the electrostatic work performed in bringing together the islands, which initially are kept infinitely far apart, in a close-packed arrangement where they occupy an area $A_{\text{c.p.}}$. Π_d is the (kinetic + electrostatic) contribution to the spreading pressure due to the islands when allowed to equilibrate with their surroundings and is formally identical to the pressure of a 2D fluid composed of rigid disks with radii R and smeared-out dipole moments $\mu \pi R^2$.¹²

In the following sections the implications of the free energy expression (eq 2.2) with regard to the equilibrium behavior of the film under variation of the experimental control variables (T , A , and N_s) will be investigated. Before proceeding with this task, however, the quantity G_{mix} needs to be examined in greater detail.

3. Free Energy of Mixing

The evaluation of G_{mix} warrants special consideration, as it is the most difficult and subtle problem that has to be dealt with in completing the expression for G_{mono} .

First of all, from the definition of $F_{\text{el}}^{\text{int}}(\text{c.p.})$ it follows that it is equal to the difference in electrostatic energy between a situation where the islands are far apart and one in which the same amount of surfactant is present as an almost uniform film of densely packed disks with negligible edge energy and nearly all of the electrostatic energy contained in the area term $j N_d \lambda_{s,d}^*$. Here, and in the following discussion, the line excess will be assumed to be negligible (mainly for the sake of transparency). As a consequence, $N_d f_{\text{el}}^{\text{edge}}$ and $F_{\text{el}}^{\text{int}}(\text{c.p.})$ should approximately compensate each other so that, for large domains and high LC surface coverage ϕ , when the Brownian motion of the disks is completely suppressed, we find that $G_{\text{mix}} \cong F_{\text{el}}^{\text{int}}$.

For mobile islands neither an analytical nor a numerical approximation is available for the pressure Π_d exerted by a collection of rigid polar disks. All that can be said with certainty is that, according to the virial theorem, Π_d should be a function of the parameters $n_d = N_d/A$, kT , R , and μ^2/ϵ_0 , the last two defining the lateral pair interaction between disks. It can readily be verified that the units of these five quantities are combinations of two (SI) units, viz., kg s^{-2} and m , so that three independent dimensionless combinations (monomials) can be formed with them, e.g.,

$$\frac{\Pi_d}{n_d kT}, \quad \phi = n_d \pi R^2, \quad \frac{\mu^2 R}{\epsilon_0 kT}$$

According to the π theorem,¹³ the desired equation of state is necessarily a functional relationship between these three monomials, which can be written as

$$\Pi_d = n_d kT f(\phi, \mu^2 R / \epsilon_0 kT) \quad (3.1)$$

thus greatly reducing the problem to that of finding the explicit form of f .

The first contribution to G_{mix} (see eq 2.3) is known exactly from the work of McConnell,¹⁴

$$F_{\text{el}}^{\text{int}}(\text{c.p.}) = N_d k' \frac{\mu^2 R}{2\epsilon_0} \phi_{\text{c.p.}}^{3/2} \mathcal{A}(\phi_{\text{c.p.}}) \quad (3.2)$$

with $k' = (3\pi/2)(\sqrt{3}/2\pi)^{3/2}$, $\phi_{\text{c.p.}} = 0.907$, and $\mathcal{A}(\phi)$ is a power series in ϕ with positive coefficients, given in ref 14.

The integral can be reformulated using eq 3.1 and $\partial\phi/\partial A = -\phi/A$ as

$$\int_{A_{\text{c.p.}}}^A \Pi_d dA = N_d kT \int_{\phi}^{\phi_{\text{c.p.}}} \phi^{-1} f(\phi, \mu^2 R / \epsilon_0 kT) d\phi \quad (3.3)$$

Equations 3.2 and 3.3 show that G_{mix} is an extensive quantity and can therefore be written formally as

$$G_{\text{mix}} = N_d g(T, R, j, n_d, a_m) \quad (3.4)$$

The integral 3.3 represents the work performed by the system in an imaginary process that starts with all domains held in a densely packed configuration by a semipermeable barrier (which only lets through individual molecules) and continues with the domain “fluid” slowly expanding toward the receding barrier, as depicted in Figure 1, during which equilibrium is maintained between the two sections into which the surface is divided (but not between the domains and their surroundings!). This means that while the barrier is moving, molecules are continually redistributed because the molecular chemical potential $\mu_{s,m}$ in

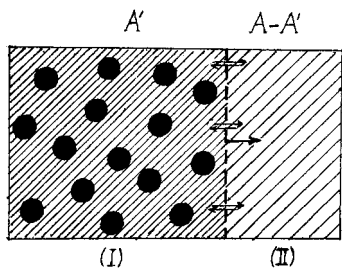


Figure 1. Illustration of the imaginary process of reversible expansion from a close-packed configuration to the final area A and the accompanying “membrane equilibrium” for a fixed number N_d of domains with fixed radii R , used in the calculation of G_{mix} .

section I is affected by the presence of the domains, which can be quantified with the aid of eqs 2.2 (putting $\Gamma_d = \Gamma_m = 0$) and 3.4,

$$\mu_{s,m} = \left(\frac{\partial G_{\text{mono}}}{\partial N_m} \right)_{T,R,j,N_d,A} = \lambda_{s,m}^* - \frac{n_d a_m^2}{1 - \phi} \left(\frac{\partial (f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \quad (3.5)$$

where we have employed the Gibbs–Duhem relation $d\lambda_{s,m}^* = a_m d\Pi_m$ and $a_m = A_m/N_m = (A - N_d \pi R^2)/(N_s - jN_d)$, while it should be kept in mind that $f_{\text{el}}^{\text{edge}}$ and Π_d depend on a_m via μ .

Conversely, if the part of the monolayer contained in section I is considered as a binary mixture of surfactant molecules and domains, eq 2.2 can again be used to calculate a chemical potential per domain, μ'_d (the prime indicating that domain and medium are not in equilibrium for this imaginary system), as

$$\mu'_d = \left(\frac{\partial G_{\text{mono}}}{\partial N_d} \right)_{T,A,N_m,R,j} = j\lambda_{s,d}^* + f_{\text{el}}^{\text{edge}} + g + n_d \left(\frac{\partial g}{\partial n_d} \right)_{T,R,j,a_m} + 2\pi R\Lambda - (\Pi_c - \Pi_m) \pi R^2 - \frac{\phi a_m}{1 - \phi} \left(\frac{\partial (f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \quad (3.6)$$

where the second Gibbs–Duhem relation, $d\lambda_{s,d}^* = a_d d\Pi_c$, has been invoked.

The two chemical potentials $\mu_{s,m}$ and μ'_d are not independent but should obey the cross relation

$$\left(\frac{\partial \mu_{s,m}}{\partial n_d} \right)_{T,R,j,n_m} = \left(\frac{\partial \mu'_d}{\partial n_m} \right)_{T,R,j,n_d} \quad (3.7)$$

defining $n_m = N_m/A$.

Equation 3.7 can be cast in a form that can be more readily applied by means of elementary manipulation of the partial derivatives (eliminating n_m in favor of a_m), leading to the equivalent condition

$$\left[(1 - \phi) \left(\frac{\partial \mu_{s,m}}{\partial n_d} \right)_{a_m} - a_m \pi R^2 \left(\frac{\partial \mu_{s,m}}{\partial a_m} \right)_{n_d} = -a_m^2 \left(\frac{\partial \mu'_d}{\partial a_m} \right)_{n_d} \right]_{T,R,j} \quad (3.8)$$

Substitution of the above expressions for $\mu_{s,m}$ and μ'_d shows, after a somewhat lengthy calculation, that this equality is indeed valid, which at least demonstrates their mutual consistency.

Returning to the system sketched in Figure 1, equilibrium between sections I and II of the surface obviously requires that at each instant

$$\mu_{s,m}(T, R, j, n'_d, a_{m,I}) = \lambda_{s,m}^*(T, a_{m,II}) \quad (3.9)$$

with $n'_d = N_d/A'$ and $a_{m,I} = A'/(N_m - (A - A')/a_{m,II})$, from which $a_{m,II}$ could be solved, in principle, as a function of A' were it not for the unfortunate circumstance that the unknown function g appears in $\mu_{s,m}$ (see eq 3.5), which means that g will also occur in Π_d in some awkward way so that its solution from eq 2.3 (after substitution of eqs 3.2–3.4) seems quite impossible by analytical methods, even if the form of the function f in eq 3.1 were known.

After having stated the problem in general terms, its solution will not be pursued here. Instead, the analysis will be continued using the generic form of G_{mix} , eq 3.4. At least, the above discussion clearly brings to light the fact that there is a great deal more to this problem than just “simple” electrostatics.

4. Equilibrium Conditions

In order to find the minimum of G_{mono} , which will naturally lead to the equilibrium conditions for the monolayer, we need to calculate dG_{mono} . This differential can be simplified considerably by using the following Gibbs–Duhem relations between intrinsic variables pertaining to the interior of each surface phase:

$$j' d\lambda_{s,d}^* = \pi R^2 d\Pi_c - [j' s_{s,d}^* + \pi R^2 (S_d^\sigma - S_o^\sigma)] dT \quad (4.1)$$

and

$$N'_m d\lambda_{s,m}^* = A_m d\Pi_m - [N'_m s_{s,m}^* + A_m (S_m^\sigma - S_o^\sigma)] dT \quad (4.2)$$

where $s_{s,d}^*$ and $s_{s,m}^*$ denote the average entropies per surfactant molecule in the corresponding phases, S_m^σ and S_d^σ are the entropies of adsorption per unit area at the fractions $(1 - \phi)$ and ϕ of the film covered by the LE and LC phases, respectively, due to the components present in the substrate, while S_o^σ represents the adsorption entropy density in the absence of surfactant.

The necessity to include these subphase contributions follows from the definition of G_{mono} , eq 2.1.

To work out the differential of the line tension, $d\Lambda$, we can employ an argument similar to that which leads to the Gibbs adsorption equation. First of all, it should be realized that, in general, Λ will depend on four variables, viz., T , R , $\lambda_{s,d}^*$, and $\lambda_{s,m}^*$.

The R -dependence is included so as to be able to account for the possible effect of boundary elasticity.¹ The chemical potentials $\lambda_{s,d}^*$ and $\lambda_{s,m}^*$, in turn, are functions of T and the density in the respective phases, as measured in terms of a_d or a_m .

Thus, we can write

$$d\Lambda = \left(\frac{\partial \Lambda}{\partial T} \right)_{R,\lambda_{s,d}^*,\lambda_{s,m}^*} dT + \left(\frac{\partial \Lambda}{\partial R} \right)_{T,\lambda_{s,d}^*,\lambda_{s,m}^*} dR + \left(\frac{\partial \Lambda}{\partial \lambda_{s,d}^*} \right)_{T,R,\lambda_{s,m}^*} d\lambda_{s,d}^* + \left(\frac{\partial \Lambda}{\partial \lambda_{s,m}^*} \right)_{T,R,\lambda_{s,d}^*} d\lambda_{s,m}^* = -S_b dT + \left(\frac{\partial \Lambda}{\partial R} \right)_{T,a_d,a_m} dR - \Gamma_d d\lambda_{s,d}^* - \Gamma_m d\lambda_{s,m}^* \quad (4.3)$$

where S_b is the excess entropy per unit length of the boundary.¹⁵

Next, in order to avoid the expression for dG_{mono} becoming too unwieldy, we will again assume that the equilibrium will not be affected seriously if we neglect the line excess, i.e., putting $\Gamma_d = \Gamma_m = 0$, thus assuming a sharp boundary to separate the LE and LC phases, as in part 1. As a consequence, Λ will depend only on T and R .

In carrying out the calculation of dG_{mono} , it is important to realize that variations of j , R , N_d at constant T , A , N_s will affect Π_m and $\lambda_{s,m}^*$ via a_m .

Starting from eq 2.2, the above considerations allow dG_{mono} to be expressed as

$$dG_{\text{mono}} = \mu_{s,m} dN_s + N_d \left[\lambda_{s,d}^* + \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial j} \right)_{T,R,j,n_d,a_m} - \mu_{s,m} \right] dj + \left[j(\lambda_{s,d}^* - \mu_{s,m}) + \pi R^2(\Pi_m - \Pi_c) + 2\pi R\Lambda + f_{\text{el}}^{\text{edge}} + g + n_d \left(\frac{\partial g}{\partial n_d} \right)_{T,R,j,a_m} - \frac{j n_d a_d a_m}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \right] dN_d + N_d \left[2\pi R \left(\Pi_m - \Pi_c + \frac{\Lambda}{R} + \left(\frac{\partial \Lambda}{\partial R} \right)_T - \frac{n_d a_m}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \right) + \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial R} \right)_{T,j,n_d,a_m} \right] dR - \left[\Pi_m + n_d \left(n_d \left(\frac{\partial g}{\partial n_d} \right)_{T,R,j,a_m} - \frac{a_m}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \right) \right] dA - \left[N_m s_{s,m}^* + j N_d s_{s,d}^* + 2\pi R N_d S_b - N_d \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial T} \right)_{R,j,n_d,a_m} + N_d \pi R^2 S_d^\sigma + A_m S_m^\sigma - A S_o^\sigma \right] dT \quad (4.4)$$

where use has been made of the mass balance equation $N_s = N_m + jN_d$ and the relations $\partial a_m / \partial j = N_d a_m / N_m$, $\partial a_m / \partial R = -2\pi R N_d / N_m$, $\partial a_m / \partial N_d = j(a_m - a_d) / N_m$, and $N_d / N_m = n_d a_m / (1 - \phi)$.

The conditions for internal equilibrium now follow from the general requirement $(dG_{\text{mono}})_{T,A,N_s} = 0$.

First, one could consider a simultaneous variation in the radii of all N_d islands, while keeping the number j of molecules contained in each of them fixed; that is, we impose the restrictions $dN_d = dj = 0$.

Equilibrium with respect to this change obviously requires the coefficient of dR in eq 4.4 to vanish; hence,

$$\Delta \Pi = \Pi_c + \Pi_{\text{el,mix}} - \Pi'_m = \frac{\Lambda}{R} + \left(\frac{\partial \Lambda}{\partial R} \right)_T \quad (4.5)$$

where we have introduced the notations

$$\Pi_{\text{el,mix}} = - \frac{1}{2\pi R} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial R} \right)_{T,j,n_d,a_m} \quad (4.6)$$

and

$$\Pi'_m = \Pi_m - \frac{n_d a_m}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \quad (4.7)$$

As was already noted in part 1, eq 4.5 expresses the condition of mechanical equilibrium between a domain and its environment and should be compared with the classical Young–Laplace relation with $\Delta \Pi$ the surface pressure drop across the domain boundary. The contribution $\Pi_{\text{el,mix}}$ to $\Delta \Pi$ accounts for the electrostatic edge effect and lateral interdomain repulsion

between the head groups, whereas an additional kinetic (“osmotic”) contribution is also included. The significance of the latter result lies in the recognition of the fact that $\Delta \Pi$ contains a collective contribution that is expected to become important in monolayers at more advanced stages of compression. This conclusion applies generally to any kind of dispersed system but seems to have been overlooked in earlier studies of, for example, droplet-type microemulsions.¹⁶

The second condition is that of material equilibrium between the dispersed and contiguous phases; that is, dG_{mono} should equal zero if a small number $dN_m = -N_d dj$ of molecules were to be transferred between them, with N_d and R remaining constant.

The second term in eq 4.4 should then be equal to zero; thus,

$$\mu_s = \lambda_{s,d}^* + \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial j} \right)_{T,R,n_d,a_m} = \mu_{s,m} \quad (4.8)$$

Equation 4.8 implies uniformity of the (electro-) chemical potential for which we can therefore use the symbol μ_s defined by eq 2.1.

Finally, the third condition states that G_{mono} should be stationary for the spontaneous condensation of j molecules from the medium into a new domain of radius R . This will only be the case if the factor of dN_d in eq 4.4 disappears. Applying eqs 4.5–4.8, we then arrive at the following relation:

$$j \lambda_{s,d}^* + \pi R \left(\Lambda - R \left(\frac{\partial \Lambda}{\partial R} \right)_T + R \Pi_{\text{el,mix}} \right) + f_{\text{el}}^{\text{edge}} + g + n_d \left(\frac{\partial g}{\partial n_d} \right)_{T,R,j,a_m} = j \mu_s \quad (4.9)$$

which is essentially a statement of the law of mass action, be it in a restricted form in view of the isodispersity constraint, with the expression on the left-hand side representing the chemical potential, μ_d , of a domain in mechanical equilibrium with its surroundings.¹

Equations 4.5, 4.8, and 4.9 constitute three relations between the six variables T , A , N_s , N_d , R , and j , from which the intrinsic variables N_d , R , and j can be eliminated, in principle, in favor of the control parameters T , A , and N_s .

In terms of reversible variations of the independent variables, dG_{mono} is now seen to assume the expected phenomenological form,

$$dG_{\text{mono}} = \mu_s dN_s - \Pi dA - S_{\text{mono}} dT \quad (4.10)$$

defining

$$\Pi = \Pi'_m + n_d^2 \left(\frac{\partial g}{\partial n_d} \right)_{T,R,j,a_m} \quad (4.11)$$

while comparison between the factors of dT in eqs 4.10 and 4.4 shows that the entropy of the monolayer breaks down into several easily identifiable contributions:

$$S_{\text{mono}} = N_m s_{s,m}^* + j N_d s_{s,d}^* + 2\pi R N_d S_b - N_d \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial T} \right)_{R,j,n_d,a_m} + N_d \pi R^2 (S_d^\sigma - S_m^\sigma) + A (S_m^\sigma - S_o^\sigma) \quad (4.12)$$

For the purpose of solving eqs 4.8 and 4.9, the difference $\lambda_{s,d}^* - \lambda_{s,m}^*$ can be written more conveniently in terms of the equation of state for a uniform film, $\Pi_s(T, a)$, noting that $\Pi_c = \Pi_s(T, a_d)$ and $\Pi_m = \Pi_s(T, a_m)$, as follows:

$$\lambda_{s,d}^* - \lambda_{s,m}^* = \int_{\Pi_m}^{\Pi_c} a d\Pi_s = \Pi_c a_d - \Pi_m a_m + \int_{a_d}^{a_m} \Pi_s da \quad (4.13)$$

The last integration is typically carried out across a van der Waals loop, which is a hallmark of instability in a uniform film.

Ultimately, solving eqs 4.5, 4.8, and 4.9 after inserting explicit expressions for $\Pi_s(T, a)$ as well as the line tension $\Lambda(T, R)$ and $g(T, R, j, n_d, a_m)$, if available, eq 4.11 will yield the relationship between the measured surface pressure Π and the parameters T , A , and N_s (or, rather, T and the average area per molecule, $a = A/N_s$), in other words, the equation of state of the monolayer in the LE/LC coexistence region. In section 6 we will return to this important point.

The thermodynamic formalism developed here can be readily extended to incorporate mixed monolayers. If there are r (nonreactive) surfactant components present in the film, in amounts N_1, \dots, N_r , the number of them in each domain can be represented by j_1, \dots, j_r , thus, together with T , A , R , and N_d , bringing to $2r + 4$ the total number of variables in G_{mono} . The dependence of each λ_i^* upon composition should follow from a description of a continuous monolayer, e.g., in terms of a regular mixture model.¹⁷

The number of equilibrium conditions is now raised to $r + 2$; that is, for mechanical equilibrium we still have eq 4.5, the law of mass action, eq 4.9, which is now generalized to $\mu_d = \sum_{i=1}^r j_i \mu_i$, and r equations like eq 4.8, leaving T , A , and the N_i as $r + 2$ independent variables.

5. Stability Criteria

The three equations derived in the previous section provide the necessary conditions for equilibrium. However, this does not mean that the values for R , j , and N_d obtained in terms of T , A , and N_s are unique. One could, for instance, conceive of a stationary yet unstable state, e.g., a collective "critical nucleus" corresponding to a maximum in G_{mono} , even though such a state of the monolayer is evidently to be regarded as an artifact of our model, resulting from the isodispersity constraint.

To establish the nature of the stationary state, we therefore need to look at higher derivatives of G_{mono} and check if the condition for a minimum, $(d^2 G_{\text{mono}})_{T,A,N_s} > 0$, is indeed fulfilled.

From the definition of G_{mono} it is clear that these differentiations will not affect G_0 so that we may legitimately drop the subscript when taking derivatives, which will at the same time allow a more concise notation.

A necessary requirement¹⁸ for a minimum is that the Hessian

$$H = \begin{vmatrix} \partial^2 G / \partial j^2 & \partial^2 G / \partial R \partial j & \partial^2 G / \partial N_d \partial j \\ \partial^2 G / \partial j \partial R & \partial^2 G / \partial R^2 & \partial^2 G / \partial N_d \partial R \\ \partial^2 G / \partial j \partial N_d & \partial^2 G / \partial R \partial N_d & \partial^2 G / \partial N_d^2 \end{vmatrix}_{T,A,N_s} \quad (5.1)$$

and every principal minor (of whatever order, obtained by successively erasing one row and one column which intersect at a diagonal element) be either positive or zero. Moreover, any of these that is positive must have every principal minor also positive. A sufficient condition that G_{mono} (and G) be minimum in a stationary state is that there the Hessian and a sequence of principal minors be positive.

A corollary to this theorem states that if $H > 0$, then a necessary and sufficient condition for a minimum is that there exists a sequence of principal minors that are positive.

As a starting point for the evaluation of the various entries of the determinant eq 5.1, we should use the first-order

derivatives of G with respect to j , N_d , and R , which follow directly from eq 4.4,

$$\left(\frac{\partial G}{\partial j} \right)_{T,A,N_s,N_d,R} = N_d \left[\lambda_{s,d}^* - \lambda_{s,m}^* + \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial j} \right)_{T,R,n_d,a_m} + \frac{n_d a_m^2}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \right] \quad (5.2)$$

$$\left(\frac{\partial G}{\partial N_d} \right)_{T,A,N_s,j,R} = j(\lambda_{s,d}^* - \lambda_{s,m}^*) + \pi R^2(\Pi_m - \Pi_c) + 2\pi R\Lambda + f_{\text{el}}^{\text{edge}} + g + n_d \left(\frac{\partial g}{\partial n_d} \right)_{T,R,j,a_m} + \frac{j n_d a_m (a_m - a_d)}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \quad (5.3)$$

$$\left(\frac{\partial G}{\partial R} \right)_{T,A,N_s,j,N_d} = 2\pi R N_d \left[\Pi_m - \Pi_c + \frac{\Lambda}{R} + \left(\frac{\partial \Lambda}{\partial R} \right)_T - \frac{n_d a_m}{1 - \phi} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} \right)_{T,R,j,n_d} \right] + N_d \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial R} \right)_{T,j,n_d,a_m} \quad (5.4)$$

With the surface pressure Π_s for a continuous film introduced in the previous section, the notation $(\partial \Pi_s / \partial a)_{T,a_d}$ will be used rather than $(\partial \Pi_c / \partial a_d)_T$, and similarly for Π_m .

For the diagonal elements we then find, with eqs 5.2–5.4,

$$\left(\frac{\partial^2 G}{\partial j^2} \right)_{T,A,N_s,N_d,R} = N_d \left[-\frac{a_d^2}{j} \left(\frac{\partial \Pi_s}{\partial a} \right)_{T,a_d} - \frac{N_d a_m^2}{N_m} \left(\frac{\partial \Pi_s}{\partial a} \right)_{T,a_m} + \frac{\partial^2(f_{\text{el}}^{\text{edge}} + g)}{\partial j^2} + \frac{N_d a_m}{N_m} \left(2 \frac{\partial^2(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m \partial j} + \frac{2 N_d}{N_m} \frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} + \frac{N_d a_m}{N_m} \frac{\partial^2(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m^2} \right) \right] \quad (5.5)$$

from which $d\lambda_{s,d}^*$ and $d\lambda_{s,m}^*$ have been eliminated using the Gibbs–Duhem relations 4.1 and 4.2 (at constant T);

$$\left(\frac{\partial^2 G}{\partial N_d^2} \right)_{T,A,N_s,R,j} = -\frac{j^2(a_m - a_d)^2}{N_m} \left(\frac{\partial \Pi_s}{\partial a} \right)_{T,a_m} + \frac{2j(a_m - a_d)}{N_m} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} + n_d \frac{\partial^2 g}{\partial a_m \partial n_d} + \frac{j N_d}{N_m} \frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} + \frac{j N_d (a_m - a_d)}{2 N_m} \frac{\partial^2(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m^2} \right) + A^{-1} \left(2 \frac{\partial g}{\partial n_d} + n_d \frac{\partial^2 g}{\partial n_d^2} \right) \quad (5.6)$$

using $a_d = \pi R^2 / j$;

$$\left(\frac{\partial^2 G}{\partial R^2} \right)_{T,A,N_s,N_d,j} = 2\pi N_d \left[-2a_d \left(\frac{\partial \Pi_s}{\partial a} \right)_{T,a_d} + \frac{j N_d}{N_m} \left(\frac{\partial \Pi_s}{\partial a} \right)_{T,a_m} + 2 \left(\frac{\partial \Lambda}{\partial R} \right)_T + R \left(\frac{\partial^2 \Lambda}{\partial R^2} \right)_T + \Pi_m - \Pi_c - \frac{N_d}{N_m} \left(\frac{\partial(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m} + 2R \frac{\partial^2(f_{\text{el}}^{\text{edge}} + g)}{\partial a_m \partial R} \right) \right] + N_d \frac{\partial^2(f_{\text{el}}^{\text{edge}} + g)}{\partial R^2} \quad (5.7)$$

The calculation of the off-diagonal elements of H provides a useful consistency check in the requirement that cross-derivatives should be equal. This can be tested on the basis of the relationships presented above and the fact that free use can be made of the equilibrium conditions, eqs 4.5–4.9, since the second derivatives are all taken at the stationary point. This yields the following expressions:

$$\left(\frac{\partial^2 G}{\partial j \partial N_d}\right)_{T,A,N_s,R} = \left(\frac{\partial^2 G}{\partial N_d \partial j}\right)_{T,A,N_s,R} = \frac{jN_d(a_m - a_d)}{N_m} \left[-a_m \left(\frac{\partial \Pi_s}{\partial a}\right)_{T,a_m} + \frac{\partial^2(f_{el}^{edge} + g)}{\partial a_m \partial j} + \frac{N_d}{N_m} \frac{\partial(f_{el}^{edge} + g)}{\partial a_m} + \frac{N_d a_m}{N_m} \frac{\partial^2(f_{el}^{edge} + g)}{\partial a_m^2} \right] + \frac{a_m N_d N_s}{N_m^2} \frac{\partial(f_{el}^{edge} + g)}{\partial a_m} + n_d \left(\frac{\partial^2 g}{\partial n_d \partial j} + \frac{N_d a_m}{N_m} \frac{\partial^2 g}{\partial n_d \partial a_m} \right) \quad (5.8)$$

$$\left(\frac{\partial^2 G}{\partial R \partial N_d}\right)_{T,A,N_s,j} = \left(\frac{\partial^2 G}{\partial N_d \partial R}\right)_{T,A,N_s,j} = \frac{2\pi R N_d}{N_m} \left[j(a_m - a_d) \left(\frac{\partial \Pi_s}{\partial a}\right)_{T,a_m} - \frac{N_d}{N_m} \frac{\partial^2(f_{el}^{edge} + g)}{\partial a_m^2} + \frac{1}{2\pi R} \frac{\partial^2(f_{el}^{edge} + g)}{\partial a_m \partial R} \right] - \frac{N_s}{N_m} \frac{\partial(f_{el}^{edge} + g)}{\partial a_m} - n_d \frac{\partial^2 g}{\partial n_d \partial a_m} + n_d \frac{\partial^2 g}{\partial n_d \partial R} \quad (5.9)$$

$$\left(\frac{\partial^2 G}{\partial j \partial R}\right)_{T,A,N_s,N_d} = \left(\frac{\partial^2 G}{\partial R \partial j}\right)_{T,A,N_s,N_d} = \frac{2\pi R N_d}{N_m} \left[\frac{N_m a_d}{j} \left(\frac{\partial \Pi_s}{\partial a}\right)_{T,a_d} + N_d a_m \left(\frac{\partial \Pi_s}{\partial a}\right)_{T,a_m} - \frac{\partial^2(f_{el}^{edge} + g)}{\partial a_m \partial j} - \frac{N_d}{N_m} \left(\frac{\partial(f_{el}^{edge} + g)}{\partial a_m} + a_m \frac{\partial^2(f_{el}^{edge} + g)}{\partial a_m^2} \right) \right] + N_d \frac{\partial^2(f_{el}^{edge} + g)}{\partial R \partial j} + \frac{N_d^2 a_m}{N_m} \frac{\partial^2(f_{el}^{edge} + g)}{\partial R \partial a_m} \quad (5.10)$$

Next, we proceed with an analysis of the stability of the dotted superstructures via the behavior of Π as a function of film area (at constant T and N_s) or, equivalently, the variation of $(\partial \Pi / \partial a)_T$ along that part of the isotherm that passes through the two-phase region. If the monolayer is to be thermodynamically stable, this quantity should not become positive or else another van der Waals loop would appear, which in this case heralds the onset of some secondary phase transformation. However, the nature of such a transition is not at all obvious within the framework of this model. The reason is that the spatial separation into two homogeneous phases, characterized by two sets of parameters (j , R , n_d), which is usually associated with this type of instability, can not be made compatible with the equilibrium conditions. This is so because, first of all, $\mu_s = \mu_{s,m}$ should remain uniform, while on the other hand the uniform surface pressure Π of the system can be found by means of a Maxwell construction, thus fixing the value of a for each phase. The values for j , R , and n_d follow from eqs 4.5–4.9 so that for

each phase $a_m = (1 - n_d \pi R^2) / (a^{-1} - j n_d)$ can be determined. Since the two values of $\mu_{s,m}$ that follow from this are not necessarily identical, the first equilibrium condition would be violated.

Here, no attempt will be made to elucidate the nature of the stable phase, but it is likely that the anomaly is due to the exclusion of domain shapes other than circular and can be removed by taking different morphologies into consideration.

To demonstrate that an instability of the type identified above may indeed follow from the model as it has been developed so far, we start with the identity

$$\left(\frac{\partial \Pi}{\partial a}\right)_T = \left(\frac{\partial \Pi}{\partial j}\right) \left(\frac{\partial j}{\partial a}\right)_T + \left(\frac{\partial \Pi}{\partial R}\right) \left(\frac{\partial R}{\partial a}\right)_T + \left(\frac{\partial \Pi}{\partial n_d}\right) \left(\frac{\partial n_d}{\partial a}\right)_T + \left(\frac{\partial \Pi}{\partial a_m}\right) \left(\frac{\partial a_m}{\partial a}\right) \quad (5.11)$$

where $(\partial a_m / \partial a)_{j,R,n_d} = a_m N_s / a N_m$ and

$$\left(\frac{\partial \Pi}{\partial j}\right)_{T,A,N_s,n_d,R} = \left(\frac{\partial \Pi}{\partial j}\right)_{T,R,n_d,a_m} + \frac{n_d a_m^2}{1 - \phi} \left(\frac{\partial \Pi}{\partial a_m}\right)_{T,R,j,n_d} \quad (5.12)$$

$$\left(\frac{\partial \Pi}{\partial R}\right)_{T,A,N_s,n_d,j} = \left(\frac{\partial \Pi}{\partial R}\right)_{T,j,n_d,a_m} - \frac{2\pi R n_d a_m}{1 - \phi} \left(\frac{\partial \Pi}{\partial a_m}\right)_{T,R,j,n_d} \quad (5.13)$$

$$\left(\frac{\partial \Pi}{\partial n_d}\right)_{T,A,N_s,R,j} = \left(\frac{\partial \Pi}{\partial n_d}\right)_{T,R,j,a_m} + \frac{j a_m (a_m - a_d)}{1 - \phi} \left(\frac{\partial \Pi}{\partial a_m}\right)_{T,R,j,n_d} \quad (5.14)$$

The derivatives $(\partial j / \partial a)_T$, $(\partial R / \partial a)_T$, and $(\partial n_d / \partial a)_T$ can be written more explicitly by noting that at each point along the isotherm $(\partial G / \partial j)_{T,A,N_s,N_d,R} = (\partial G / \partial R)_{T,A,N_s,N_d,j} = (\partial G / \partial N_d)_{T,A,N_s,R,j} = 0$ so that, for example, $d(\partial G / \partial j) = 0$ for an isothermal change of film area from A to $A + dA$. When written out in full, this equation reads

$$\left[\left(\frac{\partial^2 G}{\partial j^2}\right)_{N_d,R} dj + \left(\frac{\partial^2 G}{\partial R \partial j}\right)_{N_d} dR + \left(\frac{\partial^2 G}{\partial N_d \partial j}\right)_R dN_d \right]_{T,A,N_s} + \left(\frac{\partial^2 G}{\partial A \partial j}\right)_{T,N_s,N_d,R} dA = 0$$

or, equivalently,

$$\left(\frac{\partial^2 G}{\partial j^2}\right) \left(\frac{\partial j}{\partial a}\right)_T + \left(\frac{\partial^2 G}{\partial R \partial j}\right) \left(\frac{\partial R}{\partial a}\right)_T + N_s \left(\frac{\partial^2 G}{\partial N_d \partial j}\right) \left(\frac{\partial N_d}{\partial a}\right)_{T,N_s} = N_s \left(\frac{\partial \Pi}{\partial j}\right) \quad (5.15)$$

The remaining two equilibrium conditions give rise to similar equations. They can be summarized conveniently in matrix notation, after substitution of $n_d + a(\partial n_d / \partial a)_T$ for $(\partial N_d / \partial a)_{T,N_s}$, as follows:

$$\begin{pmatrix} \partial^2 G / \partial j^2 & \partial^2 G / \partial j \partial R & \partial^2 G / \partial j \partial N_d \\ \partial^2 G / \partial R \partial j & \partial^2 G / \partial R^2 & \partial^2 G / \partial R \partial N_d \\ \partial^2 G / \partial N_d \partial j & \partial^2 G / \partial N_d \partial R & \partial^2 G / \partial N_d^2 \end{pmatrix}_{T,A,N_s} \times \begin{pmatrix} N_s^{-1} \partial j / \partial a \\ N_s^{-1} \partial R / \partial a \\ n_d + a \partial n_d / \partial a \end{pmatrix}_T = \begin{pmatrix} \partial \Pi / \partial j \\ \partial \Pi / \partial R \\ A^{-1} \partial \Pi / \partial n_d \end{pmatrix}_{T,A,N_s} \quad (5.16)$$

from which $(\partial j/\partial a)_T$, $(\partial R/\partial a)_T$, and $(\partial n_d/\partial a)_T$ can be easily solved, e.g., in determinantal form using Cramer's rule. If this solution is inserted into eq 5.11, the resulting expression can be reorganized, after a somewhat lengthy but straightforward calculation, into

$$\begin{aligned}
 HN_s^{-1} \left(\frac{\partial \Pi}{\partial a} \right)_T &= \left(\frac{\partial \Pi}{\partial j} \right)^2 \left| \frac{\partial^2 G/\partial R^2}{\partial^2 G/\partial N_d \partial R} \frac{\partial^2 G/\partial R \partial N_d}{\partial^2 G/\partial N_d^2} \right|_{T,A,N_s} + \\
 &\quad \left(\frac{\partial \Pi}{\partial R} \right)^2 \left| \frac{\partial^2 G/\partial j^2}{\partial^2 G/\partial N_d \partial j} \frac{\partial^2 G/\partial j \partial N_d}{\partial^2 G/\partial N_d^2} \right|_{T,A,N_s} + \\
 &\quad A^{-2} \left(\frac{\partial \Pi}{\partial n_d} \right)^2 \left| \frac{\partial^2 G/\partial j^2}{\partial^2 G/\partial R \partial j} \frac{\partial^2 G/\partial j \partial R}{\partial^2 G/\partial R^2} \right|_{T,A,N_s} - \\
 &\quad 2 \left(\frac{\partial \Pi}{\partial j} \right) \left(\frac{\partial \Pi}{\partial R} \right) \left| \frac{\partial^2 G/\partial j \partial R}{\partial^2 G/\partial N_d \partial R} \frac{\partial^2 G/\partial j \partial N_d}{\partial^2 G/\partial N_d^2} \right|_{T,A,N_s} - \\
 &\quad 2A^{-1} \left(\frac{\partial \Pi}{\partial j} \right) \left(\frac{\partial \Pi}{\partial n_d} \right) \left| \frac{\partial^2 G/\partial N_d \partial j}{\partial^2 G/\partial R \partial j} \frac{\partial^2 G/\partial N_d \partial R}{\partial^2 G/\partial R^2} \right|_{T,A,N_s} - \\
 &\quad 2A^{-1} \left(\frac{\partial \Pi}{\partial R} \right) \left(\frac{\partial \Pi}{\partial n_d} \right) \left| \frac{\partial^2 G/\partial N_d \partial R}{\partial^2 G/\partial j \partial R} \frac{\partial^2 G/\partial N_d \partial j}{\partial^2 G/\partial j^2} \right|_{T,A,N_s} - \\
 &\quad HA^{-1} n_d \left(\frac{\partial \Pi}{\partial n_d} \right) + \frac{Ha_m}{N_m a} \left(\frac{\partial \Pi}{\partial a_m} \right) \quad (5.17)
 \end{aligned}$$

with H given by eq 5.1. The first three terms on the right-hand side are positive, on account of the criteria for stable equilibrium, whereas the last two are negative. This shows that, under certain circumstances, a positive value for $(\partial \Pi/\partial a)_T$, and hence a negative lateral isothermal compressibility, $\kappa_T = -[a(\partial \Pi/\partial a)_T]^{-1}$, is indeed a possibility, in which case the theory is no longer applicable, as pointed out earlier.

6. Specific Formulation of the Problem. Equation of State

In the preceding sections a general framework has been developed for the thermodynamic description of dotted superstructures. The theory has been kept as general as possible with the functions f_{el}^{edge} , Λ , Π_s , and Π_d left unspecified. At this time only the first of these is known exactly in terms of μ and R ,¹⁴

$$f_{el}^{edge} = -\frac{\mu^2 R}{2\epsilon_0} \ln \left(\frac{4R}{e^2 \Delta} \right) \quad (6.1)$$

where Δ is a cutoff distance (of closest approach between two surfactant molecules). This obviously leaves open the question of the functional dependence of μ on T , R , j , and a_m , which should follow from a statistical theory. Accurate structural data can be obtained with X-ray diffraction methods, elucidating the in-plane and vertical structures of Langmuir monolayers¹⁹ which could be used to directly test such theories.

As far as the line tension is concerned, only the R -dependence is known from an argument presented in part 1,

$$\Lambda = \Lambda_0 + K \left(\frac{1}{2R^2} - \frac{c_0}{R} \right) \quad (6.2)$$

where K is the bending elastic modulus, c_0 the spontaneous curvature of the boundary, and Λ_0 the line tension of a straight boundary. It should be pointed out that reasonable data fits for the equilibrium radii of solid DMPA domains as a function of

solid area fraction could be achieved assuming $K = 0$, although a more decisive test would also have to include domain size distributions¹ in the fit procedure, should more accurate data become available. A microscopic theory for the line tension Λ_0 has not yet been given, but a successful approach to this problem will undoubtedly follow the line of argument set out by Fowler²⁰ in his statistical theory of surface tension, which recognizes attractive forces between molecules as an essential ingredient that ensures a positive value for the surface (or line) tension.

In the case of an amphiphile monolayer dispersion forces between the hydrocarbon tails are apparently responsible for line tension, and since these interactions are greatly diminished in an oil-type medium, it is to be expected that structure formation is not as pronounced at an oil/water interface as it is at an air/water interface.

The evaluation of the third thermodynamic function, the surface pressure Π_s of a uniform monolayer, has attracted more attention, and quite a considerable body of literature exists that deals with the statistical mechanics of monolayers of long chain amphiphile molecules with attractive chain-chain interactions.

These treatments, which share a mean field approach as a common feature, have led to a satisfactory explanation of the two phase transitions (gaseous to LE and LE to LC) that are typical for these systems.^{21,22} Unfortunately, all of these theories lead to an equation of state that can only be obtained by iterative methods; that is, no expression exists for the non-electrostatic part of $\Pi_s(T, a)$ in a closed analytical form. Nevertheless, as a simple mathematical description of the unstable section of a pressure-area isotherm, we might still use a van der Waals-type equation and write

$$\Pi_s(T, a) = \frac{kT}{a - \beta} - \frac{\alpha}{a^2} \quad (6.3)$$

retaining the original meaning of the parameters α and β .

Besides having a simple analytical form, eq 6.3 has an additional advantage as it naturally incorporates the Maxwell pressure Π_{el} due to the vertical dipole moments,²³ provided that it can be assumed that the average vertical component of the dipole moment on a surfactant molecule, henceforth denoted by p , is approximately independent of a . This model assumption first of all implies that we can write $\mu = p(a_d^{-1} - a_m^{-1})$. Secondly, modeling the dipole layer as a parallel plate condenser with spacing t , the electric field is $E = p/(ta\epsilon\epsilon_0)$, with ϵ an effective dielectric constant, leading to the following a -dependence of Π_{el} :

$$\Pi_{el} = \frac{1}{2} \epsilon \epsilon_0 E^2 t = \frac{p^2}{2\epsilon \epsilon_0 t a^2} \quad (6.4)$$

which is automatically included in the second term of Π_s .

This only leaves the free energy of mixing per domain, g , to be determined. It was already noted in section 3 that this is the most pernicious problem that has to be dealt with, but it is nevertheless possible to circumvent it by making the reasonable approximation $n_d a_m \cong 0$, meaning that the number density of islands is far less than that of the molecules in the LE background.²⁴ (N.B.: This assumption is weaker than that implicit in the treatment presented in ref 9, i.e. $n_d \cong 0$, to avoid interactions between domains.)

This assumption greatly contributes to making the problem more transparent since now we have $\mu_{s,m} \cong \lambda_{s,m}^*$ (eq 3.5) and $\Pi'_m \cong \Pi_m$ (eq 4.7), so that there will be negligible redistribution of molecules during the reversible expansion process

described in section 3. An immediate consequence is that the excess dipole moment density μ remains constant and the reversible work of mixing, eq 3.3, can be calculated directly once the function f is known. For large domains and moderately high coverage ϕ we can safely use the "stagnant island" approximation, in which case¹⁴

$$g \cong F_{\text{el}}^{\text{int}}/N_{\text{d}} = k \frac{\mu^2 R}{2\epsilon_0} \phi^{3/2} \mathcal{A}(\phi) \quad (6.5)$$

Within this approximation the equation of state (eq 4.11) can then be written as

$$\Pi \cong \Pi_{\text{m}} + \Pi_{\text{d}} \cong \Pi_{\text{s}}(T, a_{\text{m}}) + \frac{k\mu^2}{2\pi\epsilon_0 R} \phi^2 (\phi^{3/2} \mathcal{A}(\phi))' \quad (6.6)$$

where a_{m} , μ , R , and ϕ follow as functions of T and a from the simplified versions of eqs 4.5–4.9 with eqs 6.1–6.3 and 6.5 as input.

Even with these rather drastic approximations the solution can only be obtained numerically, however. This will not be attempted here, but it may suffice to point out that eq 6.6 suggests that Π increases monotonically with increasing $\phi = n_{\text{d}}\pi R^2$ as R is known to increase in the course of film compression,^{1,14} while n_{d} tends to level off to a constant value. The anomaly that was anticipated at the end of section 5 (κ_T negative) is therefore not likely to occur under the given circumstances.

7. Discussion and Conclusion

It is well established that an understanding of the trends observed in (LE/LC) phase equilibria in an amphiphilic monolayer requires a formulation of the monolayer free energy at a mesoscopic level; that is, contributions due to nonuniformities within the colloidal size range are considered separately. Sections 2 and 3 of this paper are primarily concerned with this problem, and in particular with the elucidation of the exact nature of the free energy of mixing, G_{mix} , which turns out to involve a 2D "membrane equilibrium", an aspect that had not been recognized before (or at least has never been stated clearly). Even though the discussion of this point seems to aim at a higher degree of rigor than strictly necessary, it is nevertheless important to be fully aware of all the subtleties inherent to the argument and of possible pitfalls one might encounter, especially for a deceptively simple-looking system as the one under consideration, i.e., a film consisting of a single amphiphile component and condensed islands that are identical and circular.

The remaining sections essentially comprise a systematic analysis of the free energy expression which naturally leads to the conditions for stable equilibrium and the way in which it shifts with a change in the experimental variables, the temperature T , trough area A , and total number of surfactant molecules N_{s} .

In particular, these results allow the formulation of the equation of state for the monolayer within the coexistence region, although this only becomes feasible with the introduction of a simplification of the theory as discussed in section 6.

The free energy minimum arrived at by applying the equilibrium conditions, eqs 4.5, 4.8, and 4.9, is necessarily a

local one because polydispersity and departures from the circular domain shape are excluded. Lifting the first restriction is not expected to alter the picture significantly in view of the results obtained in ref 1, which point toward a low degree of equilibrium polydispersity in most practical cases. The main purpose of considering the size distributions is to obtain values for important model parameters such as μ , Δ , and Λ from data fits.

The second limitation can of course be removed by including other geometry parameters next to, or instead of, the domain radius R , with respect to which G_{mono} should be minimized. This program has been followed in numerous studies on shape transitions, particularly those observed in lipid monolayers.

Concerning the latter point, an interesting observation that has been made in the context of the present study is the possibility of an instability of a surfactant monolayer in the form of a negative compressibility (section 5), which is inherently due to the restriction placed upon domain shape.

Even though the theory presented in this paper was developed with the aim to investigate the equilibrium behavior of surfactant monolayers in the LE/LC coexistence region, the treatment has been kept as general as possible so as to render it potentially useful as a paradigm for the application of thermodynamics to similar (dispersed) systems.

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