

Equilibrium Size Distributions of Circular Domains in Amphiphilic Monolayers

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An expression is derived for the free energy of a surfactant monolayer at the interface between two immiscible bulk phases for a range of surface pressures in which two surface phases coexist. The condensed phase is assumed to be present in dispersed form, viz., as circular domains embedded in the less dense phase. The domains are kept in fixed positions as a result of electrostatic trapping. A thermodynamic analysis is presented on the basis of the free energy expression for the case of a single amphiphilic component using a mass-action equilibrium condition, which yields the equilibrium distribution of domain sizes. The distribution function is shown to be the result of a competition between a collective entropy effect (which favors dispersion), line tension, electrostatic edge effects, and interdomain repulsion, while a possible contribution due to bending elasticity of the phase boundary is taken into account. A numerical example illustrates that for practical systems the distributions are fairly narrow and that both the domain size and the width of the distribution increases with the fractional surface coverage of the condensed phase, but in such a way that the degree of polydispersity decreases.

1. Introduction

Over the past 10 years, extensive experimental and theoretical studies of surfactant monolayers at the air/water (or oil/water) interface have led to rapid and substantial progress in our understanding of the relationship between molecular constitution and the thermodynamic and structural properties of these systems.

In recent times experimental research on monolayer-forming amphiphiles has been mainly focused on phospholipids, with their obvious relevance to the investigation of biological membranes, alcohols, and saturated fatty acids.^{1–3} As is well-known, the classical technique employed in the study of monolayers is based on measurement of surface pressure (Π) as a function of film area (A) using a Langmuir film balance. The data, when plotted in a Π versus A phase diagram in the form of a set of isotherms, reveal the occurrence of phase transitions that differ in at least two respects from those observed in three-dimensional systems.

Firstly, two types of liquid-like phase appear to exist; one has been termed liquid-expanded (LE), the other liquid-condensed (LC), which coexist within a certain region of the Π – A plane. A second coexistence region is observed at large areas corresponding to a gas to liquid-expanded ($G \rightarrow LE$) transition.

The second observation that points toward unconventional phase behavior in two-dimensional systems is that of a finite isothermal compressibility of the film within the two-phase domains for monolayers consisting of a single component, in apparent conflict with the phase rule, a type of behavior that is most pronounced in the LE/LC region.

The occurrence of the two phase transitions has been explained both qualitatively and quantitatively on the basis of statistical mechanical (mean field) models.^{4–6} The $G \rightarrow LE$ transition has been associated with a loss of translational freedom of free hydrocarbon chains and thus represents an ordinary condensation, while the $LE \rightarrow LC$ transition has been

interpreted as being the result of an interplay between purely conformational entropy and energy of the chains.⁶ However, the statistical theories have not as yet been developed to a point where it is possible to account for the second anomalous effect. The sections of the isotherms that pass through the coexistence regions were simply obtained by means of a Maxwell construction. That the theory is certainly inadequate in this respect is obvious from the microscopic evidence obtained by means of fluorescence microscopy, a technique that has been in use since the early 1980s,^{7,8} and the more recently developed Brewster angle microscopy (BAM).^{9,10} The images obtained with these techniques during 2D condensation have revealed the existence of surface textures that display long-range ordering and a rich variety of morphologies. In the simplest case a dotted superstructure is observed with circular islands of the condensed phase arranged in a hexagonal array, a type of pattern that persists all across the transition region. This is usually the case with one-component films, e.g., dimyristoyl phosphatidic acid (DMPA).¹²

In the case of lipids the domains undergo a series of shape transitions upon compression of the film, which starts with the elongation of the disks to elliptical domains that evolve into striped or spiral superstructures.² That these structures are not necessarily of a temporary nature but may actually represent equilibrium shapes has become clear after extensive experimental and theoretical work, notably by the groups of McCornell and Möhwald.

The present study is devoted to an aspect of the dotted superstructures that has so far received little attention, viz., the question of their polydispersity. To the author's knowledge only one paper has appeared in which a statistical analysis of domain sizes is presented.¹²

However, it is well-known that colloidal dispersions like micelles, vesicles, and microemulsions, stabilized by a surfactant, exhibit rather wide size distributions and that this is an entropy-driven phenomenon, characteristic of large numbers of particles in the colloidal size range of which the condensed-surfactant islands in monolayers are just one example.

Recently,^{13,14} considerable progress has been reported in the theoretical description of particle size distributions based on a critical review of the concept of configurational entropy in

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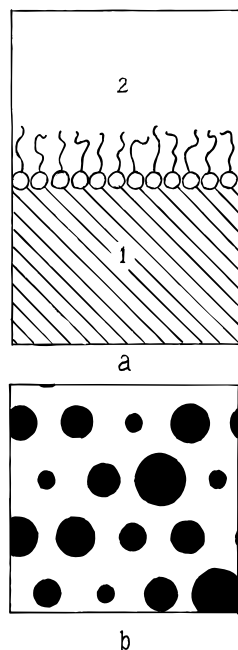


Figure 1. (a) Schematic cross section of the three-phase system under consideration. The bulk phases 1 and 2 are an aqueous support and either air or oil, respectively. (b) Top view of the film when present in the LE/LC coexistence region, with slightly exaggerated polydispersity.

mesoscopic systems. The objective of this paper is to implement these ideas in the study of phase equilibria in amphiphilic monolayers.

2. The Model

A vertical cross section of the system of interest is depicted schematically in Figure 1a. The amphiphile, which is supposed to consist of a single component, s , is confined to the interface between two immiscible bulk phases, 1 and 2, at least for surface pressures below the collapse pressure. The substrate (phase 1) is usually an aqueous solution, whereas phase 2 could be either air or an oil. If a surface pressure is applied that carries the film into the (LE/LC) coexistence region at the prevailing temperature, an epifluorescence or BAM micrograph might show a typical hexagonal pattern of islands as shown in Figure 1b, which covers a fraction, say ϕ , of the surface. For sufficiently high values of ϕ the domains are effectively immobilized as a result of the mutual electrostatic repulsion between their parallel dipole moments, which are a consequence of the fact that the molecules in the domains (d) are more densely packed than those in the surrounding phase (the "medium", m) leading to an excess dipole moment perpendicular to the film surface due to the head groups.

In the following the domains will be grouped into categories according to the number of molecules (j) they contain.

3. Free Energy of the Monolayer

The Gibbs energy of the system shown in Figure 1 can be written as

$$G = \sum_k \mu_k N_k + \mu_s N_s + \gamma A \quad (3.1)$$

where k labels the bulk components, N = number of molecules, μ = molecular chemical (or rather electrochemical) potential, and γ is the interfacial tension.

In the absence of the amphiphile (indicated by a subscript 0) this reduces to

$$G_0 = \sum_k \mu_k N_k + \gamma_0 A \quad (3.2)$$

if other parameters (pressure, p , and temperature, T) remain the same.

Subtracting eq 3.2 from 3.1 yields the Gibbs energy of the monolayer, G_{mono} , which for an interfacial system with negligible volume is indistinguishable from the Helmholtz energy, F_{mono} ; thus

$$G_{\text{mono}} = F_{\text{mono}} = \mu_s N_s - \Pi A \quad (3.3)$$

where $\Pi = \gamma_0 - \gamma$ is the macroscopic surface pressure as measured with, e.g., a film balance (N.B.: A more appropriate name to denote the excess quantity G_{mono} would be "semigrand potential"; however, henceforth we will simply use the more commonly employed generic term "free energy").

The monolayer free energy can also be written as

$$G_{\text{mono}} = -kT \ln Q \quad (3.4)$$

with k Boltzmann's constant and Q the partition function of the two-phase surfactant film.

In calculating Q a distinction has to be made between microscopic states of the film corresponding to different classifications of the islands in terms of the categories j defined previously.

Suppose we first consider all those microstates that correspond to a total number N_m of molecules in the outer (connected) phase and the remaining $N_s - N_m$ molecules divided among the islands for a given distribution $\{n_{dj}\}$, where n_{dj} is the number of domains in category j , assuming the boundaries of each one of them to be fixed in space.^{13,14}

The corresponding (restricted) partition function will be denoted by Q^* , which may be written as a product of partition functions Q_m and Q_d pertaining to the outer and the dispersed condensed phases, respectively, where the phase boundary is being considered to be part of the latter

$$Q^* = Q_m Q_d \quad (3.5)$$

(this partition function is, of course, understood to include a redundancy factor $1/N_s!$).

The partition function Q_m can be expressed in terms of thermodynamic quantities characteristic of the medium as

$$Q_m = \exp(-(N_m \lambda_{s,m}^* - \Pi_m A_m)/kT) \quad (3.6)$$

where $\lambda_{s,m}^*$ is the chemical potential of a surfactant molecule in the medium, which occupies an area A_m , evaluated at the local excess (surface) pressure Π_m .

The partition function of the $N_d = \sum_j n_{dj}$ frozen (and hence distinguishable) domains, on the other hand, takes the form of a product over categories multiplied by an exponential factor that accounts for the free energy $F_{\text{el}}^{\text{int}}$ associated with the long-range interdomain repulsion

$$Q_d = \prod_j (q_{dj})_{\text{fixed}}^{n_{dj}} \exp(-F_{\text{el}}^{\text{int}}/kT) \quad (3.7)$$

with $(q_{dj})_{\text{fixed}}$ the partition function of a single domain of type j , which can also be expressed as

$$(q_{dj})_{\text{fixed}} = \exp(-f_{dj}/kT) \quad (3.8)$$

In this formula, the free energy of an isolated category- j domain is given as

$$(f_{dj})_{\text{fixed}} = j\lambda_{s,j}^* - \Pi_j^{\text{od}} a_j + f_{\text{el},j}^{\text{self}} + \Lambda_j l_j \quad (3.9)$$

The meaning of the symbols in this expression is as follows: $\lambda_{s,j}^*$ is the chemical potential at a local surface pressure Π_j^{od} that would prevail in the domain interior in the absence of electrostatic interactions between the head groups (which would then only have a purely osmotic, or kinetic, component plus a contribution due to dispersion forces between the hydrocarbon chains, as indicated by the superscript 'od'), while the electrostatic contribution is contained in the self-energy $f_{\text{el},j}^{\text{self}}$. The free energy of the domain boundary is given by the last term where Λ_j is the line tension and $l_j = 2\pi R_j$ is the boundary length if R_j is the radius, in terms of which the domain area is $a_j = \pi R_j^2$.

In order to calculate the full partition function Q of the film, the next step would be to remove the restriction on the mobility of the islands and sum the above Q^* over all possible different (quantum) states in the phase space of the monolayer. For each spatial configuration $Q^*(\{n_{dj}\})$ can then be assigned a statistical weight factor $P(\{n_{dj}\}, F_{\text{el}}^{\text{int}})$, which counts the number of microstates consistent with a given distribution $\{n_{dj}\}$ and a certain value of the total interaction energy $F_{\text{el}}^{\text{int}}$; hence we find

$$Q = \sum_{\{n_{dj}\}, F_{\text{el}}^{\text{int}}} P(\{n_{dj}\}, F_{\text{el}}^{\text{int}}) Q_m \prod_j (q_{dj})_{\text{fixed}}^{n_{dj}} \exp(-F_{\text{el}}^{\text{int}}/kT) \quad (3.10)$$

The exact evaluation of P is clearly a formidable task, and in order to proceed it is therefore unavoidable to make rather drastic simplifying assumptions. A very plausible approximation can be made on the basis of the fact that for sufficiently large average domain sizes the mutual repulsion is rather strong, to the effect that all domains are essentially held in fixed positions in a hexagonal arrangement ("electrostatic trapping"). In the most extreme approximation the value of $\exp(-F_{\text{el}}^{\text{int}}/kT)$ is nonzero only for this array, in which case P reduces to a simple combinatorial factor, counting only the permutations among the stagnant islands that lead to different patterns, i.e.

$$P = \frac{N_d!}{\prod_j n_{dj}!} \quad (3.11)$$

(N.B.: In order to avoid similar mathematical complications as pointed out above, the authors of ref 14 had to limit their considerations to extremely dilute dispersions.)

Substituting eq 3.10 into eq 3.4, retaining only the maximum term in eq 3.10 under the logarithm, as usual, together with eqs 3.6, 3.8, 3.9, and 3.11, yields the following expression for the free energy of the monolayer

$$G_{\text{mono}} = N_m \lambda_{s,m}^* + \sum_j n_{dj} j \lambda_{s,j}^* - \Pi_m A_m - \sum_j \Pi_j^{\text{od}} n_{dj} a_j + \sum_j \Lambda_j n_{dj} l_j + \sum_j n_{dj} f_{\text{el},j}^{\text{self}} + F_{\text{el}}^{\text{int}} + kT \sum_j n_{dj} \ln(n_{dj}/N_d) \quad (3.12)$$

where the last sum is the result of applying Stirling's approximation to $\ln P$. This term can be identified as $-TS_{\text{poly}}$ where S_{poly} may be termed the "entropy of polydispersity"

$$S_{\text{poly}} = -k \sum_j n_{dj} \ln(n_{dj}/N_d) \quad (3.13)$$

and it is a special case of the more general "entropy of mixing", S_{mix} .

It should actually be compared with the "syringe-fixed" entropy of ref 13.

Equation 3.12 can be used to derive the equilibrium conditions that ensure a minimum value of G_{mono} and that eventually lead to an expression for dG_{mono} in terms of variations of the independent variables T , A , and N_s (In a recent study¹⁵ a similar procedure was actually followed, based on a simplified version of eq 3.12 in which the effects of polydispersity and interdomain interactions were not taken into account).

One such condition is that of mechanical equilibrium between a domain and its environment, which can be formulated as the requirement that $dG_{\text{mono}} = 0$ for a small isothermal change in the size of a domain while keeping j constant. This may be expressed as follows, using $A = A_m + \sum_j n_{dj} a_j = \text{constant}$ and $dl_j/da_j = 1/R_j$

$$\frac{1}{n_{dj}} \left(\frac{\partial G_{\text{mono}}}{\partial a_j} \right)_{T, A, n_{dk}, R_{i \neq j}} = \Pi_m - \Pi_j^{\text{od}} + \frac{\Lambda_j}{R_j} + \left(\frac{\partial \Lambda}{\partial R} \right)_{T, R=R_j} + \frac{1}{2\pi R_j} \left(\frac{\partial f_{\text{el},j}^{\text{self}}}{\partial R} \right)_{T, j, R=R_j} + \frac{1}{2\pi R_j} \left(\frac{\partial f_{\text{el},j}^{\text{int}}}{\partial R} \right)_{T, j, R=R_j} = 0 \quad (3.14)$$

In the derivation of eq 3.14 it should be kept in mind that terms in dG_{mono} containing differentials of intrinsic thermodynamic parameters cancel, as usual, on account of Gibbs–Duhem relations.

In this equation, the possibility of a nonzero bending elasticity of the boundary is anticipated, as evidenced by the presence of the term $\partial \Lambda / \partial R$ (as well as the subscript in Λ_j), which allows for an explicit dependence of Λ on R , while in the last term the symbol $f_{\text{el},j}^{\text{int}}$ has been introduced to represent the (average) electrostatic free energy of interaction between a category- j domain with all the other islands.

With the abbreviations

$$f_{\text{el},j} = f_{\text{el},j}^{\text{self}} + f_{\text{el},j}^{\text{int}} \quad (3.15)$$

and

$$\Pi_{j,\text{el}} = -\frac{1}{2\pi R_j} \left(\frac{\partial f_{\text{el},j}}{\partial R} \right)_{T, j, R=R_j} \quad (3.16)$$

the latter representing the electrostatic part of the excess spreading pressure in a j -type domain, the equilibrium condition eq 3.14 takes on the form

$$\Delta \Pi_j = \Pi_j^{\text{od}} + \Pi_{j,\text{el}} - \Pi_m = \frac{\Lambda_j}{R_j} + \left(\frac{\partial \Lambda}{\partial R} \right)_{T, R=R_j} \quad (3.17)$$

where $\Delta \Pi_j$ can be interpreted as the difference in local spreading pressure across the domain boundary. Equation 3.17 may be recognized as the two-dimensional analogue of the generalized Laplace equation for droplets with nonzero bending moment.

Elimination of Π_j^{od} from eq 3.12, making use of eqs 3.17 and 3.16, gives rise to the following useful formula for G_{mono}

$$G_{\text{mono}} = N_m \lambda_{s,m}^* + \sum_j n_{dj} j \lambda_{s,j}^* - \Pi_m A + \pi \sum_j n_{dj} R_j \left(\Lambda_j - R_j \left(\frac{\partial \Lambda}{\partial R} \right) \right) + \sum_j n_{dj} \left(f_{\text{el},j}^{\text{self}} - \frac{1}{2} R_j \left(\frac{\partial f_{\text{el},j}}{\partial R} \right) \right) + F_{\text{el}}^{\text{int}} + kT \sum_j n_{dj} \ln(n_{dj}/N_d) \quad (3.18)$$

Both forms of G_{mono} , eqs 3.12 and 3.18, will serve as the basis for the derivation, in the next section, of the equilibrium domain size distribution (n_{dj}/N_d) that minimizes G_{mono} .

However, before continuing with a detailed discussion of the size distribution, we will digress a little on the possibility of generalizing the treatment that led to eq 4.12 to lower fractional coverages. This involves a reevaluation of the free energy of mixing, G_{mix} , which was approximated by $F_{\text{el}}^{\text{int}} - TS_{\text{poly}}$ in the previous discussion.

If allowance has to be made for the thermal (Brownian) motion of the domains, as is expected to become necessary if they are small and far apart, the following thought experiment can be employed to calculate G_{mix} .

First, we will imagine a reference state in which the domains are kept at fixed sites “infinitely” far apart. At this point, the term $-TS_{\text{poly}}$ enters. Subsequently, they are brought together reversibly into a close-packed (“c.p.”) configuration, which occupies a total area $A_{\text{c.p.}}$. The amount of work performed during this stage will be denoted by $F_{\text{el}}^{\text{int}}(\text{c.p.})$. Finally, the domains (each one of which is assumed to retain its molecules throughout the process) will be allowed to expand reversibly against a barrier that is permeable with respect to individual molecules only, while the domains are allowed to equilibrate with their environment. This continues until the domains occupy an area A . The work done on the expanding 2D “gas” of domains is equal to $-\int_{A_{\text{c.p.}}}^A \Pi_d dA$, where Π_d is the “osmotic” pressure exerted by the domains (which now contains both a kinetic and an electrostatic part). Consequently, the generalized form of the free energy of mixing is

$$G_{\text{mix}} = F_{\text{el}}^{\text{int}}(\text{c.p.}) - \int_{A_{\text{c.p.}}}^A \Pi_d dA - TS_{\text{poly}} \quad (3.19)$$

which simplifies to the approximate form if the kinetic part of Π_d is negligible, i.e., in the case of “ideal” trapping.

According to McMillan and Mayer¹⁶ Π_d is formally identical to the pressure of a 2D fluid of disks that interact through the potential of mean force in the actual monolayer, which can be modeled as a hard-core interaction with a superimposed long-range repulsive tail, the form of which is known exactly for identical disks.¹⁹

Unfortunately, to date no attempt has been made to derive the equation of state for even a monodisperse system of this kind, so that this avenue of progress is blocked (solving this problem is probably not any easier than evaluating P , anyway).

4. Size Distribution

Next, we return to the original expression for G_{mono} , eq 3.3, which can be rewritten in equivalent ways as

$$G_{\text{mono}} = \mu_s(N_m + \sum_j n_{dj}) - \Pi A = \mu_s N_m + \sum_j n_{dj} \mu_{dj} - \Pi A \quad (4.1)$$

defining the chemical potential μ_{dj} of a domain containing j surfactant molecules. From eq 4.1 we immediately deduce

$$\mu_{dj} = j\mu_s \quad (4.2)$$

which is just the law of mass action, and our next goal is to find explicit expressions for μ_s and μ_{dj} . This approach is analogous to that followed by Overbeek¹⁷ in a study of polydispersity in microemulsions.

First, μ_s will be calculated and eq 3.12 will prove to be the appropriate expression for this purpose. By definition, μ_s is the average reversible work of inserting a surfactant molecule into the film, and because of the heterogeneity of the monolayer

there are several options. Depending on the part of the film to which the molecule is added, we can distinguish between chemical potentials $\mu_{s,m}$ and $\mu_{s,j}$, which all lead to different expressions for μ_s . Of course, phase equilibrium of the outer and dispersed phases requires that

$$\mu_{s,m} = \mu_{s,j} = \mu_s \quad (4.3)$$

From eq 3.12 one obtains first of all

$$\mu_{s,m} = \left(\frac{\partial G_{\text{mono}}}{\partial N_m} \right)_{T,A,n_{dj}} = \lambda_{s,m}^* \quad (4.4)$$

which is not a particularly useful form of μ_s in view of the present purpose, though.

On the other hand, $\mu_{s,j}$ represents the work of inserting a molecule into a domain of type j , which should be performed in such a way as to keep the radius R_j fixed (for otherwise expansion of the domain would involve work done against the line tension that is not supposed to be part of $\mu_{s,j}$).

Furthermore, it should be realized that adding a molecule to a domain of category j will promote it to category $j+1$, which will affect G_{mono} through the entropy of polydispersity, S_{poly} (without changing the total number of domains, N_d , of course). This will give rise to a term

$$kT \left[\frac{\partial(n_{dj+1} \ln(n_{dj+1}/N_d))}{\partial n_{dj+1}} - \frac{\partial(n_{dj} \ln(n_{dj}/N_d))}{\partial n_{dj}} \right]_{N_d} = kT \ln \left(\frac{n_{dj+1}/N_d}{n_{dj}/N_d} \right) = kT \left(\frac{\partial \ln(n_{dj}/N_d)}{\partial j} \right)_{N_d}$$

appearing in $\mu_{s,j}$.

From eq 3.12, with the above considerations kept in mind, the following equation for $\mu_{s,j}$ is obtained

$$\mu_{s,j} = \lambda_{s,j}^* + \left(\frac{\partial f_{\text{el},j}}{\partial j} \right)_{R_j} + kT \left(\frac{\partial \ln(n_{dj}/N_d)}{\partial j} \right)_{N_d} \quad (4.5)$$

Still, this form of $\mu_{s,j}$ is not quite suitable for use in the law of mass action, eq 4.2, because our aim is eventually to arrive at a distribution function in terms of R , the domain radius. This requires the derivatives $\partial/\partial j$ in eq 4.5 to be transformed into derivatives $\partial/\partial R$. To this end, we need to introduce the notion of the average nearest-neighbor distance δ , between molecules in the condensed phase from which the average molecular area follows as δ^2 . This allows us to write $a_j = \pi R_j^2 = j\delta^2$. It should also be clear from this discussion that two types of R -derivatives can be distinguished, i.e. $(\partial/\partial R)_j$ and $(\partial/\partial R)_\delta$, and it is the latter that is of most interest to us here. The operator $j(\partial/\partial j)_{R_j}$ can now be transformed using $j = \pi R_j^2/\delta^2$ and the relation $(\partial/\partial j)_R = (\partial/\partial j)_\delta - (\partial R/\partial j)_\delta (\partial/\partial R)_j$ into

$$j \left(\frac{\partial}{\partial j} \right)_{R_j} = \frac{1}{2} R_j \left(\left(\frac{\partial}{\partial R} \right)_\delta - \left(\frac{\partial}{\partial R} \right)_j \right) \quad (4.6)$$

which, upon application to eq 4.5, leads to

$$j\mu_s = j\lambda_{s,j}^* + \frac{1}{2} R_j \left(\frac{\partial f_{\text{el},j}}{\partial R} \right)_\delta - \frac{1}{2} R_j \left(\frac{\partial f_{\text{el},j}}{\partial R} \right)_j + \frac{1}{2} R_j kT \left(\frac{\partial \ln(n_{dj}/N_d)}{\partial R} \right)_\delta \quad (4.7)$$

where the derivative in the last term is to be understood as being taken along the size distribution (so that the condition $N_d = \text{constant}$ is automatically fulfilled).

Next, we turn our attention to μ_{dj} , which is interpreted as the reversible work of adding a whole domain of size j to the monolayer.

Since the added domain is in mechanical equilibrium with its environment, eq 3.18 will be employed in the calculation of μ_{dj} , which is a relatively straightforward task, as follows

$$\mu_{dj} = \left(\frac{\partial G_{\text{mono}}}{\partial n_{dj}} \right)_{T, A, N_m, n_{d \neq j}} = j\lambda_{s,j}^* + \pi R_j \left(\Lambda_j - R_j \left(\frac{\partial \Lambda}{\partial R} \right) \right) + f_{\text{el},j} - \frac{1}{2} R_j \left(\frac{\partial f_{\text{el},j}}{\partial R} \right) + kT \ln \left(\frac{n_{dj}}{N_d} \right) \quad (4.8)$$

Application of eq 4.2 and comparison of eqs 4.7 and 4.8 yields an ordinary differential equation for the size distribution

$$\frac{1}{2} R_j kT \left(\frac{\partial \ln(n_{dj}/N_d)}{\partial R} \right)_\delta - kT \ln(n_{dj}/N_d) = \pi R_j \left(\Lambda_j - R_j \left(\frac{\partial \Lambda}{\partial R} \right)_\delta \right) + f_{\text{el},j} - \frac{1}{2} R_j \left(\frac{\partial f_{\text{el},j}}{\partial R} \right)_\delta \quad (4.9)$$

in which all R -derivatives are now of the same type (the subscript δ added to $\partial \Lambda / \partial R$ is purely optional). The right-hand side of eq 4.9 is a known function of R , which will be abbreviated as $f(R)$.

Then, defining $y(R) = kT \ln(n_{dj}/N_d)$ this equation reads

$$\frac{1}{2} R \frac{dy}{dR} - y(R) = f(R) \quad (4.10)$$

which has the general solution

$$y(R) = -CR^2 + 2R^2 \int^R dx f(x)/x^3 \quad (4.11)$$

with C an arbitrary constant.

The integral can be readily evaluated after substitution for $f(R)$ from eq 4.9,

$$2\pi R_j^2 \int^{R_j} dR \left(\frac{\Lambda}{R^2} - \frac{1}{R} \frac{\partial \Lambda}{\partial R} \right) + 2R_j^2 \int^{R_j} dR \left(\frac{f_{\text{el}}}{R^3} - \frac{1}{2R^2} \frac{\partial f_{\text{el}}}{\partial R} \right) = -2\pi R_j^2 \int^{R_j} dR \frac{\partial(\Lambda/R)}{\partial R} - R_j^2 \int^{R_j} dR \frac{\partial(f_{\text{el}}/R^2)}{\partial R} = -2\pi R_j \Lambda_j - f_{\text{el},j} \quad (4.12)$$

Hence, with eq 4.11 and the definition of y , the size distribution becomes

$$\frac{n_{dj}}{N_d} = \exp\{-(CR_j^2 + 2\pi R_j \Lambda_j + f_{\text{el},j})/kT\} \quad (4.13)$$

The constant C can be determined from the normalization condition $\sum_j (n_{dj}/N_d) = 1$, where the sum over j can be converted into an integral over R using an appropriate weight factor, according to $\sum_j \equiv \int_0^\infty dR \, 2\pi R / \delta^2$. Thus C (which should obviously be positive) must be solved from the equation

$$\int_0^\infty dR R \exp\{-(CR^2 + 2\pi R \Lambda + f_{\text{el}})/kT\} = \delta^2 / (2\pi) \quad (4.14)$$

Written as a probability density in terms of R the distribution now assumes the form

$$\frac{n_d(R)}{N_d} = \frac{2\pi}{\delta^2} R \exp\{-(CR^2 + 2\pi R \Lambda + f_{\text{el}})/kT\} \quad (4.15)$$

A useful alternative representation of the distribution considers the fractional coverage of the surface by domains of a

particular size as a function of R , with the obvious definition $\phi(R) = n_d(R) \pi R^2 / A = (2\pi^2 N_d / A \delta^2) R^3 \exp\{\dots\}$. The total fractional coverage is then equal to $\phi = \int_0^\infty dR \phi(R)$ so that the distribution can be characterized equally well by the partial coverage $\phi(R)/\phi$, which, when written out in full, reads

$$\frac{\phi(R)}{\phi} = \frac{R^3 \exp\{-(CR^2 + 2\pi R \Lambda + f_{\text{el}})/kT\}}{\int_0^\infty dR' R'^3 \exp\{-(CR'^2 + 2\pi R' \Lambda + f_{\text{el}})/kT\}} \quad (4.16)$$

In order to complete the above expressions we clearly need to know the functional dependence of Λ and f_{el} ($= f_{\text{el}}^{\text{self}} + f_{\text{el}}^{\text{int}}$) upon R .

$\Lambda(R)$ can be obtained from an adaptation of Helfrich's equation¹⁸ for the curvature free energy of a surface, which in this simple case adopts the form

$$f_c = \frac{1}{2} K \left(\frac{1}{R} - c_0 \right)^2 \quad (4.17)$$

with f_c the curvature free energy per unit length, K the bending elastic modulus, and c_0 the spontaneous curvature.

The bending stress coefficient

$$c = \frac{\partial f_c}{\partial(1/R)} = \frac{\partial \Lambda}{\partial(1/R)} \quad (4.18)$$

can thus be readily integrated, leading to

$$\Lambda(R) = \Lambda_0 + K \left(\frac{1}{2R^2} - \frac{c_0}{R} \right) \quad (4.19)$$

where Λ_0 is the line tension for a straight boundary.

The electrostatic self-energy has been calculated by McConnell¹⁹ as

$$f_{\text{el}}^{\text{self}}(R) = \frac{\mu^2}{4\pi\epsilon_0} \left(2\pi R \ln \left(\frac{e^2 \delta}{4R} \right) + \frac{2\pi^2 R^2}{t} \right) \quad (4.20)$$

where μ is the excess dipole moment density in the domain with respect to that of its surroundings and t is a measure of the thickness of the dipole layer. The first term denotes the finite-size (or edge) effect, while the second gives the electrostatic energy of the domain which it would have had if it had been part of an infinite, uniform film. This last term should not appear explicitly in the exponent, however, because it is simply proportional to R^2 and all such terms will be absorbed into CR^2 .

Finally, the contribution $f_{\text{el}}^{\text{int}}$ can only be estimated since the interaction energy of a single domain of radius R with a polydisperse set of domains cannot be calculated exactly. However, it will be shown later that the size distributions in most practical cases are fairly narrow so that a reasonable approximation might be to calculate $f_{\text{el}}^{\text{int}}$ from the electrostatic interaction between equally sized domains that are arranged in a regular hexagonal array. This problem has also been solved by McConnell,¹⁹ and the result can be quoted in the form

$$f_{\text{el}}^{\text{int}}(R, \phi) = 2\pi R k' (g(\phi) \phi^{5/2})' \mu^2 / 4\pi\epsilon_0 \quad (4.21)$$

where $k' = (3\pi/2)(\sqrt{3}/2\pi)^{3/2}$ and $g(\phi)$ is a power series that is given explicitly in ref 19. $f_{\text{el}}^{\text{int}}$ is seen to depend parametrically on ϕ , so that the same will be true for C and the distribution functions $n_d(R)/N_d$ and $\phi(R)/\phi$.

That a judicious choice of $f_{\text{el}}^{\text{int}}$ is of critical importance can be illustrated by investigating as an alternative a seemingly

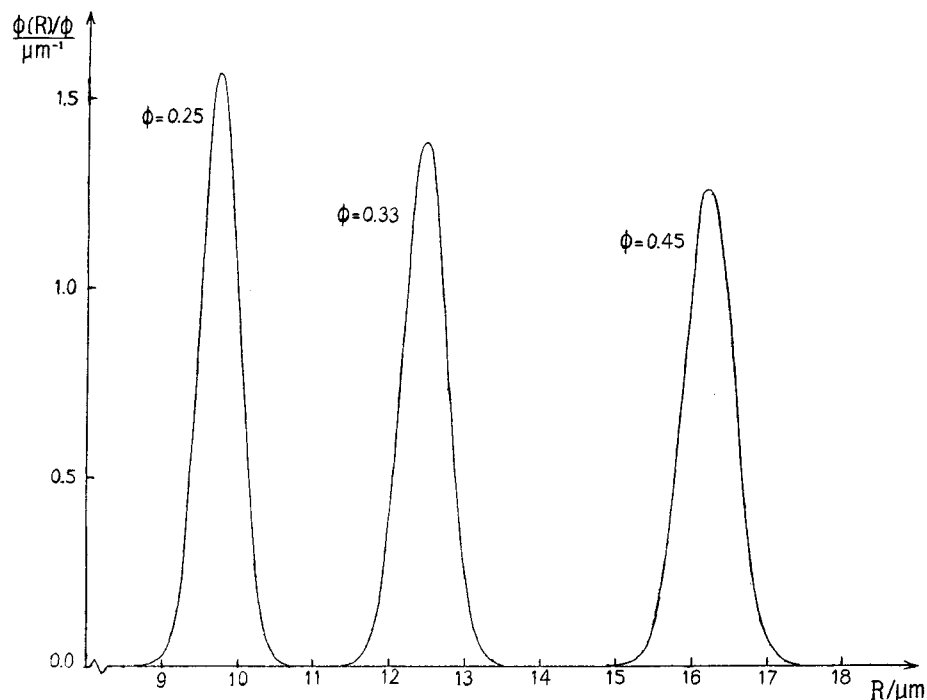


Figure 2. Size distributions in terms of partial fractional coverage $\phi(R)/\phi$ vs. R according to eq 4.16 for three values of the fractional coverage ϕ , as indicated. Parameter values are $\delta = 10 \text{ \AA}$, $2\pi\Lambda_0/kT = 1071 \text{ } \mu\text{m}^{-1}$, $2\pi\mu^2/4\pi\epsilon_0kT = 153 \text{ } \mu\text{m}^{-1}$, and $K = 0$.

reasonable model in which $f_{\text{el}}^{\text{int}}$ is calculated as the electrostatic work of inserting a polar disk of radius R and dipole moment density μ in a fictitious film with uniform dipole moment density $\mu\phi$, which results if the excess dipole moments of all domains are smeared out uniformly over the entire surface. This mean field approach can be shown to amount to simply replacing μ in $f_{\text{el}}^{\text{self}}$ by $\mu(1 - \phi)$. The resulting trends in the average domain sizes with varying ϕ are, however, in strong disagreement with those observed experimentally, and this approach therefore has to be discarded as fruitless (N.B.: Yet another weak point of this model is its apparent inability to account for trapping).

It might be possible to further improve upon the approximation implicit in eq 4.21 if an expression were available for the interaction energy of a domain of variable radius R with an infinite array of domains all having equal (averaged) radii $\langle R \rangle$. This average radius can then be calculated in a self-consistent manner with the aid of the number distribution, eq 4.15, in conjunction with the normalization condition, eq 4.14, leading to a size distribution that is likely to be more accurate, considering the dynamic nature of the equilibrium.

In the following section the implications of eq 4.16 (with eqs 4.19–4.21) will be explored by means of a typical example.

5. Numerical Example

The availability of microscopic images of amphiphile superstructures allows the direct verification of some of the results predicted by the theory developed in the preceding sections. In particular, the variation of average size with monolayer compression, measured in terms of LC fractional coverage (ϕ), can be easily followed. A well-documented case is presented by DMPA,¹² which displays hexagonal arrangements of circular domains over a rather wide range of ϕ values.

A theoretical analysis of this type has been conducted by McConnell¹⁹ assuming monodispersity, which led to good quantitative agreement with experimental trends. By virtue of the nature of the model this could be achieved with just one fit parameter.

Within the framework of the present theory a similar agreement can only be arrived at after specifying the values of no less than five adjustable parameters, viz., μ , δ , Λ_0 , K , and c_0 , but here the payoff will be in the form of more detailed information regarding the size distributions (and remember there is a different one for each ϕ).

In the case of DMPA a good fit is obtained if we put $K = 0$, which then leaves only the three parameters μ , δ , and Λ_0 to be evaluated as is evident from eq 4.19.

The lack of boundary stiffness is most likely due to an absence of tilt organization within the domains. That this need not always be the case has become clear after the observation of radial tilt regions ("star defects"). These domain substructures (which typically contain 5–7 segments) result from discontinuous changes in molecular orientation at the segment boundaries. Examples of this sort are presented by 1-monoglyceride monolayers.²⁰

Figure 2 depicts the results of substituting parameter values $\delta = 10 \text{ \AA}$, $2\pi\Lambda_0/kT = 1071 \text{ } \mu\text{m}^{-1}$, and $2\pi\mu^2/4\pi\epsilon_0kT = 153 \text{ } \mu\text{m}^{-1}$ into eqs 4.14, 4.16, 4.20, and 4.21. Three ϕ values are considered, $\phi = 0.25, 0.33$, and 0.45 , which are expected to be high enough for the domains to be immobilized. If we define a scaled normalization factor as $C\delta^2/kT$, its values for the three curves are calculated as 15.520, 12.179, and 9.373, respectively, on the basis of eq 4.14.

Looking at this figure we see that the distributions $\phi(R)/\phi$ are fairly narrow, are peaked at typical values of R in the order of $10 \text{ } \mu\text{m}$, and have a Gaussian shape. Two trends are obvious: first a steady increase in the average domain radius $\langle R \rangle$, which agrees well with experimental observations, and second a slight broadening of the distribution with increasing ϕ .

It is interesting to note that, at the same time, the width of the distribution with respect to the average, which defines the degree of polydispersity $\sigma = \sqrt{\langle R^2 \rangle / \langle R \rangle^2 - 1}$, decreases, as is to be expected.

The alternative representation of the distribution in terms of number fractions, $n_d(R)/N_d$ (eq 4.15), leads to curves that look

very similar to those shown in Figure 2, and have been omitted for this reason.

6. Discussion and Conclusion

The aim of the present study is to determine how a one-component amphiphilic monolayer, when present in a semi-condensed state, strives to minimize its free energy via dispersion of one phase into the other (under certain restrictions that justify the application of simplifying assumptions). This tendency toward dispersion is prompted by the resulting gain in entropy of mixing, a purely collective phenomenon.

However, other effects come into play as a result of dispersion, which either counteract this trend, as is the case with line tension, or boost it, like the negative contribution to the electrostatic self-energy of a domain due to its fringe field (see eq 4.20), the effect of which is, in turn, partly offset by the interdomain repulsion (eq 4.21).

In the case of surfactants with dissociable head groups, the electrostatic effects can be manipulated via the parameter μ , which is proportional to the surface charge density and the Debye screening length and hence depends on pH and ionic strength of the aqueous support.

The overall effect of the competition between the various tendencies described above on the distribution function is contained in a Boltzmann-like factor, in line with other results reported for microemulsions and vesicles.¹⁴

An unusual feature is the occurrence of a normalization factor C in the exponent, which attests to the fact that our result is by no means trivial.

From the example given in section 5 it can be inferred that for domains with radii on the order of 10 μm the distributions are narrow, a circumstance that may be taken as a justification, with hindsight, of the assumption that was implicitly made in

writing P as in eq 3.11, implying that $F_{\text{el}}^{\text{int}}$ is virtually invariant under permutations of the N_d domains, as well as for the use of eq 4.21 for $f_{\text{el}}^{\text{int}}$.

Moreover, the narrowness of the distributions gives support to the statement that equilibrium polydispersity is a hallmark of the mesoscopic regime of particle sizes, which is roughly demarcated by microscopic objects having sizes typical for the LC islands found in amphiphilic monolayers.

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