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Phase transitions of a confined complex fluid

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The effect of confinement on a microemulsion, a disordered, fluid phase with two characteristic length scales, ξ the correlation length, and d the wavelength of oil and water density variations, is studied within a simple Ginzburg-Landau theory. We find a qualitative difference between those systems which contain a strong amphiphile as opposed to a weak one. As the distance between walls is increased in the former, a series of first-order transitions occurs which, in principle, can continue without limit, while in the latter, only a small number of such transitions are expected. Such transitions will be manifest in discontinuities in the forces between the walls. In our model calculation, the boundary between strong and weak amphiphiles is $2\pi\xi/d=\sqrt{3}$, a value easily accessible experimentally.

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I. INTRODUCTION

The effect of confinement between two walls on ordinary, simple fluids has received much attention in recent years. Significant changes in the fluid's properties can occur when the distance between walls becomes comparable to some characteristic length of the system. For example, the thickness of a wetting layer is such a characteristic length. If capillary condensation occurs when the thickness of the wetting layer is comparable to the distance between walls, the pressure at which it occurs differs significantly from the equilibrium condensation pressure [1]. If the walls favor different bulk phases, then two-phase coexistence is greatly affected when these lengths are comparable, and can be suppressed entirely [2]. Another important length is the molecular size, as each wall can induce layering that extends out into the fluid to several such lengths. When the distance between walls becomes of this order, such structures overlap, causing an increase in viscosity of orders of magnitude. Confined to sufficiently small spacing, the entire film becomes glassy or crystalline [3].

Besides these lengths, which characterize an ordinary, simple fluid, an additional length becomes important in complex fluids, such as bicontinuous [4] microemulsions and polymer-copolymer melts. In such systems, correlation functions show exponentially damped *oscillatory* behavior [5]. The fluid appears to have internal structure that is periodic, due to the tendency of the amphiphile to order the other two components, and this new wavelength is crucial in describing the properties of the system.

The effect of confinement on amphiphilic systems has, so far, been studied mainly in lamellar phases, in which the order induced by the amphiphile is long ranged and the isotropy is lost. As computer simulations show, the transition from the ordered phase with lamellar parallel to the walls is relatively unaffected by the confinement if the spacing between walls is a multiple of the lamellar spacing, whereas it is strongly suppressed if the wall distance is half odd-integer times the spacing [6]. It is found experimentally [7] that, within the lamellar phase, the forces between the walls oscillate as a function of their separation, with a periodicity matching the lamellar spacing. Within a period, the force need not be a smooth function of distance, but can exhibit discontinuities. This has been studied theoretically for systems of amphiphiles [8] and copolymers [9]. The discontinuities are related to the change in the number of layers between the walls from n to $n\pm1$ or $n\pm2$.

That macroscopic quantities, such as the force between walls, reflect the properties of a bulk ordered phase confined by them is not surprising. However, when the confined phase is a microemulsion, which is also characterized by a period d as well as correlation length ξ but yet is disordered, it is not clear what effect will be manifest at the walls. It is this issue that we study here. A one-component Ginzburg-Landau theory is employed [10]. We find that there is a qualitative difference in the behavior between strong and weak amphiphiles, with the former giving rise to oscillatory forces between the walls whose amplitude is damped exponentially with the separation, while the latter are characterized by only a small number of oscillations followed by a monotonic exponential decay. In the model, the sharp change in behavior at finite separations is a consequence of a surface phase transition that occurs in the semi-infinite system. Interestingly, this transition does not occur when the ratio of the two lengths of the microemulsion $2\pi\xi/d$ vanishes, as at the disorder line, or takes the value unity, as at the Lifshitz line, but at an independent value, which in our calculation is $\sqrt{3}$. This is easily attainable with a good amphiphile [5,11].

Our paper is organized as follows. After introducing the model in Sec. II, we derive in Sec. III a general expression for the density profile and the free energy of a slab of oil, or water, or of middle phase. We study in Sec.

IV the effect of confinement on the middle phase, with particular emphasis on the free energy, the wall forces, and the phase diagram. We summarize and discuss our results in Sec. V.

II. MODEL

We employ an extension of the Ginzburg-Landau functional introduced by Gompper and Schick [10],

$$\mathcal{F}=\int d^3r[c(\Phi)(\nabla^2\Phi)^2+g(\Phi)(\nabla\Phi)^2+f(\Phi)]\ , \qquad (1)$$

where the scalar order parameter $\Phi(\mathbf{r})$ is the difference between the local concentrations of oil and water. For a fluid confined between parallel walls, we assume that Φ varies only in the direction perpendicular to them. We also introduce surface fields h_1 and κ_1, which couple to Φ and its first derivative, respectively. With these fields, one can describe the preference of the walls for oil, water, or amphiphile. We have for the total free energy then,

$$\mathcal{F}=\int_0^L dz\left[c(\Phi)\left[\frac{d^2\Phi}{dz^2}\right]^2+g(\Phi)\left[\frac{d\Phi}{dz}\right]^2+f(\Phi)\right]$$
$$-h_1(\Phi(0)+\Phi(L))$$
$$-\kappa_1\left[\left[\frac{d\Phi}{dz}\right]_{z=0}-\left[\frac{d\Phi}{dz}\right]_{z=L}\right]. \qquad (2)$$

The order-parameter profile which minimizes (2) satisfies the Euler-Lagrange equation

$$2c(\Phi)\frac{d^4}{dz^4}\Phi+c'(\Phi)\left[4\frac{d}{dz}\Phi\frac{d^3}{dz^3}\Phi+3\left[\frac{d^2}{dz^2}\Phi\right]^2\right]$$
$$+2c''(\Phi)\left[\frac{d}{dz}\Phi\right]^2\frac{d^2}{dz^2}\Phi-2g(\Phi)\frac{d^2}{dz^2}\Phi$$
$$-g'(\Phi)\left[\frac{d}{dz}\Phi\right]^2+f'(\Phi)=0\ , \qquad (3)$$

and the boundary conditions

$$h_1+2g\frac{d}{dz}\Phi-2\frac{d}{dz}\left[c\frac{d^2}{dz^2}\Phi\right]\Bigg|_0=0\ ,$$
$$-h_1+2g\frac{d}{dz}\Phi-2\frac{d}{dz}\left[c\frac{d^2}{dz^2}\Phi\right]\Bigg|_L=0\ , \qquad (4)$$

and

$$\kappa_1+2c\frac{d^2}{dz^2}\Phi\Bigg|_0=0\ ,$$
$$\kappa_1+2c\frac{d^2}{dz^2}\Phi\Bigg|_L=0\ . \qquad (5)$$

The first integral of (3) is

$$U\equiv2\frac{d}{dz}\left[c\frac{d}{dz}\Phi\frac{d^2}{dz^2}\Phi\right]-3c\left[\frac{d^2}{dz^2}\Phi\right]^2$$
$$-g\left[\frac{d}{dz}\Phi\right]^2+f(\Phi) \qquad (6)$$
$$=\text{const}\ . \qquad (7)$$

These are general considerations. The particular model is defined by the specific form of $f(\Phi)$, $g(\Phi)$, and $c(\Phi)$. In order to describe three-phase coexistence between an oil-rich phase, a water-rich phase, and a middle phase in the bulk, $f(\Phi)$ must have three minima. Furthermore, the middle phase is a fluid with internal structure as revealed by its structure factor $S(q)\sim1/(cq^4+gq^2+\frac{1}{2}f''(\Phi)_{\text{middle}})$, which has a pronounced peak at a nonzero value of q. This implies $g<0$ in the middle phase. In contrast, the oil-rich and water-rich phases are considered to be simple liquids, i.e., the structure factors there are Lorentzian functions characterized by just one width. Hence g is positive and c can be ignored in that region. Analytic calculations are readily performed utilizing a piecewise quadratic approximation for f,

$$f(\Phi)=\begin{cases}(\Phi-1)^2-a\ , & \Phi>\phi\\ \omega_0\Phi^2\ , & |\Phi|<\phi\\ (\Phi+1)^2-a\ , & \Phi<-\phi\ ,\end{cases} \qquad (8)$$

where ϕ is determined by requiring that $f(\Phi)$ be a continuous function. The functions c and g are taken to be piecewise constant:

$$g(\Phi)=\begin{cases}g_0\ , & |\Phi|<\phi\\ g_2>0\ , & \text{otherwise}\ ,\end{cases} \qquad (9)$$

$$c(\Phi)=\begin{cases}c_0>0\ , & |\Phi|<\phi\\ c_2>0\ , & \text{otherwise}\ .\end{cases} \qquad (10)$$

The general solution of the Euler-Lagrange equation within one parabolic piece of $f(\Phi)$ is

$$\tilde{\Phi}=\Phi=a_1e^{\lambda_1z}+a_2e^{-\lambda_1z}+a_3e^{\lambda_2z}+a_4e^{-\lambda_2z}+a_5\ ,$$

where (11)

$$\lambda_{1,2}^2=\frac{g}{2c}\left[1\mp\left[1-\frac{4c\omega}{g^2}\right]^{1/2}\right]\ ,$$

where $\omega=\omega_0$ if $|\Phi|<\phi$, and equals unity otherwise. In the oil-rich and water-rich phases, the $\lambda_{1,2}$ are real and $\lambda_1\equiv\xi\approx1/g_2\ll\lambda_2\approx g_2/c_2$. In the middle phase, the λ_i are complex: $\lambda_1\equiv q$, $\lambda_2\equiv\bar{q}$, with $|q|^4=\omega_0/c_0$. The real part of q is related to the usual correlation length $q_r=\text{Re}(q)=1/\xi$, whereas the imaginary part of q gives a wave number $q_i=\text{Im}(q)=2\pi/d$. These different solutions have to be matched at the points $\pm\phi$ so that the profile $\Phi(z)$, its first derivative $d\Phi/dz$, and the invariant Eq. (6) are continuous there. In the following, we will set $\xi\equiv1$ thus fixing the units of z.

III. FREE ENERGY AND BULK STABILITY

As is shown in the Appendix, the free energy of a slab consisting of a single phase, i.e., with $\Phi(z)$ staying within one parabola of f, is given by

$$\mathcal{F}=f_b l+C_1(\tilde{\Phi}_0+\tilde{\Phi}_l)^2+C_2(\tilde{\Phi}_0-\tilde{\Phi}_l)^2 +C_3(\ddot{\Phi}_0+\ddot{\Phi}_l)^2+C_4(\ddot{\Phi}_0-\ddot{\Phi}_l)^2 , \tag{12}$$

where l is the thickness of the slab, f_b is the bulk free-energy density of the phase, and $\tilde{\Phi}_{0,l}$ and $\ddot{\Phi}_{0,l}$ are the values of $\tilde{\Phi}(z)$ and its second derivative at the edges of the slab. Contributions from surface fields are ignored for the moment. The coefficients C_i are given by

$$\begin{aligned}
C_1&=\frac{\omega}{2}\frac{\lambda_1^2\lambda_2^2}{\lambda_2^2-\lambda_1^2}\left[\frac{\tanh(\lambda_1 l/2)}{\lambda_1^3}-\frac{\tanh(\lambda_2 l/2)}{\lambda_2^3}\right] ,\\
C_2&=\frac{\omega}{2}\frac{\lambda_1^2\lambda_2^2}{\lambda_2^2-\lambda_1^2}\left[\frac{\coth(\lambda_1 l/2)}{\lambda_1^3}-\frac{\coth(\lambda_2 l/2)}{\lambda_2^3}\right] ,\\
C_3&=\frac{\omega}{2}\frac{1}{\lambda_1^2\lambda_2^2(\lambda_2^2-\lambda_1^2)}[\lambda_2\tanh(\lambda_2 l/2)-\lambda_1\tanh(\lambda_1 l/2)] ,\\
C_4&=\frac{\omega}{2}\frac{1}{\lambda_1^2\lambda_2^2(\lambda_2^2-\lambda_1^2)}[\lambda_2\coth(\lambda_2 l/2)-\lambda_1\coth(\lambda_1 l/2)] .
\end{aligned} \tag{13}$$

In the oil- and water-rich phases, where the λ_i are real, it is easy to show that all of these coefficients are always positive. Furthermore, if one makes the reasonable assumption that in these two phases $\lambda_1 \ll \lambda_2$, i.e., these phases are far from a disorder line at $g_2=\sqrt{4c}$, then the properties of the phase are governed by just one length $\lambda_1 \equiv \zeta \approx 1/g_2$, and, as stated earlier, the parameter c becomes unimportant. In this case, C_3 and C_4 turn out to be very small compared to $C_1 \approx (\omega/2\zeta)\tanh(\zeta l/2)$ and $C_2 \approx (\omega/2\zeta)\coth(\zeta l/2)$. The situation is more interesting in the middle phase. In terms of the real part q_r and the imaginary part q_i of $q=\lambda_1$, the coefficients C_i read

$$C_{1,2}=\frac{\omega_0}{4}\frac{1}{(q_r^2+q_i^2)(\cosh q_r l \pm \cos q_i l)} \times\left[(3q_r^2-q_i^2)\frac{\sinh q_r l}{q_r}\pm(3q_i^2-q_r^2)\frac{\sin q_i l}{q_i}\right] , \tag{14}$$

$$C_{3,4}=\frac{\omega_0}{4}\frac{1}{(q_r^2+q_i^2)(\cosh q_r l \pm \cos q_i l)} \times\left[\frac{\sinh q_r l}{q_r}\pm\frac{\sin q_i l}{q_i}\right] . \tag{15}$$

While C_3 and C_4 are still positive, this is no longer true for C_1 and C_2: As q_i/q_r becomes larger than 1, i.e., as the system crosses the Lifshitz line and becomes a microemulsion (see [10]), C_1 and C_2 can become negative for certain values of l. For $q_i/q_r > \sqrt{3}$, a condition which is fulfilled for strong amphiphiles [5,11], C_1 and C_2 are negative in the limit of infinitely large l. As C_1 and C_2 are essentially inverse susceptibilities of the surface free energy, which can be positive or negative, the fact that they pass through zero indicates a surface phase transition. As a consequence of these negative coefficients in the free energy, Eq. (12), the magnitude at the slab edges of the profile (2) will be nonzero, so that the profile will oscillate at the surface *irrespective* of the nature of the confining surface. Recently, such oscillations have been clearly observed at the microemulsion-air interface [12]. The implications for the confined system of the surface phase transition in the semi-infinite system will be discussed in the next section. Before doing so, we note that in order to be certain that the middle phase is stable for values of the parameters at which we have examined it, we have determined the phase boundary between lamellar and middle phases. The manner of doing this is discussed briefly in the Appendix.

IV. CONFINED MICROEMULSION

We now study the effect of confinement on the middle phase. We consider a slab of it of thickness l at bulk three-phase coexistence of a symmetric system. We must minimize the free energy [see (2), (12), and (A2) and (A3)]

$$\mathcal{F}=\mathcal{F}_{\Phi}+\mathcal{F}_{\ddot{\Phi}} , \tag{16}$$

where

$$\mathcal{F}_{\Phi}=C_1(\Phi_0+\Phi_l)^2+C_2(\Phi_0-\Phi_l)^2-\alpha_1(\Phi_0+\Phi_l) ,$$

$$\mathcal{F}_{\ddot{\Phi}}=C_3(\ddot{\Phi}_0+\ddot{\Phi}_l)^2+C_4(\ddot{\Phi}_0-\ddot{\Phi}_l)^2-\alpha_2(\ddot{\Phi}_0+\ddot{\Phi}_l) ,$$

and

$$\alpha_1=h_1+\kappa_1\frac{|q|^4}{\mathrm{Im}(q^2)}\mathrm{Im}\left[\frac{\tanh(ql/2)}{q}\right] ,$$

$$\alpha_2=-\frac{\kappa_1}{\mathrm{Im}(q^2)}\mathrm{Im}(q\tanh(ql/2)) ,$$

under the constraint that Φ_0 and Φ_l may not exceed the values at the matching points $\pm\phi=\pm 1/(1+\sqrt{\omega_0})$.

The free energy $\mathcal{F}$ is easily minimized with respect to $\ddot{\Phi}_0$ and $\ddot{\Phi}_l$. The values which minimize it are

$$\ddot{\Phi}_0=\ddot{\Phi}_l=\frac{\alpha_2}{4C_3}=-\kappa_1\frac{|q|^4}{2\omega}$$

and the minimum value is

$$\mathcal{F}_{\ddot{\Phi}}=-\frac{\alpha_2^2}{4C_3}=-\kappa_1^2\frac{1}{2\omega}\frac{|q|^4}{\mathrm{Im}(q^2)}\mathrm{Im}(q\tanh(ql/2)) .$$

The minimization with respect to Φ_0 and Φ_l is a little more complicated. Assuming $\alpha_1>0$ for simplicity, one finds four different solutions:

$$\begin{aligned}
&(\mathrm{I})\ \ \Phi_0=\Phi_l=\frac{\alpha_1}{4C_1}\ ,\ \ \mathcal{F}_\Phi=-\frac{\alpha_1^2}{4C_1}\ ,\\
&(\mathrm{II})\ \ \Phi_0=1\ ,\ \ \Phi_l=\frac{C_2-C_1+\alpha_1/2}{C_2+C_1}\ ,\ \ \mathcal{F}_\Phi=\frac{-\alpha_1^2/4+4C_1C_2-2\alpha_1C_2}{C_1+C_2}\ ,\\
&(\mathrm{III})\ \ \Phi_0=\Phi_l=1\ ,\ \ \mathcal{F}_\Phi=4C_1-2\alpha_1\ ,\\
&(\mathrm{IV})\ \ \Phi_0=1\ ,\ \ \Phi_l=-1,\ \ \mathcal{F}_\Phi=4C_2\ .
\end{aligned} \tag{17}$$

Which particular solution applies depends on the coefficients $C_{1,2}$ and α_1:

$$\begin{aligned}
&C_1,C_2>0\Longrightarrow\begin{cases}(\mathrm{I})\ \text{for}\ \alpha_1/4<C_1\\(\mathrm{III})\ \text{otherwise}\ ,\end{cases}\\
&C_1>0\ ,\ \ C_2<0\ ,\ \ C_1+C_2>0\Longrightarrow\begin{cases}(\mathrm{II})\ \text{for}\ |C_2|<\alpha_1/4<C_1\\(\mathrm{III})\ \text{for}\ \alpha_1/4>C_1\\(\mathrm{IV})\ \text{for}\ \alpha_1/4<|C_2|\ ,\end{cases}\\
&\text{otherwise}\Longrightarrow\begin{cases}(\mathrm{III})\ \text{for}\ \alpha_1/4>(C_1-C_2)/2\\(\mathrm{IV})\ \text{for}\ \alpha_1/4<(C_1-C_2)/2\ .\end{cases}
\end{aligned} \tag{18}$$

The extension to $\alpha_1<0$ is straightforward. In the asymptotic limit $l\rightarrow\infty$ the coefficients take the values

$$\begin{aligned}
&C_{1,\infty}=C_{2,\infty}=\frac{\omega}{2}\frac{3q_r^2-q_i^2}{3q_r(q_r^2+q_i^2)}\ ,\\
&\alpha_{1,\infty}=h_1-\kappa_1\frac{q_r^2+q_i^2}{2q_r}\ .
\end{aligned} \tag{19}$$

Consider first the case $h_1=\kappa_1=0$, i.e., completely neutral walls. Then $\alpha_1=\alpha_2=0$. Solution (II) never occurs; solution (I) corresponds to $\mathcal{F}_\Phi=0$, which means that the values at the walls are the same as in the bulk so that the profile is flat. In solutions (III) and (IV), the profile oscillates. Figures 1(a) and 1(b) show the free energies related to the states (I), (III), and (IV) for different amphiphilic strengths. At small wall distances, solution (IV) is always the one with lowest free energy, i.e., the order parameter at the walls take maximum, opposite values. Intuitively, this corresponds to one single sheet of amphiphile aligning itself parallel to the walls. As the wall distance l is increased, one finds the behavior is qualitatively different in systems with weak amphiphiles than in systems with strong ones. When $q_i/q_r<\sqrt{3}$, corresponding to a weak amphiphile, the solution which minimizes the free energy alternates from (IV) to (III) a few times and ends up in (I) for large l, i.e., the order-parameter profile is flat. Beyond this distance, there is no indication in the free energy that additional amphiphile is entering the system in a manner which varies periodically with the wall separation. In contrast when $q_i/q_r>\sqrt{3}$, corresponding to strong-amphiphilic systems, the solution always alternates between (III) and (IV) for any wall distance. The amplitudes of the order parameter at the walls are always maximal. Thus the insertion of amphiphile into the system appears to occur periodically even in this fluid phase, and is manifest in an infinite series of first-order transitions.

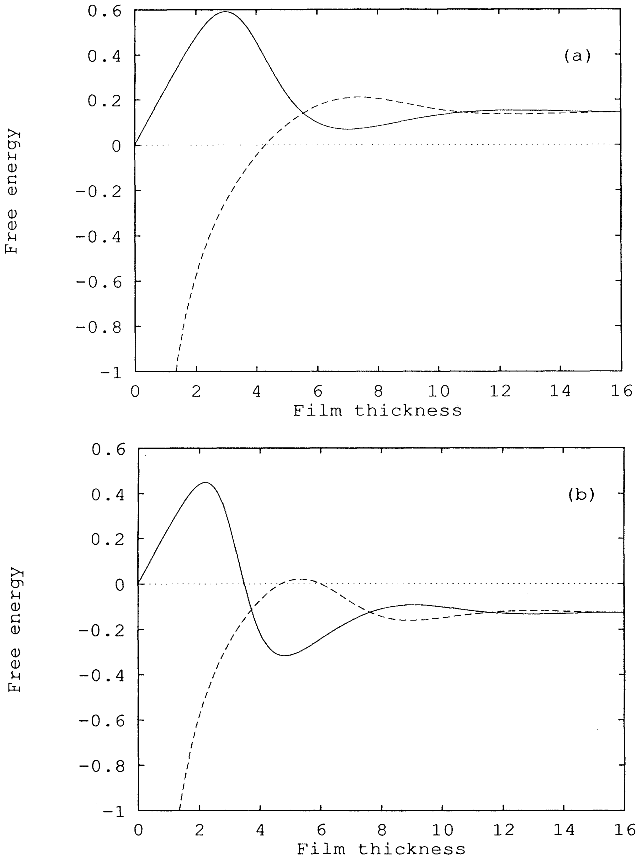

FIG. 1. Dimensionless free energy of a middle-phase film vs dimensionless film thickness at $\omega_0=0.25$, $h_1=\kappa_1=0$ for (a) a weak amphiphile ($q_i=0.6$, $q_r=0.4$, $2\pi\xi/d=1.5$) and (b) a strong amphiphile ($q_i=0.8$, $q_r=0.4$, $2\pi\xi/d=2$.) Solid line corresponds to state (III), dashed line to (IV), dotted line to (I) (see text for explanation). For a given film thickness, the state of the film corresponds to that with the lowest free energy.

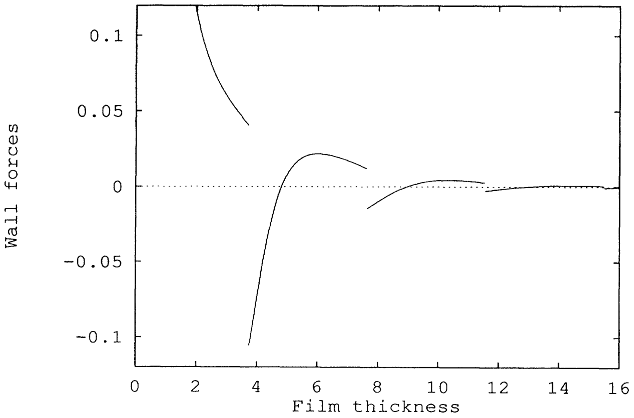

FIG. 2. Dimensionless forces between walls vs wall distance for a strong amphiphile: $\omega_0=0.25$, $h_1=\kappa_1=0$, $q_i=0.8$, $q_r=0.4$, $2\pi\xi/d=2$.

If we now include the effect that the walls will favor one component so that α_1 is not zero, then we see from Eqs. (18) and (19) that, for sufficiently large separations, the system will cease to oscillate and the lowest state will be (III) or (IV), depending on the sign of α_1. This occurs because the energy gain in having the order parameter change sign at the walls decreases exponentially with distance, whereas the energy cost in having the wrong component against a wall is independent of distance. In principle, however, there is no limit to the number of first-order transitions one can observe in strong-amphiphilic systems if the walls be suitably adjusted. In weak-amphiphilic systems, on the other hand, there is a limit inherent in the fluid.

Presumably the most straightforward way to observe this effect would be to measure the wall forces. Figure 2 shows these forces $\tau=\partial\mathcal{F}/\partial l$ between the walls as a function of l in a strong-amphiphilic system. The singularities in the free energy manifest themselves as discontinuities in the wall forces. Thermodynamic methods could also be employed to probe the first-order transitions, as could ellipsometry to study the discontinuous evolution in film thickness.

V. SUMMARY

We have used a simple Ginzburg-Landau model for mixtures of oil, water, and amphiphiles to study the effect of confinement on a microemulsion. Our model is basically the same as the one introduced by Gompper and Schick [10], with the difference that we assume the oil-rich and the water-rich phases to be simple fluids such that their structure function is well described by just one characteristic length. We find a bulk first-order transition from the middle phase to the lamellar phase.

When confined between parallel walls, strong amphiphilic systems should display behavior qualitatively different from that of weak amphiphilic systems. As the wall distance is increased, the former are predicted to undergo a series of first-order transitions, which can be related to layers of amphiphiles entering the film sequentially. If the walls are chosen properly, there is no limit to the thickness of the microemulsion at which such transitions occur. In weak-amphiphilic systems, there are only a few such transitions, and they occur at small separations of the walls. The appearance of the transitions in a slab of finite thickness is directly related to a surface phase transition in the infinitely thick system of microemulsion. In this light, the two different behaviors are quite reminiscent of two similar ones in adsorbed systems [13]. In the case of a weak substrate, one observes just a few layering transitions in a film of finite thickness even when the film becomes macroscopically large at coexistence. On the other hand, for strong substrates, an infinite sequence of layering transitions is observed. The surface transition in the amphiphilic system we have considered is one from a state in which the bulk middle phase prefers there to be no difference between the bulk and surface order parameters, to one in which this difference is maximal. It shows up therefore as a preferential adsorption of oil or water at the wall, brought on *not* by wall forces, but by the presence in the middle phase of the amphiphile which prefers such differences in oil and water concentrations. Wall forces can enhance the adsorption of course.

We found that weak and strong amphiphiles were distinguished by a particular ratio of their two characteristic lengths, $2\pi\xi/d=\sqrt{3}$, where ξ is the correlation length and d the oscillation length in the microemulsion. This is certainly a model-dependent value, but that there exists such a value we believe to be independent of the model. It would be very interesting to observe such a series of first-order transitions in a bicontinuous microemulsion, and we indicated a few ways in which this could be done. Lastly, we note that the walls need not be of the same kind, so that one could simply observe a film of finite thickness confined between some substrate and its own vapor. From the form of the structure function obtained from a scattering experiment on the bulk fluid, one could determine the values of ξ and d.

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APPENDIX

We consider a slab consisting solely of one phase, so that $\Phi(z)$ stays within one parabola of $f(\Phi)$. First we calculate the free energy of one such slab in phase p (p stands for oil o, water w, or middle phase m) with given order parameter $\Phi(z_1)$, $\Phi(z_2)$ and second derivative $d\Phi/dz|_{z_1,z_2}$ at the borders z_1 and z_2. The order-parameter profile $\widetilde{\Phi}(z)=\Phi(z)-\Phi_{b,p}$ is

$$\widetilde{\Phi}=a_1e^{\lambda_1 z}+a_2e^{-\lambda_1 z}+a_3e^{\lambda_2 z}+a_4e^{-\lambda_2 z} ,$$

where $\underline{a}=(a_1,a_2,a_3,a_4)$ is connected to $\underline{b}=(\widetilde{\Phi}(z_1),\ddot{\Phi}(z_1)\widetilde{\Phi}(z_2),\ddot{\Phi}(z_2))$ by $\underline{M}(z_1,z_2)\underline{a}=\underline{b}$ with

$$\underline{M}(z_1,z_2)=\begin{bmatrix} e^{\lambda_1 z_1} & e^{-\lambda_1 z_1} & e^{\lambda_2 z_1} & e^{-\lambda_2 z_1} \\ \lambda_1^2 e^{\lambda_1 z_1} & \lambda_1^2 e^{-\lambda_1 z_1} & \lambda_2^2 e^{\lambda_2 z_1} & \lambda_2^2 e^{-\lambda_2 z_1} \\ e^{\lambda_1 z_2} & e^{-\lambda_1 z_2} & e^{\lambda_2 z_2} & e^{-\lambda_2 z_2} \\ \lambda_1^2 e^{\lambda_1 z_2} & \lambda_1^2 e^{-\lambda_1 z_2} & \lambda_2^2 e^{\lambda_2 z_2} & \lambda_2^2 e^{-\lambda_2 z_2} \end{bmatrix} . \tag{A1}$$

The parameters c and g are constant within the slab. Using partial integration and the Euler-Lagrange equations $c\ddddot{\Phi}-g\ddot{\Phi}+\omega\tilde{\Phi}=0$, one obtains the free energy

$$\begin{aligned}\mathcal{F}&=(z_2-z_1)f_b+c\{[\dot{\Phi}\ddot{\Phi}]_{z_1}^{z_2}-[\tilde{\Phi}\dddot{\Phi}]_{z_1}^{z_2}\}+g[\tilde{\Phi}\dot{\Phi}]_{z_1}^{z_2}\\ &=(z_2-z_1)f_b+\underline{b}^T\underline{Ab}\end{aligned}$$

with

$$\underline{A}=\begin{bmatrix} -\frac{\omega}{\lambda_1}e^{\lambda_1 z_1} & \frac{\omega}{\lambda_1}e^{-\lambda_1 z_1} & -\frac{\omega}{\lambda_2}e^{\lambda_2 z_1} & \frac{\omega}{\lambda_2}e^{-\lambda_2 z_1} \\ -c\lambda_1 e^{\lambda_1 z_1} & c\lambda_1 e^{-\lambda_1 z_1} & -c\lambda_2 e^{\lambda_2 z_1} & c\lambda_2 e^{-\lambda_2 z_1} \\ \frac{\omega}{\lambda_1}e^{\lambda_1 z_2} & -\frac{\omega}{\lambda_1}e^{-\lambda_1 z_2} & \frac{\omega}{\lambda_2}e^{\lambda_2 z_2} & -\frac{\omega}{\lambda_2}e^{-\lambda_2 z_2} \\ c\lambda_1 e^{\lambda_1 z_2} & -c\lambda_1 e^{-\lambda_1 z_2} & c\lambda_2 e^{\lambda_2 z_2} & -c\lambda_2 e^{-\lambda_2 z_2} \end{bmatrix}\underline{M}^{-1} .$$

Hence $\mathcal{F}$ is essentially a symmetric bilinear form in $\underline{b}$. Because it is symmetric, $\underline{A}$ can be replaced by the symmetric part of $\underline{A}$,

$$\underline{A}_{\text{sym}}=\begin{bmatrix} A_1 & 0 & A_2 & 0 \\ 0 & A_3 & 0 & A_4 \\ A_2 & 0 & A_1 & 0 \\ 0 & A_4 & 0 & A_3 \end{bmatrix} ,$$

with

$$A_1=\frac{\omega^2}{c}\left[\frac{1}{\lambda_1^3\tanh[\lambda_1(z_2-z_1)]}-\frac{1}{\lambda_2^3\tanh[\lambda_2(z_2-z_1)]}\right] ,$$

$$A_2=\frac{\omega^2}{c}\left[\frac{-1}{\lambda_1^3\sinh[\lambda_1(z_2-z_1)]}+\frac{1}{\lambda_2^3\sinh[\lambda_2(z_2-z_1)]}\right] ,$$

$$A_3=c\left[\frac{-\lambda_1}{\tanh[\lambda_1(z_2-z_1)]}+\frac{\lambda_2}{\tanh[\lambda_2(z_2-z_1)]}\right] ,$$

$$A_4=c\left[\frac{\lambda_1}{\sinh[\lambda_1(z_2-z_1)]}-\frac{\lambda_2}{\sinh[\lambda_2(z_2-z_1)]}\right] .$$

The diagonalization of the bilinear form finally yields Eq. (12) and (13). Note that the first derivatives $d\Phi/dz$ at the borders are given by

$$\dot{\Phi}(z_1)=(\lambda_1,-\lambda_1,\lambda_2,-\lambda_2)\underline{M}^{-1}(0,z_2-z_1)\begin{bmatrix}\tilde{\Phi}(z_1)\\ \ddot{\Phi}(z_1)\\ \tilde{\Phi}(z_2)\\ \ddot{\Phi}(z_2)\end{bmatrix} , \tag{A2}$$

$$\dot{\Phi}(z_2)=-(\lambda_1,-\lambda_1,\lambda_2,-\lambda_2)\underline{M}^{-1}(0,z_2-z_1)\begin{bmatrix}\tilde{\Phi}(z_2)\\ \ddot{\Phi}(z_2)\\ \tilde{\Phi}(z_1)\\ \ddot{\Phi}(z_1)\end{bmatrix} . \tag{A3}$$

To calculate the free energy of a lamellar phase, we consider a periodic array of such slabs consisting of different phases, oil, middle, water, middle, oil, etc. Each slab of middle phase is of thickness l_1 and each slab of oil or of water is of thickness l_0. At the matching points between a slab p_1, $z \subset [z_1, z_2 = z_1 + l_1]$ and a slab p_2, $z \subset [z_2, z_3 = z_2 + l_0]$ the order-parameter profile $\Phi(z)$ and its first derivative $(d/dz)\Phi(z)$ must be continuous. Because the profile $\Phi(z)$ in a slab is determined by $\Phi(z)$ and $\ddot{\Phi}(z)$ at the borders in our formalism, Φ itself can be made continuous very naturally. The continuity of $\dot{\Phi}$ requires that $\ddot{\Phi}(z_1)$, $\ddot{\Phi}(z_2)$, and $\ddot{\Phi}(z_3)$ fulfill

$$(\lambda_1^{p_1}, -\lambda_1^{p_1}, \lambda_2^{p_1}, -\lambda_2^{p_1}) \underline{\boldsymbol{M}}_{p_1}^{-1}(0, z_2 - z_1) \begin{bmatrix} \Phi(z_2) - \Phi_{b,p_1} \\ \ddot{\Phi}(z_2) \\ \Phi(z_1) - \Phi_{b,p_1} \\ \ddot{\Phi}(z_1) \end{bmatrix} + (\lambda_1^{p_2}, -\lambda_1^{p_2}, \lambda_2^{p_2}, -\lambda_2^{p_2}) \underline{\boldsymbol{M}}_{p_2}^{-1}(0, z_3 - z_2) \begin{bmatrix} \Phi(z_2) - \Phi_{b,p_2} \\ \ddot{\Phi}(z_2) \\ \Phi(z_3) - \Phi_{b,p_2} \\ \ddot{\Phi}(z_3) \end{bmatrix} = 0 . \tag{A4}$$

One can simplify this expression by using $\lambda_1 \equiv \zeta \ll \lambda_2$ in the oil- or water-rich phases. Once the free energy is expressed in terms of the thicknesses l_0 and l_1, it is minimized with respect to them to determine the free energy of the lamellar phase. It is then compared with that of the pure middle phase to determine which is stable. The lamellar phase is stable if

$$\min_{l_0, l_1} \left[(f_{b,w} - f_{b,m}) l_1 + 2\omega_0 \tanh(l_1/2) + 2\omega_0 \frac{\mathrm{Im}(q^{-3}\coth(q l_0/2))}{\mathrm{Im}(1/q^2)} + \frac{2\omega_0}{|q|^4} \frac{\mathrm{Im}(q \coth(q l_0/2))}{\mathrm{Im}(q^2)} \ddot{\Phi}^2 \right] < 0 , \tag{A5}$$

with

$$\ddot{\Phi} = \frac{\mathrm{Im}(q^2)}{\mathrm{Im}(q \coth(q l_0/2))} \left[-\sqrt{\omega_0} \tanh(l_0/2) + \frac{\mathrm{Im}(q^{-1}\coth(q l_0/2))}{\mathrm{Im}(1/q^2)} \right] .$$

In the general case in which $c(\Phi)$ is only piecewise constant, $c_0 \neq c_2$, we find the transition between lamellar and middle phases to be first order.

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[1] R. Evans, J. Phys. Condens. Matter **2**, 8989 (1990).

[2] A. O. Parry and R. Evans, Physica A **181**, 250 (1991); Phys. Rev. Lett. **64**, 439 (1990); M. R. Swift, A. L. Owczarek, and J. O. Indekeu, Europhys. Lett. **14**, 475 (1991).

[3] R. G. Horn and J. N. Israelachvili, J. Chem. Phys. **75**, 1400 (1981); D. Y. C. Chan and R. G. Horn, *ibid.* **83**, 5311 (1985); R. G. Horn, S. J. Hirz, G. Holziioannou, C. W. Frank, and J. M. Catala, *ibid.* **90**, 6767 (1989); P. A. Thompson and G. A. Grest, Phys. Rev. Lett. **68**, 3448 (1992).

[4] We draw the distinction between bicontinuous microemulsions and micellar microemulsions. In the latter, the micelle can act as a component particle whose size provides a characteristic length. See J. L. Parker, P. Richetti, P. Kékicheff, and S. Sarman, Phys. Rev. Lett. **68**, 1955 (1993). The structure of the bicontinuous microemulsion is not characterized by micelles, but by sheets of surfactant separating coherent regions of water from coherent regions of oil.

[5] M. Teubner and R. Strey, J. Chem. Phys. **87**, 3195 (1987).

[6] D. Chowdhury and D. Stauffer, J. Phys. (Paris) **49**, 625 (1988); M. Kikuchi and K. Binder (private communication).

[7] O. Abillon and E. Perez, J. Phys. (Paris) **51**, 2543 (1990); P. Kekicheff and H. K. Christenson, Phys. Rev. Lett. **63**, 2823 (1989).

[8] G. Gompper and S. Zschocke, Phys. Rev. A **46**, 4836 (1992); G. Gompper and M. Kraus, Phys. Rev. E **47**, 4301 (1993).

[9] M. S. Turner, Phys. Rev. Lett. **69**, 1788 (1992).

[10] G. Gompper and M. Schick, Phys. Rev. Lett. **62**, 1647 (1989).

[11] S. H. Chen, S. L. Chang, R. Strey, J. Samseth, and K. Mortensen, J. Phys. Chem. **95**, 7427 (1991).

[12] X-L. Zhou, L-T. Lee, S-H. Chen, and R. Strey, Phys. Rev. A **46**, 6479 (1992).

[13] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).