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Boundary Tension Between Amphiphilic Layers[1]

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The structure and tension of the region of contact where an oil phase, a water phase, and a microemulsion phase meet, are theoretically investigated. The analysis has as a starting point a Landau theory-like expression for the free energy in which, besides the usual gradient of the density squared term, a term proportional to the second derivative of the density squared is present, while the coefficient of the squared gradient term is taken to be negative in the microemulsion phase. It is shown that a first-order wetting transition exists at which point infinitely many ($n = 0, 1, 2, \ldots$) surface phases can coexist, each described by the presence of a different thickness of the microemulsion phase between the oil and the water phase. This situation physically describes the coexistence of layers of amphiphilic molecules with different thicknesses between a water and an oil bulk phase, the thickness of one amphiphilic layer being equal to l_0. We present the calculation of the density profile and the boundary tension of the contact region of a coexisting $n = 0$ and $n = 1$ surface phase, e.g., between the oil–water interface with a single amphiphilic layer present and the oil–water interface where three amphiphilic layers are present.

KEY WORDS: amphiphiles; boundary tension; Landau theory.

1. INTRODUCTION

When oil, water, and a surfactant are mixed at different concentrations, a wide variety of phases is observed [1]. At low concentrations of added surfactant (inverted) micelles of small droplets of oil (water) are surrounded by surfactant, while at high concentrations of surfactant complex structures arise, of which the lamellar phase is probably the best known. In this phase, a large number of layers of amphiphiles are stacked between the oil and the water phase. In certain parts of the phase diagram only one or a few layers of amphiphiles will be present at the oil–water interface, but

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under proper conditions a larger number of layers can coexist at this interface. The coexisting layers of different thicknesses meet to form a contact line and it is the theoretical calculation of the structure and tension of this line that is the subject of this paper.

Recently, a number of experiments focused on measuring the line (or boundary) tension between layers of amphiphilic material on water in air [2–4]. In the experiment of Benvegnu and McConnell [2] in 1992, the boundary tension of lipid domains at the air–water interface was measured by investigating the distortion of these domains under shear. By varying the applied surface pressure they found values for the line tension ranging from 5×10^{-14} to 1.6×10^{-12} N. In 1993, the boundary tension between smectic membranes of different thicknesses was measured by Pieranski et al. [3]. This was done by measuring both the surface tension σ_N as a function of the number of layers N and the critical radius R of circular domains of smectic phase with thickness $N-1$ surrounded by a smectic phase consisting of N layers. The boundary tension τ is then calculated from the two-dimensional analogue of Laplace's law: $\sigma_N - \sigma_{N-1} = \tau/R$. They find that the boundary tension is independent of N and equal to 4.15×10^{-11} N.

Theoretical investigations [5] of the structure and tension of the contact line have been limited to the case where the three phases, that meet to form the line, are not complex. The three phases are either two liquids with their vapor [6, 7] or a liquid and its vapor near a structureless wall [8, 9]. In these cases the line tension has been calculated along three-phase coexistence when the three phases meet in a line [6, 8], as well as along the prewetting line where prewetting phases consisting of different thicknesses coexist [7–9]. In the Landau model that we will use to calculate the boundary tension, the surface free energy is a functional of only one density, m. The explicit form was first given by Gompper and Schick [10] and has been successfully used to describe a number of different microemulsion phases [10–12].

In the next section we describe the Landau theory for microemulsions and in Section 3 we extend the theory to calculate the structure and tension of coexisting amphiphilic layers. In the last section a brief summary of results is given.

2. LANDAU MODEL

The model for the free energy as a functional of the density m is taken to be of the following form [10]:

$$F[m] = \int_{-\infty}^{\infty} dz \left[\frac{1}{2} g(m) \left(\frac{\partial}{\partial z} m(z) \right)^2 + \frac{c}{2} \left(\frac{\partial^2}{\partial z^2} m(z) \right)^2 + f(m) \right] \qquad (1)$$

where we have assumed symmetry in the x and y direction so that the density is a function of z alone. The above free-energy functional is of the usual Landau form where the expansion in square gradients is up to a second derivative squared term with constant positive coefficient c. The addition of such a term is necessary for stability since we will allow $g(m)$, the coefficient of the squared gradient term, to be negative when m equals the density in the middle phase. The free-energy density $f(m)$ has to allow for the coexistence of three phases, namely, the oil phase, the water phase, and the middle phase, and should therefore exhibit three equal minima at the three bulk densities. Specifically, we assume $g(m)$ and $f(m)$ to be given by the following form [10]:

$$f(m)=\begin{cases}(m+1)^2\\ m^2\\ (m-1)^2\end{cases}\qquad g(m)=\begin{cases}1 & m<-\frac{1}{2}\\ g & -\frac{1}{2}<m<\frac{1}{2}\\ 1 & m>\frac{1}{2}\end{cases}\tag{2}$$

Units are chosen such that the curvature of $f(m)$ at its minima is equal to 2, $g(m)=1$ in the oil and water phase, and the density of the oil and water phase is equal to ± 1. The structure of $g(m)$ follows from scattering experiments in the three bulk phases. The structure factor $S(k)$ in the middle phase calculated from Eq. (1) is given by

$$S(k)\propto\frac{1}{f_2+gk^2+ck^4}\tag{3}$$

where k is the wave number of the scattered light and f_2 denotes the second derivative of $f(m)$ in the bulk middle phase. While the oil and water phases exhibit a peak in the structure factor at $k=0$, the peak in the middle phase is at $k>0$, signifying that $g<0$. The presence of amphiphiles in the middle phase indicates the fact that gradients in the density are now favored by the system. We can understand this in terms of the amphiphilic molecules trying to bring the oil and water phases, of different densities, closer together. One of the consequences of this is that the more amphiphilic a surfactant is, the more negative g will be.

The above forms for $f(m)$ and $g(m)$ are a specific case of the forms given by Gompper and Schick [10]. Here we have chosen, for simplicity, the density of the middle phase ($m=0$) to be half of the sum of the density of the water ($m=1$) and the density of the oil phase ($m=-1$). Furthermore, the values of $g(m)$ in the water and oil phase are chosen equal to each other and the value of $f(m)$ at the minimum corresponding to the stable middle phase is taken to be equal to the value at the minima for the water and oil phase. It should be noted that $g(m)$ and $f'(m)$ are discontinuous at $m = \pm\frac{1}{2}$, the value of the densities where the parabolas of $f(m)$ meet, and that therefore the density profile that minimizes Eq. (1) will not be analytic when $m = \pm\frac{1}{2}$. The minimizing density profile is found in *two* steps. First, one chooses a fixed height l defined so that $m(z = l) = \frac{1}{2}$, the height at which one of the discontinuities occurs, namely, in the *third* derivative of the density with respect to z. We choose the $z = 0$ plane such that $m(z = 0) = 0$, and by the symmetry of Eq. (2) we then have that $m(-z) = -m(z)$ and consequently $m(z = -l) = -\frac{1}{2}$. The Euler–Lagrange equations for the density profile that minimizes the free-energy functional in Eq. (1) are then solved in the three regions $z < -l$, $-l < z < l$, and $z > l$ under the constraint that the density and its first and second derivatives are continuous at $z = \pm l$. Second, the surface free energy is calculated as a function of l by inserting the density profile into Eq. (1) and is subsequently minimized with respect to l to yield the equilibrium profile.

The Euler–Lagrange equations in the three regions are

$$\begin{aligned} m''(z) &= 2(m(z)+1) + cm''''(z), && z < -l \\ gm''(z) &= 2m(z) + cm''''(z), && -l < z < l \\ m''(z) &= 2(m(z)-1) + cm''''(z), && z > l \end{aligned} \tag{4}$$

where a prime indicates differentiation with respect to its argument. The solutions of these differential equations are simple sums of exponentials

$$m(z) = \begin{cases} -1 + A_1 e^{k_1 z} + A_2 e^{k_2 z}, & z < -l \\ B_1 \sinh(k_{m,1} z)\cos(k_{m,2} z) \\ \qquad + B_2 \cosh(k_{m,1} z)\sin(k_{m,2} z), & -l < z < l \\ 1 - A_1 e^{-k_1 z} - A_2 e^{-k_2 z}, & z > l \end{cases} \tag{5}$$

where we have defined the inverse length

$$\begin{aligned} k_1 &= (2c)^{-1/2}(1 + (1-8c)^{1/2})^{1/2}, & k_{m,1} &= (2c)^{-1/2}\left(\frac{g}{2} + (2c)^{1/2}\right)^{1/2} \\ k_2 &= (2c)^{-1/2}(1 - (1-8c)^{1/2})^{1/2}, & k_{m,2} &= (2c)^{-1/2}\left(-\frac{g}{2} + (2c)^{1/2}\right)^{1/2} \end{aligned} \tag{6}$$

and where we have used $m(-z) = -m(z)$ and the fact that the densities must be equal to the bulk water and oil densities at $z = \pm\infty$. We are interested mainly in the case where all the k_i and $k_{m,i}$ are real and positive. This poses as restriction for the values of c and g, $0 < c < \frac{1}{8}$, and $|g| < 2(2c)^{1/2} \equiv -g^*$.

For fixed l, one now is able to determine the four unknowns, A_1, A_2, B_1, and B_2, by requiring the density to be equal to $\pm\frac{1}{2}$ at $z = \pm l$ and the density profile and its first and second derivative to be continuous at this point. The surface free energy as a function of l, which we denote $\sigma(l)$, is subsequently calculated by inserting the profiles from Eq. (5) into Eq. (1). The analytic answer is rather lengthy and we do not reproduce it here [14]. A typical example of $\sigma(l)$ is shown in Fig. 1. In this example $c = 0.01$ and, from top to bottom, $g = 0.3$, 0.2, 0, -0.2, $g^* = -0.282842...$. The filled circles indicate the location of a (local) minimum. The first minimum (smallest l) is the one of lowest free energy when $g^* < g < -g^*$. The system is then in the partially wet regime: Only a microscopic amount of middle phase can be present at the oil-water interface. When a bulk of middle phase is present in the system, the three phases (oil, water, and middle phase) meet at a line of contact with the three contact angles determined by the three surface tensions according to Neumann's rule [13]. It was already noted by Schick [12] that the addition of the second derivative squared term in Eq. (1) leads to the possibility of the presence of a nonwet regime in a theory with a single order parameter.

When the value of g is increased, the value of l, being (half) the thickness of the middle phase, at the first minimum, continuously increases and becomes infinite at $g = -g^*$. For $g > -g^*$ the system is in a regime of complete wetting: The middle phase completely intrudes between the oil and the water phases (top curve in Fig. 1). The three surface tensions are now related to each other by Antonow's rule [13, 15], which states that

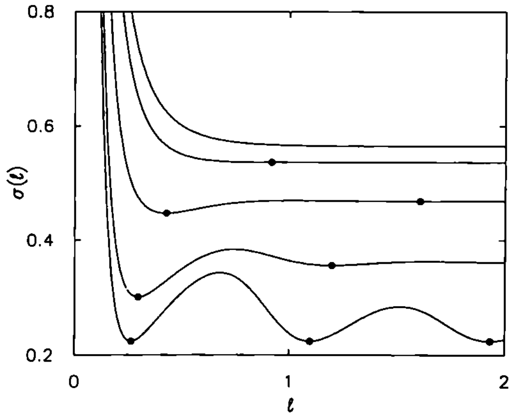

Fig. 1. The surface free energy as a function of l for $c = 0.01$ and, from top to bottom, $g = 0.3$, 0.2, 0, -0.2, $g^* = -0.282842...$. The circles indicate the location of a (local) minimum. At $g = g^*$ the values of the surface free energy at all the minima are equal.

the surface tension of the oil–water interface equals the sum of the surface tensions of the oil–middle and water–middle interfaces. The condition $g = -g^*$ denotes the location of a (continuous) wetting transition.

Upon decreasing the value of g one finds the value of the surface free energy at its minimum to decrease. This indicates that the surface tension of the oil–water interface can be lowered by adding a surfactant with increasing amphiphilicity. Figure 1 shows that the value of the free energy at the second minimum decreases as well and starts to compete with the first minimum. The density profile corresponding to the first minimum increases monotonically as a function of z, while the density profile corresponding to the second minimum exhibits a maximum and a minimum in the middle-phase region. We will interpret the shape of the curve corresponding to the second minimum as the presence of three layers of amphiphiles, while at the first minimum only one layer of amphiphiles is present.

When $g = g^*$ the surface free energy of the second minimum is exactly equal to the surface free energy of the first minimum [14]. This behavior can be seen in the lowest curve in Fig. 1. Not only does the surface free energy at the second minimum become equal to the surface free energy of the first minimum, but at $g = g^*$ *infinitely* many equal minima of the surface free energy occur as a function of l. This reflects the fact that at $g = g^*$, surface phases with 1, 3, 5,... layers of amphiphiles present can coexist. In some sense, $g = g^*$ locates a (first-order) wetting transition since the number of layers may be infinitely large.

In the next section we calculate the structure and boundary tension of the contact line where two surface structures, one corresponding to the first and the other corresponding to the second minimum at $g = g^*$ in Fig. 1, meet. Since these surface structures can coexist only when $g = g^*$ we first investigate how the above formulas are simplified when $g = g^*$. When $g = g^*$, the definition in Eq. (6) implies that $k_{m,1} = 0$. As a result the density profile, Eq. (5), is now given by

$$m(z) = \begin{cases} -1 + A_1 e^{k_1 z} + A_2 e^{k_2 z}, & z < -l \\ B_1 \sin(k_m z) + B_2 z \cos(k_m z), & -l < z < l \\ 1 - A_1 e^{-k_1 z} - A_2 e^{-k_2 z}, & z > l \end{cases} \qquad (g = g^*) \qquad (7)$$

with $k_m \equiv (2/c)^{1/4}$. Again, for fixed l we can determine the four unknowns, A_1, A_2, B_1, and B_2, by requiring the density to be equal to $\pm\frac{1}{2}$ at $z = \pm l$ and the density profile and its first and second derivatives to be continuous at this point. The surface free energy has (equal) minima when

$$l = l_{\mathrm{eq},n} \equiv \frac{1}{k_m}\left[\arctan\left(\frac{k_1 + k_2}{2k_m}\right) + n\pi\right] \qquad (n = 0, 1, 2, \ldots) \qquad (8)$$

where the subscript eq denotes that these values of l belong to the equilibrium state of the system. The (equilibrium) surface tension at these minima is given by

$$\sigma \equiv \sigma(l_{\text{eq},n}) = \frac{k_m^2 - 4}{4(k_1 + k_2)} \tag{9}$$

Here we have defined σ as the surface free energy after minimization with respect to l.

3. BOUNDARY TENSION

In this section, we calculate the structure and tension of the contact line between two surface phases with thicknesses $l = l_{\text{eq},0}$ and $l = l_{\text{eq},1}$. We will choose the contact line parallel to the y-direction and locate the surface phase with $l = l_{\text{eq},0}$ at $x = -\infty$ and the surface phase $l = l_{\text{eq},1}$ at $x = \infty$. The density profile, $m(x, z)$, will now depend not only on z but also on x. It is obtained from minimizing the surface free-energy functional in Eq. (1), generalized to accommodate for an x- and z-dependent density,

$$\begin{aligned} F[m] = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dx \left\{ \frac{1}{2} g(m) \left[\left(\frac{\partial m}{\partial x} \right)^2 + \left(\frac{\partial m}{\partial z} \right)^2 \right] \right. \\ \left. + \frac{c}{2} \left[\left(\frac{\partial^2 m}{\partial x^2} \right)^2 + \left(\frac{\partial^2 m}{\partial z^2} \right)^2 \right] + f(m) \right\} \end{aligned} \tag{10}$$

We make a variable transformation $x \to l(x)$ and investigate the density as a function of z and $l(x)$: $m(l(x), z)$ [9]. The function $l(x)$ is defined by $m(z = l(x), x) = \frac{1}{2}$, in analogy to the way it is defined in the previous section, but l is now a function of x. The line $z = l(x)$ defines a line of points where the density profile has a discontinuous third derivative with respect to z. For $x \to \pm\infty$ the function $l(x)$ is equal to the constant $l_{\text{eq},0,1}$.

With the substitution $x \to l(x)$ the surface free energy in Eq. (10) is a functional of $l(x)$,

$$F[l] = \int_{-\infty}^{\infty} dx \left[\tfrac{1}{2}\sigma_0(l)(l'(x))^2 + \tfrac{1}{2}\sigma_1(l)(l''(x))^2 + \tfrac{1}{2}\sigma_2(l)(l'(x))^4 + V(l) \right] \tag{11}$$

where we have defined

$$\sigma_0(l) \equiv \int_{-\infty}^{\infty} dz\, g(m) \left(\frac{\partial}{\partial l} m(l, z) \right)^2$$

$$\sigma_1(l) \equiv c \int_{-\infty}^{\infty} dz \left(\frac{\partial}{\partial l} m(l, z) \right)^2$$

$$\sigma_2(l) \equiv \frac{c}{3}\int_{-\infty}^{\infty} dz \left[\left(\frac{\partial^2}{\partial l^2} m(l,z)\right)^2 - 2\left(\frac{\partial}{\partial l} m(l,z)\right)\left(\frac{\partial^3}{\partial l^3} m(l,z)\right)\right]$$

$$V(l) \equiv \int_{-\infty}^{\infty} dz \left[\frac{1}{2} g(m)\left(\frac{\partial}{\partial z} m(l,z)\right)^2 + \frac{c}{2}\left(\frac{\partial^2}{\partial z^2} m(l,z)\right)^2 + f(m)\right] \tag{12}$$

The functions $\sigma_i(l)$ and $V(l)$ as defined above can be determined only if one has knowledge of the density profile $m(l,z)$. The way we proceed here is to approximate the density profile $m(l,z)$ by the density profile $m(z;l)$ as defined in Eq. (7). Then the functions $\sigma_0(l)$, $\sigma_1(l)$, $\sigma_2(l)$, and $V(l)$ can be evaluated explicitly [9]. From a comparison of the definition of $V(l)$ in Eq. (12) with Eq. (1), we immediately deduce that $V(l)$ equals the previously defined $\sigma(l)$. The surface free-energy functional has the form of the interface displacement model [8, 15] but with the addition of the $\sigma_1(l)$ and $\sigma_2(l)$ terms. The form is analogous to the Landau form in Eq. (1), and similarly to the coefficient of the gradient squared term in Eq. (1), $\sigma_0(l)$ is negative for some values of l, while the coefficient of the second derivative squared term, $\sigma_1(l)$, is positive but small.

The Euler–Lagrange equation for the minimization of the surface free-energy in Eq. (11) leads to the following, third-order, nonlinear differential equation

$$-\tfrac{1}{2}\sigma_0(l)(l')^2 - \tfrac{1}{2}\sigma_1(l)(l'')^2 - \tfrac{3}{2}\sigma_2(l)(l')^4 + \sigma_1(l)\, l'''l' + \sigma_1'(l)\, l''(l')^2 + V(l) = \sigma \tag{13}$$

Although the functions $\sigma_0(l)$, $\sigma_1(l)$, $\sigma_2(l)$, and $V(l)$ are all known analytically, the expressions for them are very lengthy and the solution to the above differential equation with the appropriate boundary conditions can be found only numerically. The resulting profile is exact when $x \to \pm\infty$ and only approximately correct in between. Since the surface free energy is minimized with respect to the whole function $l(x)$, we expect the approximation to be very accurate.

Substituting the density profile $m(x,z)$ into the expression for the surface free energy in Eq. (10) and subtracting the surface free-energy contributions from the surface phases at $\pm\infty$ gives the boundary tension, τ, between the two surface phases. The boundary tension as a function of c is shown as the circles in Fig. 2. For small c the boundary tension increases rapidly with increasing c, then it goes through a maximum and decreases until at a certain value of $c = c^* = 0.1254\ldots$ it becomes zero. For $c > c^*$ the boundary tension is negative, signifying that the interface between the two surface phases is no longer stable.

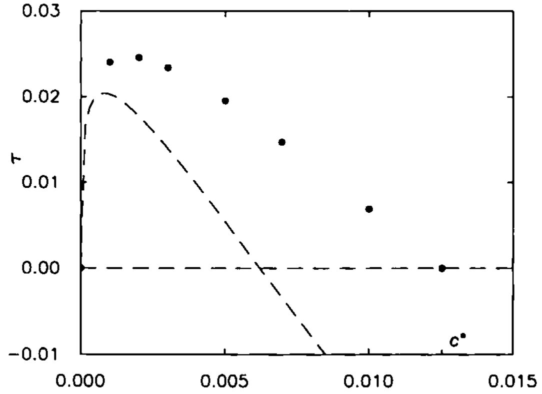

Fig. 2. Boundary tension as a function of c (circles). The boundary tension is negative for $c > c^* = 0.1254...$ and is zero when $c = 0$. The dashed curve is the result of an analytic expansion for small c [see Eq. (14)].

Although the differential equation in Eq. (13) cannot be solved analytically, the coefficients of the first two terms in an expansion in small c can be found numerically. The result is that the line tension, for small c, is given by [14]

$$\tau = 0.73632c^{3/8} - 2.6197c^{5/8} + \mathcal{O}(c^{7/8}) \qquad (14)$$

The resulting line tension in the expansion in small c is shown in Fig. 2 as the dashed curve. Although the qualitative behavior is correctly described by the above approximation, quantitatively the expansion works only for very small c.

4. SUMMARY

We have presented a mean-field calculation of the structure and tension between surface phases comprising of one and three amphiphilic layers between a bulk oil and a water phase. The theory that we have used is a single-order-parameter Landau model first proposed by Gompper and Schick in 1990 [10]. We have shown that in a closely related model a (first-order) wetting transition exists, at which point amphiphilic layers of different thicknesses can coexist. Except for an initial sharp increase, we find that the boundary tension between one and three layers of amphiphiles decreases when the amphiphilicity of the surfactant molecules is increased. This behavior is analogous to the behavior of the surface tension of the oil–water interface when surfactant is added.

A detailed comparison of the calculation presented here with experiments is not yet possible since measurements of the boundary tension have been carried out in similar systems but not for the oil–water–surfactant system. In order to make such a comparison, scattering experiments of the bulk middle phase have to be carried out in addition, in order to determine the relevant parameters g and c.

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