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Ginzburg-Landau theory of ternary amphiphilic systems.
I. Gaussian interface fluctuations

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Using a Ginzburg-Landau approach, we study the interface fluctuations in ternary mixtures of oil, water, and an amphiphile. The capillary wave spectra can be understood in terms of interfacial tension and bending rigidity of the amphiphilic monolayers. For large interface widths, the distortion of the interface profile due to curvature lowers the bending rigidity. The interfacial tension is found to depend crucially on the distance to neighboring membranes or walls. In particular, we show exactly that the interfacial tension vanishes in the infinite lamellar phase. The variation of the interfacial tension has observable consequences for a lamellar phase between walls, where we calculate the effect of the wall separation on fluctuation spectra and scattering intensities.

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I. INTRODUCTION

When a small amount of an amphiphile is added to a system of oil and water, the interfacial tension between these two phases decreases due to the formation of an amphiphilic monolayer at the oil-water interface [1]. The reduction is proportional to the amount of amphiphile, until the interfacial tension levels off as soon as the amphiphiles form a saturated two-dimensional fluid at the interface; a further increase of the amphiphile concentration leads to the formation of micelles in oil or water. When the amphiphile concentration is increased even further, new phases can be formed, phases which are characterized by an extensive amount of interface between oil-rich and water-rich regions. The most prominent of these phases are the lamellar phase, a regular one-dimensional stacking of monolayers separated alternatively by sheets of oil and water, and the microemulsion, a random array of monolayers.

The effects of fluctuations in amphiphilic systems are traditionally studied by an effective interface model, in which the monolayer is described by a two-dimensional mathematical surface, with given elastic properties [2, 3]. Since the interfacial tension between oil and water is drastically reduced by the presence of the amphiphile, interfacial fluctuations are controlled by the elastic bending energy [3] of the monolayers in these systems. The fluctuations can be investigated most easily in the lamellar phase, where they give rise to a universal repulsive force between neighboring monolayers [4].

Here, we want to describe a different approach. Our starting point is a Ginzburg-Landau theory for a single, scalar order parameter, which describes the local concentration difference between oil and water [5]. This model has been shown to describe several properties of oil-water-surfactant mixtures correctly. In particular, it can be used to calculate the elastic bending moduli of surfactant monolayers [6, 7], to describe lamellar, hexagonal, and cubic phases [6, 7], to study the wetting behavior of the oil-water interface by the microemulsion [5, 8, 9], and of a wall-oil interface by the lamellar phase [7].

Our motivation for using this approach is threefold. First, we want to show that the elastic moduli of the oil-water interface, calculated in Ref. [6] by comparing planar, cylindrical, and spherical interfaces, are the same moduli which determine the spectrum of capillary waves. We are also able to derive expressions for the elasticity of the oil-microemulsion interface, which was not possible by the method of Ref. [6]. Second, we want to show that while the oil-water interfacial tension is small but nonzero at oil-water coexistence (in the vicinity of the lamellar phase), the interfacial tension vanishes *identically* in the lamellar phase. Thus, the spectrum of capillary waves we obtain from the Ginzburg-Landau model is identical with the spectrum used in the interfacial models [4]. Finally, we consider fluctuations in a lamellar phase, which is confined between two parallel walls, with a small number of interfaces in the system. We show that the interfacial tension is a function of the wall separation, and is *negative* for depressed layers. This effect should show up in scattering experiments as a peak at nonzero wave vectors.

II. GINZBURG-LANDAU MODEL

Our analysis is based on the free-energy functional [5]

$$\mathcal{F}\{\Phi\} = \int d^3r \; [c(\Delta\Phi)^2 + g(\Phi)(\nabla\Phi)^2 + f(\Phi) - \mu\Phi] \tag{1}$$

for a scalar order-parameter field $\Phi(\mathbf{r})$, which is proportional to the local difference of the oil and water concentrations. Here, μ is the chemical potential difference between oil and water. In this approach, the amphiphile degrees of freedom are considered as being integrated out [10]. However, the properties of the amphiphile and its concentration determine the form of the functions f and g, as well as the magnitude of the constant c. In the absence of amphiphilic molecules, $f(\Phi)$ has two minima at $\Phi = \Phi_o$ and $\Phi = \Phi_w$, which describe the oil and water phases, and $g(\Phi)$ is a positive constant. When an amphiphile is added to the system, a third minimum of f appears at $\Phi = 0$, which describes the disordered microemulsion phase. Simultaneously, a minimum of g develops at $\Phi = 0$. For strong amphiphiles $g(\Phi)$ becomes negative in the microemulsion phase; this leads a scattering peak at nonzero wave vector q as observed in many neutron-scattering experiments [11, 12]. The locus of points where this first occurs is called a Lifshitz line (LL). In the Ornstein-Zernike approximation, the scattering intensity $S(q)$ has the form

$$S(q) \sim \frac{1}{cq^4 + g(0)q^2 + \frac{1}{2}f''(0)} \,. \tag{2}$$

The Lifshitz line is then given by $g(0) = 0$. The Fourier transform of $S(q)$ is the correlation function $G(r)$. It also shows interesting behavior in the microemulsion [11, 5]: for $g(0) > \sqrt{2cf''(0)} \equiv g_{\rm DO}$, the correlation function decays monotonically (weak amphiphiles), while for $g(0) < g_{\rm DO}$ it decays with exponentially damped oscillations (strong amphiphiles). The boundary line between these behaviors is called the disorder line (DOL).

Many results of the model can be obtained without specifying the detailed form of the functions f and g. For analytical purposes it is convenient to use a piecewise parabolic (constant) form of f (g) (for calculational details see the Appendix). In this case we have

$$f(\Phi) = \begin{cases} \omega_2(\Phi - \Phi_w)^2, & \Phi > \Phi_{0,w} \\ \omega_0\Phi^2 + f_0, & \Phi_{0,o} < \Phi < \Phi_{0,w} \\ \omega_2(\Phi - \Phi_o)^2, & \Phi < \Phi_{0,o} \end{cases} \tag{3}$$

where $\Phi_{0,w}$ and $\Phi_{0,o}$ are chosen such that f is continuous, and

$$g(\Phi) = \begin{cases} b_2, & \Phi > \Phi_{0,w} \\ b_0, & \Phi_{0,o} < \Phi < \Phi_{0,w} \,. \\ b_2, & \Phi < \Phi_{0,o} \end{cases} \tag{4}$$

We will focus here on systems with oil-water symmetry, so that $-\Phi_o = \Phi_w \equiv 1 = \Phi_{\rm bulk}$, and $\mu = 0$. The other parameters are taken to be $c = 1$, $\omega_0 = 1$, and $\omega_2 = 4$. Phase diagrams are then calculated in the parameters f_0 and b_0. The parameter b_2 is chosen such as to give monotonically decaying correlations functions for the bulk oil and water phases.

The mean-field phase diagram [7] (which is obtained by minimizing the free-energy functional $\mathcal{F}$) for our model is shown in Fig. 1. In addition to the three homogeneous phases, oil, water, and microemulsion, inhomogeneous phases can be computed by solving the Euler-Lagrange (EL) equation

$$2c\Delta^2\Phi - 2g(\Phi)\Delta\Phi - g'(\Phi)(\nabla\Phi)^2 + f'(\Phi) = 0 \,. \tag{5}$$

A lamellar phase appears at large enough negative b_0. Other ordered spatially modulated phases, such as a hexagonal or a droplet phase, have been shown to be stable only when the oil-water symmetry is broken [7].

The order-parameter profile of an interface between two homogeneous phases, located at $z = 0$, is obtained as the solution of the Euler-Lagrange equation (5), with the boundary conditions $\Phi_\pm(\pm\infty) = \pm\Phi_{\rm bulk}$ for the oil-water interface, and $\Phi_\pm(+\infty) = \Phi_{\rm bulk}$, $\Phi_\pm(-\infty) = 0$ for the microemulsion-water interface.

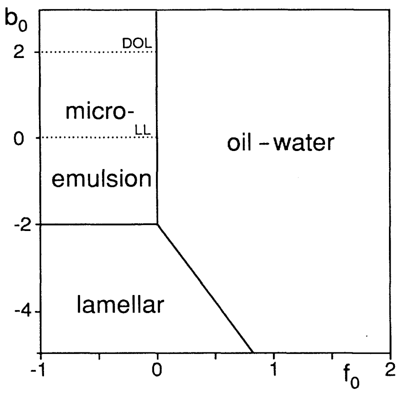

FIG. 1. Mean-field phase diagram of the piecewise parabolic model (3). The locus of the transition lines does not depend on the choice of b_2. The Lifshitz line (LL), where the scattering intensity of the microemulsion phase loses its peak at $q > 0$, and the disorder line (DOL), where the oscillations in the correlation function vanish, are indicated. The lamellar phase can be stable for $b_0 \le -g_{\rm DO} \equiv -\sqrt{4c\omega_0}$.

For general solutions $\overline{\Phi}(z)$ of (5) varying in only one dimension there is a first integral of the Euler-Lagrange equation [5],

$$2c[\overline{\Phi}'\overline{\Phi}''' - \tfrac{1}{2}(\overline{\Phi}'')^2] - g(\overline{\Phi})(\overline{\Phi}')^2 + f(\overline{\Phi}) = \text{const} \tag{6}$$

with $\overline{\Phi}' = d\overline{\Phi}/dz$. It is clear that if $\overline{\Phi} \to \Phi_{\rm bulk}$ for $z \to \infty$, as is the case for $\Phi_\pm$ (but not for the lamellar phase), the constant in (6) will be $f(\Phi_{\rm bulk})$. Then, by using (6) to substitute $f(\Phi)$ in Eq. (1), one finds [6]

$$\sigma = \frac{\mathcal{F}}{A} = \int dz\ [2g(\Phi_\pm)(\nabla\Phi_\pm)^2 + 4c(\Delta\Phi_\pm)^2] \tag{7}$$

for the interfacial free energy per unit area.

III. FLUCTUATIONS OF INTERFACES BETWEEN TWO HOMOGENEOUS PHASES

A. Curvature Hamiltonian

On length scales much larger than the intrinsic thickness, an interface can be described by a two-dimensional mathematical surface. The shapes and fluctuations of this surface are determined by a Hamiltonian, which can be derived from symmetry arguments. For interfaces in fluid systems, the Hamiltonian must be invariant under translations and rotations in three-dimensional space, and reparametrization invariant because the fluidity ensures that no coordinate system is preferable to any other. This leads to the well-known Helfrich Hamiltonian [3]

$$\mathcal{H} = \int dS[\sigma + 2\kappa(H - H_0)^2 + \bar{\kappa}K], \tag{8}$$

where the integral is taken over the whole surface. Here, $H = (c_1 + c_2)/2$ is the mean curvature and $K = c_1 c_2$ the Gaussian curvature, both expressed in terms of the local principal curvatures c_1 and c_2. The elastic properties of the interface are thus determined by the interfacial tension σ, the spontaneous curvature H_0, the bending rigidity κ, and the saddle splay modulus $\bar{\kappa}$. We focus our attention here on oil-water-symmetric systems, where $H_0 = 0$.

Almost flat configurations can be described by a single-valued function $u(\mathbf{x})$, which measures the displacement of a membrane from a planar reference state. In this case, the Hamiltonian can be expanded to second order in the displacements, which gives in Fourier space

$$\mathcal{H} = \sigma A + \sum_{\mathbf{q}} [\tfrac{1}{2}\sigma q^2 + \tfrac{1}{2}\kappa q^4] u_{\mathbf{q}} u_{-\mathbf{q}} + O(u^4)\,, \qquad (9)$$

where A is the projected area of the membrane.

B. Effective interface model

An effective interface model can also be derived from the Ginzburg-Landau free-energy functional (1). It is possible to derive a simple approximation for the spectrum of capillary waves of the interface by introducing a "collective coordinate," such that the order-parameter field of an almost flat interface is given by

$$\Phi(\mathbf{r}) = \Phi_{\pm}(z - u(\mathbf{x})), \quad \mathbf{r} = (\mathbf{x}, z)\,. \qquad (10)$$

By inserting this ansatz into the free-energy functional, and expanding to second order in the fluctuations $u(\mathbf{x})$, we find

$$\mathcal{F}\{u\} = \sigma \int d^2x [1 + \tfrac{1}{2}(\nabla_{\|} u)^2] + \tfrac{1}{2}\kappa_0 \int d^2x \, (\Delta_{\|} u)^2 + O(u^4), \qquad (11)$$

where

$$\sigma = \int dz [c(\Delta\Phi_{\pm})^2 + g(\Phi_{\pm})(\nabla\Phi_{\pm})^2 + f(\Phi_{\pm})] \qquad (12)$$

is the interfacial tension of the kink profile, and

$$\kappa_0 = 2c \int dz \, (\Phi_{\pm}')^2 \qquad (13)$$

can be identified with the bending rigidity of the interface. These expressions agree with the results of a calculation of the bending elasticity of the oil-water interface by comparing the free energy of planar interfaces, and of cylinders and spheres [6].

C. Gaussian fluctuations

We want to go now beyond the approximation (10) and calculate the exact spectrum of Gaussian fluctuations of the interface [13, 5]. To do so, we consider a small fluctuation of the order-parameter field around the mean-field solution,

$$\Phi(\mathbf{r}) = \overline{\Phi}(z) + \eta(\mathbf{r}), \qquad (14)$$

and expand the free-energy functional to second order in $\eta(\mathbf{r})$. Since the linear term in η vanishes due to the stationarity of $\overline{\Phi}$, we find

$$\mathcal{F}\{\Phi\} = \mathcal{F}\{\overline{\Phi}\} + \langle \eta, \hat{D}\eta \rangle\,, \qquad (15)$$

where $\langle , \rangle$ is the usual scalar product. The differential operator $\hat{D}$ can be written in the self-adjoint form [5]

$$\hat{D} = c\Delta^2 - g(\overline{\Phi})\Delta - g'(\overline{\Phi})(\nabla\overline{\Phi})\nabla - g'(\overline{\Phi})\Delta\overline{\Phi} - \tfrac{1}{2}g''(\overline{\Phi})(\Delta\overline{\Phi})^2 + \tfrac{1}{2}f''(\overline{\Phi})\,. \qquad (16)$$

The fluctuations can now be expressed as a linear combination of eigenfunctions of $\hat{D}$,

$$\hat{D}\, \eta_{\lambda}(\mathbf{r}) = E_{\lambda}\, \eta_{\lambda}(\mathbf{r})\,. \qquad (17)$$

Due to the translational symmetry of the mean-field solution parallel to the interface, the eigenmodes can be written in the form

$$\eta_{\lambda}(\mathbf{r}) = \eta_{n\mathbf{q}}(z)\, e^{i\mathbf{q}\cdot\mathbf{x}} \qquad (18)$$

so that

$$\eta(\mathbf{r}) = \sum_n \int d^2q \, \xi_{n\mathbf{q}}\, \eta_{n\mathbf{q}}(z)\, e^{i\mathbf{q}\cdot\mathbf{x}}, \qquad (19)$$

which leads to the simple form

$$\langle \eta, \hat{D}\eta \rangle = \sum_n \int d^2q \, |\xi_{n\mathbf{q}}|^2\, E_{n\mathbf{q}} \langle \eta_{n\mathbf{q}}, \eta_{n\mathbf{q}} \rangle \qquad (20)$$

for the contribution of the fluctuations to the free energy. Here, the index n stands for both the discrete and the continuous parts of the spectrum.

Equation (17) has a solution $\eta_{00}(z) = \overline{\Phi}'(z)$ with eigenvalue $E_0 = 0$ because it costs no energy to displace the interface in the z direction. We are mainly interested in the wave-vector dependence of the translational mode $\eta_{0\mathbf{q}}(z)$, which is the zero mode for $q = 0$.

Our aim is to derive expressions for the coefficients of the q^2 and q^4 contributions of the spectrum. Thus, we expand

$$\eta_{n\mathbf{q}}(z) = \eta_n^{(0)}(z) + q^2\eta_n^{(2)}(z) + q^4\eta_n^{(4)}(z) + O(q^6). \qquad (21)$$

We choose the normalization

$$\langle \eta_n^{(0)}, \eta_{n\mathbf{q}} \rangle = \int dz [\overline{\Phi}'(z)]^2\,, \qquad (22)$$

which implies in particular $\langle \eta_n^{(0)}, \eta_n^{(0)} \rangle = \int dz [\overline{\Phi}'(z)]^2$ and $\langle \eta_n^{(0)}, \eta_n^{(2)} \rangle = 0$; in this case ξ_{00} can be identified with the displacement $u(\mathbf{x})$ of Eq. (10),

$$\overline{\Phi}(z - u) = \overline{\Phi}(z) - u\overline{\Phi}'(z) + \cdots\,. \qquad (23)$$

The expansion (21) can be inserted back into Eq. (17) to give

$$\hat{D}\eta_\lambda(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{x}}[\hat{D}_z\eta_{n\mathbf{q}}(z) + q^2\{[g(\overline{\Phi}(z)) - 2c\Delta_z]\eta_n^{(0)}(z)\} + q^4\{c\eta_n^{(0)} + [g(\overline{\Phi}(z)) - 2c\Delta_z]\eta_n^{(2)}(z)\} + O(q^6)]$$
$$= e^{i\mathbf{q}\cdot\mathbf{x}}[\hat{D}_z + q^2\hat{\Gamma} + cq^4 + \cdots]\eta_{n\mathbf{q}}(z)\,, \tag{24}$$

where we have introduced an operator

$$\hat{\Gamma} = g(\overline{\Phi}(z)) - 2c\Delta_z\,. \tag{25}$$

The operator $\hat{D}_z$ in (24) is the operator $\hat{D}$ for $q = 0$, i.e., $\hat{D}_z\eta_{n\mathbf{0}}(z) = E_{n\mathbf{0}}\eta_{n\mathbf{0}}(z)$. Since $\hat{D}$ is self-adjoint, we obtain for the contribution of a single mode to the free energy

$$\langle\eta_{n\mathbf{q}}, \hat{D}\eta_{n\mathbf{q}}\rangle = E_{n\mathbf{0}}\langle\eta_n^{(0)}, \eta_n^{(0)}\rangle + \langle\eta_n^{(0)}, \hat{\Gamma}\eta_n^{(0)}\rangle q^2 + c\langle\eta_n^{(0)}, \eta_n^{(0)}\rangle q^4$$
$$+q^4(\langle\eta_n^{(2)}, \hat{\Gamma}\eta_n^{(0)}\rangle + \langle\eta_n^{(0)}, \hat{\Gamma}\eta_n^{(2)}\rangle + \langle\eta_n^{(2)}, \hat{D}_z\eta_n^{(2)}\rangle) + O(q^6)\,. \tag{26}$$

The first term in q^4 is just $\kappa_0/2$, compare Eq. (13). The other terms of order q^4 in this equation can be simplified further by taking into account that $\eta_{n\mathbf{q}}$ is an eigenfunction of $\hat{D}$. By expanding the eigenvalue $E_{n\mathbf{q}}$ in the form

$$E_{n\mathbf{q}} = E_n^{(0)} + q^2E_n^{(2)} + q^4E_n^{(4)} + O(q^6)\,, \tag{27}$$

together with Eq. (17) we obtain a hierarchy of inhomogeneous differential equations,

$$\hat{D}_z\eta_n^{(0)} = E_n^{(0)}\eta_n^{(0)}, \tag{28}$$

$$\hat{D}_z\eta_n^{(2)} = E_n^{(0)}\eta_n^{(2)} + E_n^{(2)}\eta_n^{(0)} - \hat{\Gamma}\eta_n^{(0)}, \tag{29}$$

$$\hat{D}_z\eta_n^{(4)} = E_n^{(0)}\eta_n^{(4)} + E_n^{(2)}\eta_n^{(2)} + E_n^{(4)}\eta_n^{(0)}$$
$$-\hat{\Gamma}\eta_n^{(2)} - c\eta_n^{(0)}. \tag{30}$$

Equation (29) yields

$$E_n^{(2)} = \frac{\langle\eta_n^{(0)}, \hat{\Gamma}\eta_n^{(0)}\rangle}{\langle\eta_n^{(0)}, \eta_n^{(0)}\rangle} \equiv \gamma_n\,. \tag{31}$$

When the equation for $\eta_n^{(2)}$ is used in Eq. (26), we finally arrive at

$$\langle\eta_{n\mathbf{q}}, \hat{D}\eta_{n\mathbf{q}}\rangle = E_{n\mathbf{0}}\langle\eta_n^{(0)}, \eta_n^{(0)}\rangle + \tfrac{1}{2}\gamma_n\langle\eta_n^{(0)}, \eta_n^{(0)}\rangle q^2$$
$$+\left(\frac{\kappa_0}{2} + \langle\eta_n^{(2)}, \hat{\Gamma}\eta_n^{(0)}\rangle\right)q^4 + O(q^6)\,. \tag{32}$$

For the translational mode we have $E_0^{(0)} = 0$. Thus we can write (32) in the form

$$\langle\eta_{0\mathbf{q}}, \hat{D}\eta_{0\mathbf{q}}\rangle = \tfrac{1}{2}\sigma_t q^2 + \tfrac{1}{2}\kappa q^4 + O(q^6)\,, \tag{33}$$

with

$$\sigma_t = \gamma_0\langle\eta_0^{(0)}, \eta_0^{(0)}\rangle = \langle\eta_0^{(0)}, \hat{\Gamma}\eta_0^{(0)}\rangle \tag{34}$$

and

$$\kappa = \kappa_0 + 2\langle\eta_0^{(2)}, \hat{\Gamma}\eta_0^{(0)}\rangle\,. \tag{35}$$

In the following we shall refer to both σ_t and γ_0 as "interfacial tension," keeping in mind that the two are related by a normalization constant $\langle\eta_0^{(0)}, \eta_0^{(0)}\rangle$. For a free interface Eq. (7) gives $\sigma_t = \sigma$.

Numerically, the eigenvalues $E = \langle\eta, \hat{D}\eta\rangle/\langle\eta, \eta\rangle$ are indistinguishable from the eigenvalues determined by solving Eq. (17) directly (for details see the Appendix). It turns out that instead of solving (29) for $\eta^{(2)}$, it is easier to calculate the third term in (32) from the full solution as

$$\langle\eta^{(2)}, \hat{\Gamma}\eta^{(0)}\rangle = \lim_{q\to 0}\frac{1}{2q^2}[\langle\eta, \hat{\Gamma}\eta\rangle - \langle\eta^{(0)}, \hat{\Gamma}\eta^{(0)}\rangle]\,. \tag{36}$$

The results for the piecewise parabolic model (3) are shown in Fig. 2(a) for the oil-water interface, and in Fig. 2(b) for the oil-microemulsion interface. We see that for the *oil-water* interface, the approximation of the local order-parameter profile by the mean-field profile gives very good results for $b_0 \lesssim -1$, i.e., in a region of the phase diagram, where the correlation function in the mi-

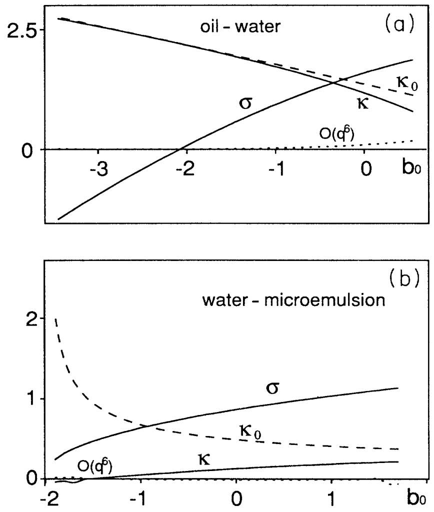

FIG. 2. Interfacial tension σ and bending rigidity κ of the interface between two homogeneous phases at oil-microemulsion-water coexistence, as calculated from the spectrum of capillary waves, with $b_2 = 4.5$ and $f_0 = 0$. (a) Oil-water interface. (b) Water-microemulsion interface. The values for σ and κ calculated from the direct solution of (17) and from (32) agree perfectly. The tension σ is positive at oil-water coexistence; for $\sigma < 0$, the lamellar phase is stable. Note that κ, which takes into account the curvature-induced change of the profile, can differ significantly from κ_0 (dashed lines). Terms of order q^6 (dotted lines) in the spectrum are very small, and contribute only for the water-microemulsion interface near $b_0 = -2$, where κ is negative, so that the excitation energy is always positive.

croemulsion has strong oscillations, so that the interface can be considered to be covered by a saturated amphiphilic monolayer. In this case, the $\langle \eta^{(2)}, \hat{\Gamma}\eta^{(0)} \rangle$ term in (32) can be neglected, and the bending rigidity is given to a very good approximation by (13). For larger values of b_0, the $\langle \eta^{(2)}, \hat{\Gamma}\eta^{(0)} \rangle$ term, which arises from the deviation of the profile of the curved interface from the simple form (10), becomes more and more important. We have to keep in mind that the width of the interface grows when the wetting transition [5], which occurs at $b_0 = 2$, is approached; at this point, a second zero mode appears in the spectrum. This second zero mode describes fluctuations of the interface width.

For the *water-microemulsion* interface, on the other hand, the simple approximation (10) never gives good results. Thus, we conclude that this interface is a much more complicated object, with an interfacial profile which is strongly distorted when the interface is bent. Its description by means of a curvature model breaks down completely near $b_0 = -2$, where the term of order q^6 ensures the stability of the interface.

IV. FLUCTUATIONS OF THE LAMELLAR PHASE

We want to consider now the fluctuations of an infinite stack of oil-water interfaces, i.e., of the lamellar phase. In this case, the undulation modes have an additional degree of freedom, the phase shift φ between the capillary waves of neighboring monolayers. It is well known that the undulation modes destroy the long-range order in lamellar phases [14]. We want to focus in this section on the modes with $\varphi = 0$. We will show that the interfacial tension term σ_t in the spectrum vanishes identically in this case. To do so, we study the variational problem of minimizing the free-energy functional (1) in more detail. In the case of a spatially modulated phase, the free-energy density is not only minimized with respect to the order-parameter profile, but also with respect to the periodicity length. Thus, the vanishing of the interfacial tension means physically that the system is stationary with respect to the formation of interfacial area.

Let us consider a general functional of the form

$$\mathcal{S} = \frac{1}{z_1} \int_0^{z_1} \mathcal{L}(\Phi, \Phi', \Phi'')\, dz\,. \tag{37}$$

To obtain a variational problem with fixed boundaries, we reparametrize [15]: a continuous function $z = z(t)$ is chosen with the periodicity of Φ, $z(t_1) = z_1$ with fixed t_1, and $\dot{z} = \frac{dz}{dt} > 0$ for $0 < t < t_1$. This yields

$$\Phi' = \frac{d\Phi}{dz} = \frac{d\Phi}{dt}\frac{dt}{dz} = \frac{\dot{\Phi}}{\dot{z}}, \tag{38}$$

$$\Phi'' = \frac{d}{dz}\left(\frac{\dot{\Phi}}{\dot{z}}\right) = \frac{\ddot{\Phi}\dot{z} - \dot{\Phi}\ddot{z}}{\dot{z}^3}, \tag{39}$$

$$\mathcal{S}\{\Phi, \dot{\Phi}, \ddot{\Phi}, \dot{z}, \ddot{z}\} = \frac{1}{z_1} \int_0^{t_1} dt\; \tilde{\mathcal{L}}(\Phi, \dot{\Phi}, \ddot{\Phi}, \dot{z}, \ddot{z}), \tag{40}$$

$$\tilde{\mathcal{L}}(\Phi, \dot{\Phi}, \ddot{\Phi}, \dot{z}, \ddot{z}) = \dot{z}\mathcal{L}\left(\Phi, \frac{\dot{\Phi}}{\dot{z}}, \frac{\ddot{\Phi}\dot{z} - \dot{\Phi}\ddot{z}}{\dot{z}^3}\right)\,. \tag{41}$$

Here and below we use the notation $\Phi' = d\Phi/dz$ and $\dot{\Phi} = d\Phi/dt$. $\mathcal{S}$ can now be minimized by a variation of $\Phi(t)$ and $z(t)$,

$$\Phi(t, \epsilon_1) = \overline{\Phi}(t) + \epsilon_1 \eta(t), \tag{42}$$

$$z(t, \epsilon_2) = \overline{z}(t) + \epsilon_2 \zeta(t). \tag{43}$$

We have already discussed the boundary conditions for z; Φ is taken to be a periodic function with continuous first and second derivatives. The stationarity of $\mathcal{S}$ with respect to Φ leads to

$$\begin{aligned} \left.\frac{\partial \mathcal{S}}{\partial \epsilon_1}\right|_{\epsilon_1=0} &= \int_0^{t_1} dt\; \left[\frac{\partial \tilde{\mathcal{L}}}{\partial \Phi}\frac{\partial \Phi}{\partial \epsilon_1} + \frac{\partial \tilde{\mathcal{L}}}{\partial \dot{\Phi}}\frac{\partial \dot{\Phi}}{\partial \epsilon_1} + \frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{\Phi}}\frac{\partial \ddot{\Phi}}{\partial \epsilon_1}\right] \\ &= \int_0^{t_1} dt\; \left\{\left[\frac{\partial \tilde{\mathcal{L}}}{\partial \Phi} - \frac{d}{dt}\frac{\partial \tilde{\mathcal{L}}}{\partial \dot{\Phi}} + \frac{d^2}{dt^2}\frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{\Phi}}\right]\eta(t)\right\} \\ &\quad + \left[\frac{\partial \tilde{\mathcal{L}}}{\partial \dot{\Phi}}\eta + \frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{\Phi}}\dot{\eta} - \frac{d}{dt}\left(\frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{\Phi}}\right)\eta\right]_0^{t_1} = 0. \end{aligned} \tag{44}$$

The boundary terms in η vanish due to the boundary conditions; the $\dot{\eta}$ contribution is

$$\frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{\Phi}}\dot{\eta} = \frac{1}{\dot{z}}\frac{\partial \mathcal{L}}{\partial \Phi''}\dot{\eta} = \frac{\partial \mathcal{L}}{\partial \Phi''}\eta' \tag{45}$$

and thus vanishes identically due to the periodicity of Φ. Finally, the integral vanishes for all functions Φ, for which

$$\dot{z}\left(\frac{\partial \mathcal{L}}{\partial \Phi} - \frac{d}{dz}\frac{\partial \mathcal{L}}{\partial \Phi'} + \frac{d^2}{dz^2}\frac{\partial \mathcal{L}}{\partial \Phi''}\right) = 0, \tag{46}$$

which is (since $\dot{z} > 0$) just the Euler-Lagrange equation for the mean-field profile [see Eq. (5)].

The stationarity of $\mathcal{S}$ with respect to z leads to

$$\begin{aligned} \left.\frac{d\mathcal{S}}{d\epsilon_2}\right|_{\epsilon_2=0} &= -\frac{\zeta(t_1)}{z_1}\mathcal{S}(\overline{\Phi}, \overline{z}) + \frac{1}{z_1}\int_0^{t_1} dt\; \left[\frac{\partial \tilde{\mathcal{L}}}{\partial \dot{z}}\frac{\partial \dot{z}}{\partial \epsilon_2} + \frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{z}}\frac{\partial \ddot{z}}{\partial \epsilon_2}\right] \\ &= -\frac{\zeta(t_1)}{z_1}\mathcal{S}(\overline{\Phi}, \overline{z}) + \frac{1}{z_1}\int_0^{t_1} dt\; \left\{\left[-\frac{d}{dt}\frac{\partial \tilde{\mathcal{L}}}{\partial \dot{z}} + \frac{d^2}{dt^2}\frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{z}}\right]\zeta(t)\right\} \\ &\quad + \frac{1}{z_1}\left[\frac{\partial \tilde{\mathcal{L}}}{\partial \dot{z}}\zeta + \frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{z}}\dot{\zeta} - \frac{d}{dt}\left(\frac{\partial \tilde{\mathcal{L}}}{\partial \ddot{z}}\right)\zeta\right]_0^{t_1} = 0. \end{aligned} \tag{47}$$

We first study the integral, where we have

$$
\begin{aligned}
-\frac{d}{dt}\left(\frac{\partial\tilde{\mathcal{L}}}{\partial\dot{z}}-\frac{d}{dt}\frac{\partial\tilde{\mathcal{L}}}{\partial\ddot{z}}\right)
&=-\frac{d}{dt}\left[\mathcal{L}-\frac{\partial\mathcal{L}}{\partial\Phi'}\Phi'-\frac{\partial\mathcal{L}}{\partial\Phi''}\Phi''+\Phi'\frac{d}{dz}\left(\frac{\partial\mathcal{L}}{\partial\Phi''}\right)\right]\\
&\equiv-\frac{d}{dt}\mathcal{H}=0. \qquad (48)
\end{aligned}
$$

Here, $\mathcal{H}$ is just the first integral of the EL equation [which is Eq.(5) for our functional (1)]. Therefore, the integral vanishes.

The boundary term in $\dot{\zeta}$ is written as

$$
\frac{\partial\tilde{\mathcal{L}}}{\partial\ddot{z}}\dot{\zeta}=-\frac{\partial\mathcal{L}}{\partial\Phi''}\left(\frac{\dot{\Phi}}{\dot{z}^2}\right)\dot{\zeta}=-\Phi'\frac{\partial\mathcal{L}}{\partial\Phi''}\frac{\dot{\zeta}}{\dot{z}} \qquad (49)
$$

and vanishes due to the periodicity of Φ and $\dot{z}$. Thus, the only terms left are those containing $\zeta(t_1)$, so that

$$
-\mathcal{S}(\overline{\Phi},\overline{z})+\left(\frac{\partial\tilde{\mathcal{L}}}{\partial\dot{z}}-\frac{d}{dt}\frac{\partial\tilde{\mathcal{L}}}{\partial\ddot{z}}\right)(t_1)=0. \qquad (50)
$$

We conclude that for periodic phases the first integral of the EL equation equals the free-energy density,

$$
\mathcal{S}(\overline{\Phi},\overline{z})=\mathcal{H}. \qquad (51)
$$

We can now return to our Ginzburg-Landau model. In this case the first integral is [see Eq. (6)]

$$
f(\overline{\Phi})+2c[\overline{\Phi}'\overline{\Phi}'''-\tfrac{1}{2}(\overline{\Phi}'')^2]-g(\overline{\Phi})(\overline{\Phi}')^2=\mathcal{H}, \qquad (52)
$$

so that

$$
\int_0^{z_1}dz\;f(\overline{\Phi})=\int_0^{z_1}dz\;[g(\overline{\Phi})(\overline{\Phi}')^2+3c(\overline{\Phi}'')^2+\mathcal{H}]. \qquad (53)
$$

The free-energy density is therefore given by

$$
\mathcal{S}=\frac{1}{z_1}\int_0^{z_1}dz\;[2g(\overline{\Phi})(\overline{\Phi}')^2+4c(\overline{\Phi}'')^2]+\mathcal{H}. \qquad (54)
$$

Together with (51) this implies

$$
\int_0^{z_1}dz\;[g(\overline{\Phi})(\overline{\Phi}')^2+2c(\overline{\Phi}'')^2]=\int_0^{z_1}dz\;\overline{\Phi}'\hat{\Gamma}\overline{\Phi}'=0. \qquad (55)
$$

This is just the result we were looking for. A comparison with Eq. (34) shows that (55) is the interfacial tension term σ_t in the spectrum of capillary waves. Our result shows that in the lamellar phase, the leading term in the spectrum is controlled by the bending energy. We want to emphasize that the absence of q^2 contributions does *not* imply that the interfacial free energy of a single oil-water interface vanishes. Quite the contrary is true: the interfacial free energy is essentially always nonzero, and usually negative in the region of the phase diagram, where the lamellar phase is stable.

V. INTERFACES IN FINITE SYSTEMS

A. Mean-field theory and Gaussian fluctuations

In experiments on lamellar phases, the system is usually confined between walls. The walls orient the stack of monolayers, so that "monocrystalline" samples can be obtained. Furthermore, the walls introduce an important new variable into the system: the distance between monolayers can be varied by changing the wall separation.

To describe a ternary mixture between walls, the interactions of the molecules with the walls have to be added to our Ginzburg-Landau free-energy functional (1). We study here the case of two parallel walls, located at $z=z_r$ and $z=z_l$, with the free-energy functional

$$
\begin{aligned}
\mathcal{F}\{\Phi\}=\int_{z_l}^{z_r}dz\int d^2x\;\{&c(\Delta\Phi)^2+g(\Phi)(\nabla\Phi)^2+f(\Phi)+\delta(z-z_l)[f_1(\Phi)+g_1(\Phi)(\nabla\Phi)^2+\mu_1\Phi]\\
&+\delta(z-z_r)[f_2(\Phi)+g_2(\Phi)(\nabla\Phi)^2+\mu_2\Phi]\}. \qquad (56)
\end{aligned}
$$

Here, $\mu_{1/2}$ is a chemical potential which describes the hydrophobicity of the wall. The functions $f_{1/2}(\Phi)$ and $g_{1/2}(\Phi)$ arise from the change in the interaction energies of the various molecules near the walls, and from the change in entropy due to the missing neighbors. We choose

$$
f_{1/2}(\Phi)=a_{1/2}\Phi^2, \qquad (57)
$$

$$
g_{1/2}(\Phi)=g_{1/2}=\text{const}. \qquad (58)
$$

The order-parameter profile, which minimizes the free-energy functional (56), satisfies the EL equation (5) with the boundary conditions [7]

$$
\begin{aligned}
\mp 2c\nabla^2\overline{\Phi}'\pm 2g(\overline{\Phi})\overline{\Phi}'+f'_{1/2}(\overline{\Phi})+g'_{1/2}(\overline{\Phi})(\overline{\Phi}')^2&\\
+\mu_{1/2}\Big|_{z=z_{r/l}}=0, &\qquad (59)
\end{aligned}
$$

$$
\pm 2c\nabla^2\overline{\Phi}+2g_{1/2}(\overline{\Phi})\overline{\Phi}'\Big|_{z=z_{r/l}}=0, \qquad (60)
$$

where the upper (lower) sign applies to the right (left) wall.

We want to consider again Gaussian fluctuations by expanding the free-energy functional to second order in the deviations η from the mean-field profile $\overline{\Phi}$,

$$
\mathcal{F}\{\Phi\}=\mathcal{F}\{\overline{\Phi}\}+\langle\eta,\hat{D}\eta\rangle+\mathcal{F}^{+}_{\text{wall}}+\mathcal{F}^{-}_{\text{wall}}, \qquad (61)
$$

where $\hat{D}$ is the self-adjoint operator (16) of the infinite system, and

$$\mathcal{F}^{\pm}_{\text{wall}} = \int d^2x \; [\mp c\eta\nabla^3\eta \pm c\nabla^2\eta\boldsymbol{\nabla}\eta \pm g(\overline{\Phi})\eta\boldsymbol{\nabla}\eta \pm g'(\overline{\Phi})(\boldsymbol{\nabla}\overline{\Phi})\eta^2 + g_{1/2}(\overline{\Phi})(\boldsymbol{\nabla}\eta)^2 +2g'_{1/2}(\overline{\Phi})(\boldsymbol{\nabla}\overline{\Phi})\eta\boldsymbol{\nabla}\eta + \tfrac{1}{2}g''_{1/2}(\overline{\Phi})(\boldsymbol{\nabla}\overline{\Phi})^2\eta^2 + \tfrac{1}{2}f''_{1/2}(\overline{\Phi})\eta^2]_{z=z_{r/l}} \,. \tag{62}$$

Due to the presence of the walls, the translational mode has now a finite energy even at zero wave vector q; this allows the calculation of correlation functions. In particular we are interested in the pair-correlation function

$$G(\mathbf{r},\mathbf{r}') \equiv \langle\Phi(\mathbf{r})\Phi(\mathbf{r}')\rangle - \langle\Phi(\mathbf{r})\rangle\langle\Phi(\mathbf{r}')\rangle = \langle\eta(\mathbf{r})\eta(\mathbf{r}')\rangle \,. \tag{63}$$

In the Gaussian approximation, $G(\mathbf{r},\mathbf{r}')$ can be written as

$$G(\mathbf{r},\mathbf{r}') = \sum_{\lambda} \frac{\eta_\lambda(\mathbf{r})\eta_\lambda(\mathbf{r}')}{E_\lambda} \,. \tag{64}$$

It satisfies the differential equation

$$\hat{D}G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{65}$$

and is therefore the Green's function of the operator $\hat{D}$.

Equation (64) indicates that the boundary conditions for $G(\mathbf{r},\mathbf{r}')$, with fixed $\mathbf{r}'$, and for $\eta(\mathbf{r})$ must be identical. When a spatially inhomogeneous chemical potential term $\int d^3r\, \mu(\mathbf{r})\Phi(\mathbf{r})$ is added formally to the functional (56), the average order-parameter profile is obtained as

$$\overline{\Phi}(\mathbf{r}) = \langle\Phi(\mathbf{r})\rangle = \left[\frac{\delta}{\delta\mu(\mathbf{r})}\mathcal{F}[\Phi,\mu]\right]_{\mu=0} , \tag{66}$$

and similarly the correlation function as

$$G(\mathbf{r}_1,\mathbf{r}_2) = \left[\frac{\delta}{\delta\mu(\mathbf{r}_1)}\langle\Phi(\mathbf{r}_2)\rangle\right]_{\mu=0} . \tag{67}$$

Thus a functional derivative of the boundary conditions [16] for the order-parameter profile yields the boundary conditions for the fluctuations and for the correlation functions in the harmonic approximation,

$$\mp 2c\nabla^2\eta' \pm 2g'(\overline{\Phi})\overline{\Phi}'\eta \pm 2g(\overline{\Phi})\eta' + f''_{1/2}(\overline{\Phi})\eta + g''_{1/2}(\overline{\Phi})(\overline{\Phi}')^2\eta + 2g'_{1/2}(\overline{\Phi})\overline{\Phi}'\eta' = 0, \tag{68}$$

$$\pm 2c\nabla^2\eta + 2g'_{1/2}(\overline{\Phi})\overline{\Phi}'\eta + 2g_{1/2}(\overline{\Phi})\eta' = 0, \tag{69}$$

where $\eta' = d\eta/dz$. By comparing with (62), we see that these boundary conditions imply

$$\mathcal{F}^{\pm}_{\text{wall}} = 0. \tag{70}$$

This relation ensures that $\hat{D}$ can be diagonalized as usual [17].

For the piecewise parabolic model, the correlation function $G(q_{\|},z,z')$ can be calculated most easily from Eq. (65) after a Fourier-transform parallel to the walls. A few details are given in Appendix A. The scattering intensity $S(\mathbf{q})$ has an additional contribution from the mean-field profile itself,

$$S(\mathbf{q}) = \left\langle \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}\Phi(\mathbf{r}) \int d\mathbf{r}'\, e^{i\mathbf{q}\cdot\mathbf{r}'}\Phi(\mathbf{r}') \right\rangle = A \int dz \int dz'\, e^{iq_\perp(z-z')}\, [\overline{\Phi}(z)\overline{\Phi}(z')\,\delta(\mathbf{q}_{\|}) + G(q_{\|},z,z')] \,. \tag{71}$$

B. Phase diagram for lamellar phase between walls

The order-parameter profile now depends on the separation of the walls, as well as on the boundary conditions. We study systems for which the infinite system is in the lamellar phase, not too far from the three-phase coexistence with the oil-rich and water-rich phases. To study the behavior of the system near the walls, we have determined the effective wall-interface interaction V by calculating the free energy of the oil-water interfacial profile as a function of the distance to the wall, see Fig. 3. For $\mu_{1/2} = 0$ the interaction is purely attractive. The free energy is minimized by a configuration, where $\Phi(z_{r/l}) = \pm\Phi_0$; the interface is adsorbed at the wall. For $\mu_{1/2} < 0$ an intermediate maximum develops and it depends on the values of $g_{1/2}$ and $a_{1/2}$ whether an adsorbed or a free interface is more favorable. Thus the adsorption transition is first order. In the following, the boundary conditions are always chosen such that the interface is desorbed, i.e., the surface order parameters are $\Phi(z_{r/l}) > \Phi_0$ or $\Phi(z_{r/l}) < -\Phi_0$.

When the separation of the walls is increased, the system will try to maintain the interface separation of the infinite system as closely as possible. Figure 4 shows the

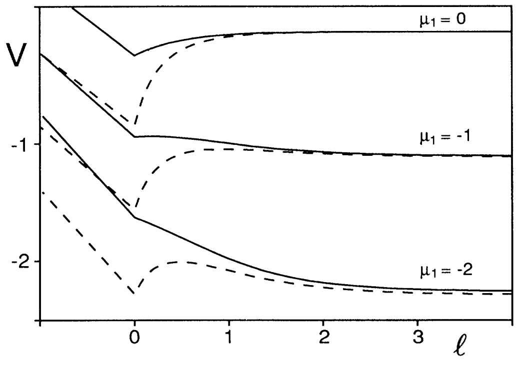

FIG. 3. Effective wall-interface potential V for $\mu_{1/2} \in \{0,-1,-2\}$, $g_{1/2} = 0$ (full lines), and $g_{1/2} = 2$ (dashed lines). ℓ is the distance from the wall to the first matching point, where $\Phi = \Phi_0$. For small μ_1 and g_1, V has a minimum at a finite distance d, which indicates adsorption of a monolayer to the wall. The other parameters are $a_{1/2} = 0$, $b_0 = -2.1$, $b_2 = 4.25$, and $f_0 = 0$.

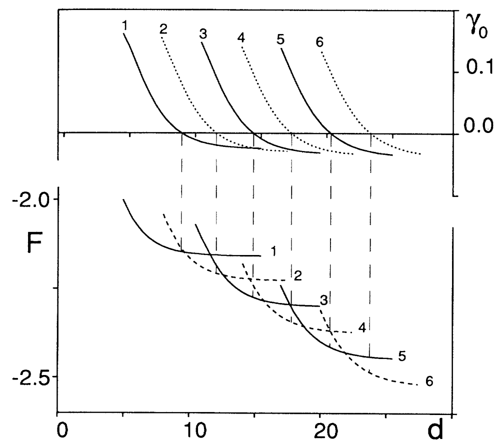

FIG. 4. The lamellar phase between two parallel walls, as a function of the wall separation d. The lower part shows the d dependence of the free energy for various numbers of monolayers. The full lines correspond to antisymmetric boundary conditions ($\mu_1 = -\mu_2$), and therefore to an odd number of monolayers, while the dotted lines correspond to symmetric boundary conditions with an even number of monolayers. The upper part shows the interfacial tension γ_0. Note that $\gamma_0 = 0$ always occurs when the configuration is stable. The parameters are $b_0 = -2.1$, $b_2 = 4.25$, $f_0 = 0$, $a_{1/2} = 0$, $\mu_1 = -1$, and $g_1 = 2$.

free energies of systems with a different number of oil-water interfaces as a function of the wall separation. It can be seen that as the wall separation increases, the interface separation also increases until at some point it becomes more favorable to squeeze an additional pair of interfaces into the system. A very similar behavior of the free energy has been observed experimentally for a system of a small number of membranes, studied with the surface force apparatus [18–20].

The spectrum of capillary waves of a single oil-water interface, and of the lamellar phase, is changed by the presence of the walls. We have shown in Sec. III C that the effective interface model (the curvature Hamiltonian) describes the fluctuations of the oil-water interfaces very well for systems where the lamellar phase is stable. In particular, we have found that modes other than the undulation modes have a much higher energy and can therefore be completely ignored. However, we have to take into account the interaction between the membrane and the wall.

The upper part of Fig. 4 shows the coefficient γ_0 of the translational mode, whose spectrum now reads

$$E_0(q,d) = E_0(d) + \gamma_0(d)q^2 + cq^4 + O(q^6), \tag{72}$$

where d is the wall separation. The optimal separation of interfaces is given by $\gamma_0 = 0$. Due to boundary effects, this separation only approximately equals the periodicity of the infinite lamellar phase. For smaller interface separations, γ_0 becomes positive, i.e., the interfacial area decreases due to a reduced amplitude of capillary waves, while for larger interface separation, the interfacial tension γ_0 becomes *negative*, i.e., the interfacial area increases due to an increased amplitude of the capillary waves. When the distance between interfaces is made very large and $4cE_0 < \gamma_0^2$, negative-energy eigenvalues appear. In this case, the stack of planar membranes becomes unstable with respect to a new phase, in which the undulations of wave vector $q_{\min} = \sqrt{-\gamma_0/2c}$ form a regular pattern with long-range correlations. This instability occurs only in the metastable region, where a system with the same wall separation but a larger number of interfaces is stable, and may therefore be difficult to observe experimentally.

C. Fluctuations of a single membrane between walls

We now want to study the consequences of the d dependence of the coefficients $E_0(d)$ and $\gamma_0(d)$ for a single membrane in detail. When only the translational mode, Eq. (72), is taken into account, the correlation function in a plane parallel to the walls can be written as

$$G(\mathbf{x}, z, z) = \eta_0(z)\eta_0(z) \int \frac{d^2q}{(2\pi)^2} e^{i\mathbf{q}\cdot\mathbf{x}} \frac{1}{E_0(q,d)}. \tag{73}$$

For large x and $4cE_0 > \gamma_0^2$, the correlations decay exponentially with oscillations, with a (parallel) correlation length

$$\xi_{\|} = \left(\frac{\gamma_0}{4c} + \frac{1}{2}\sqrt{\frac{E_0}{c}} \right)^{-\frac{1}{2}}. \tag{74}$$

The perpendicular correlation length is determined by the displacement of the interface perpendicular to the walls. For a single membrane between two walls at $z = \pm d/2$, it is found from (73) to be

$$\xi_\perp^2 = \int \frac{d^2q}{(2\pi)^2} G(q,0,0)$$
$$\propto \begin{cases} \left\{ \frac{\pi}{2} - \arctan(\gamma_0/\sqrt{4cE_0 - \gamma_0^2}) \right\} / \{2\pi\sqrt{4cE_0 - \gamma_0^2}\}, & 4cE_0 > \gamma_0^2 \\ \left(4\pi\sqrt{\gamma_0^2 - 4cE_0}\right)^{-1} \ln\{(\gamma_0 + \sqrt{\gamma_0^2 - 4cE_0})/(\gamma_0 - \sqrt{\gamma_0^2 - 4cE_0})\}, & 4cE_0 < \gamma_0^2 \end{cases} \tag{75}$$

The simplest case is certainly $\gamma_0 = 0$, where the following scaling relations [21, 22] can be obtained easily (in D dimensions):

$$\xi_{\parallel} \propto E_0^{-1/4}, \tag{76}$$

$$\xi_{\perp}^2 \propto \int d^{D-1}q \, \frac{1}{q^4 + \xi_{\parallel}^{-4}} = \xi_{\parallel}^{5-D} \int d^{D-1}(q\xi_{\parallel}) \frac{1}{(q\xi_{\parallel})^4 + 1}. \tag{77}$$

Therefore, in three-dimensional systems $\xi_{\perp} \propto \xi_{\parallel} \propto E_0^{-1/4}$. However, we have to keep in mind that due to the d dependence of γ_0 shown in Fig. 4, $\gamma_0(d)$ vanishes for *all d* nowhere in the phase diagram.

We can now determine the eigenvalues $E_0(q, d)$ numerically, and thus calculate the two correlation lengths (74) and (75), using the expression (31) for γ_0. At coexistence of the oil-rich, water-rich, and lamellar phases, where $\gamma_0(d = \infty) \approx 0$, the scaling relation $\xi_{\perp} \propto \xi_{\parallel} \propto E_0^{-1/4}$ is found to be satisfied quite well.

We want to consider next the d dependence of the free energy and the coefficients of the spectrum (72). Due to the exponential decay of the order-parameter profile towards the bulk value, the (mean-field) free energy also converges exponentially towards the free energy of a free interface, plus boundary contributions. The characteristic length scale must be the bulk correlation length of the homogeneous oil and water phases. We have to remember that the asymptotic decay of the profile actually has two length scales, even for $b_2 > b_{\mathrm{DO}} \equiv \sqrt{4c\omega_2}$. For large d, the larger of the two dominates; this is the length scale to be identified with the bulk correlation length. Figure 5 shows the excess free energy (without fluctuation contributions, see Sec. IV D) $F_d = F(d) - F(\infty)$, the energy eigenvalue $E_0(d)$, and the interfacial tension $\gamma_0(d)$. All three quantities are found to decay exponentially with the distance of the interface from the wall, i.e., $d/2$. The length scale is essentially the bulk correlation length, as expected. The agreement becomes better the further b_2 gets away from b_{DO}, where the two length scales separate. This can be seen clearly in Fig. 5(b). Thus, we have

$$\gamma_0(d) = \gamma_{\infty} + \overline{\gamma} e^{-d/\xi} + \cdots \tag{78}$$

with $\overline{\gamma} > 0$. Exactly the same behavior of the interfacial tension has been derived recently by Fisher and Jin [23] in the context of the wetting phenomena. In our model, the interfacial tension of the free oil-water interface, γ_{∞}, is negative (in the region of the phase diagram where the lamellar phase is stable); when the wall separation decreases, $\gamma_0(d)$ increases and equals zero when the optimal membrane distance is reached.

Experimentally, the fluctuations of a membrane can be studied by x-ray and neutron scattering. We calculate the scattering intensity (71) by Fourier transforming the correlation function; it contains *all* eigenmodes. Figure 6 shows $S(\mathbf{q})$ for wave vectors $\mathbf{q}$ parallel to the walls, and various wall separations. The negative interfacial tension γ_0 leads to a peak in the scattering intensity at finite wave vector for wall separations larger than the optimal lamellar distance. The peak position is given by $q_{\max} = \sqrt{-\gamma_0(d)/2c} = \sqrt{-\sigma_t(d)/2\kappa}$. Thus, by studying the peak position as a function of d the distance dependence of the interfacial tension can be determined.

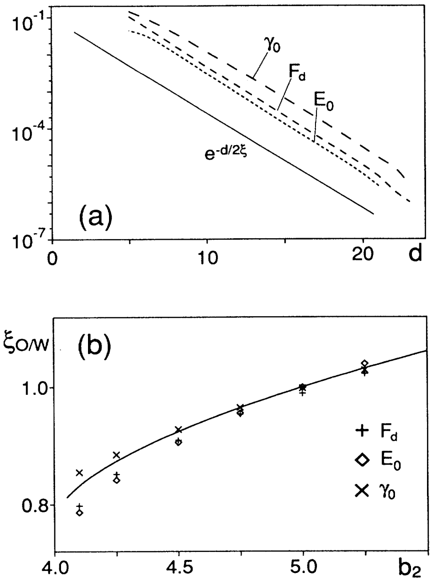

FIG. 5. (a) Exponential decay with wall separation d of excess free energy $F_d = F(d) - F(\infty)$, energy eigenvalue E_0, and interfacial tension γ_0 of the translation mode, at coexistence of the oil, water, and lamellar phases. The parameters are $b_0 = -2.5$, $f_0 = 0.1346$, $h_1 = -1$, $g_1 = 2$, and $b_2 = 4.25$. (b) The typical lengths of exponential decay of excess free energy F_d, energy eigenvalue E_0, and interfacial tension γ_0, compared with the larger of the two bulk correlation lengths in the homogeneous oil-water phases (full line), as a function of b_2.

D. Fluctuation-induced interaction

When the Gaussian fluctuations of the order parameter are taken into account, the free energy of an interface between walls, compared to the free energy of an uncon-

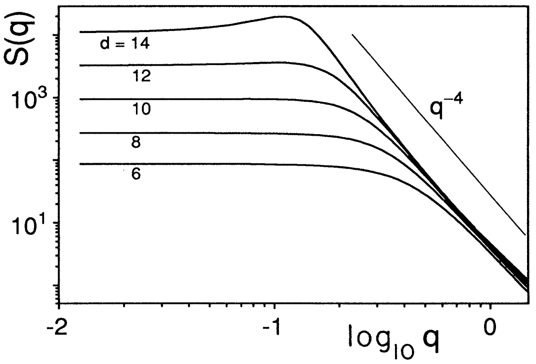

FIG. 6. Scattering intensity $S(q)$ for a single monolayer between walls, with wave vector $\mathbf{q}$ parallel to the walls, for various wall separations d, as indicated. For separations $d \geq 10$, a peak appears at $q > 0$, indicating a negative sign of the interfacial tension. Parameters are the same as in Fig. 3.

strained interface, has the additional contribution

$$\Delta F_e(d) = \Delta F(d) - \Delta F(\infty) = \tfrac{1}{2}\sum_n \int_{q<q_{\max}} d^{D-1}q \, \ln \frac{E_n + \gamma_n q^2 + cq^4}{E_{n,\infty} + \gamma_{n,\infty} q^2 + cq^4} \,. \tag{79}$$

For $\gamma_0 = 0$ this excess free energy scales as

$$\Delta F_e \propto \int d^{D-1}q \, \ln \frac{q^4 + \xi_{\|}^{-4}}{q^4} = \xi_{\|}^{-(D-1)} \int d^{D-1}(q\xi_{\|}) \ln \frac{1 + (q\xi_{\|})^4}{(q\xi_{\|})^4} \,. \tag{80}$$

Thus, $\Delta F_e \propto \sqrt{E_0}$ for $D = 3$. Since E_0 depends exponentially on the wall separation, so does ΔF_e. By numerically evaluating (79), we have checked that the excess free energy indeed decays exponentially with increasing wall separation.

Thus, on the level of Gaussian fluctuations, interfaces with $\gamma_0 = 0$ between walls do not lead to a fluctuation-induced steric interaction with an algebraic d^{-2} decay, as expected from an analysis of the effective curvature Hamiltonian [4]. This can be easily traced back to the exponential dependence of the perpendicular correlation length $\xi_\perp$ on the wall separation d, whereas $\xi_\perp \propto d$ in the curvature model. To arrive at such a relation, the interaction of capillary waves, which is neglected on the level of Gaussian fluctuations studied here, has to be taken into account.

E. Fluctuations of a stack between walls

When the wall separation is much larger than the spacing of the infinite lamellar phase, a stack of oil-water interfaces is present between the walls. In the case of N membranes, there are now N undulation modes at fixed wave vector q parallel to the walls. The translational mode, where the undulations of all membranes are in phase, is still the excitation of lowest energy at small q. However, for large distances between membranes, the other modes have only slightly larger energies; the difference $E_n(q = 0) - E_0(q = 0)$ decreases exponentially with increasing wall separation (with a fixed number of membranes in the stack).

The spectrum of undulation modes for five membranes is shown in Fig. 7, in the case of the optimal lamellar spacing, so that $\gamma_0 = 0$. It can be seen that the coefficient γ_n of all undulation modes except for the translational mode are *negative*. For sufficiently large q, the energies of all undulation modes increase as κq^4; in this case the spectrum is determined by the curvature energy and depends only very weakly on the interaction between membranes. Thus, all these modes have a minimum in their spectrum as a function of q.

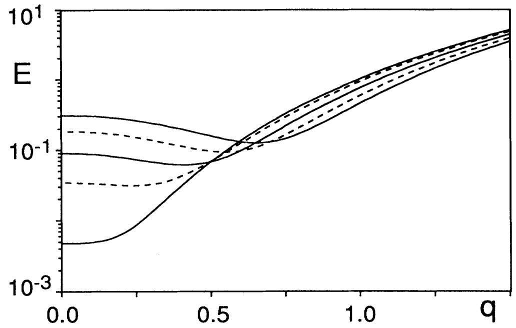

FIG. 7. Energy eigenvalues of the undulation modes for a stack of five amphiphilic monolayers with "ideal" separation ($\gamma_0 = 0$). The antisymmetric modes are shown by dotted lines. Parameters are the same as in Fig. 3.

We have calculated the scattering intensity of the stack for two cases, $q_\perp = 0$ (i.e., the wave vector is parallel to the walls) and $q_\perp = q_\|$ (i.e., the wave vector is tilted by 45° from the normal). In the first case antisymmetric modes do not contribute to the scattering intensity. For an even number of interfaces this is in particular the translational mode, so that the scattering intensity is considerably smaller than for an odd number of interfaces. The scattering intensity for five and six membranes is shown in Fig. 8 for various wall separations. We have checked numerically that the scattering intensity is dominated by the undulation modes, so that in the expression

$$S(q_\perp, \mathbf{q}_\|) = \int dz \int dz' \, e^{iq_\perp(z-z')} \sum_n \frac{\eta_{n\mathbf{q}_\|}(z)\eta_{n\mathbf{q}_\|}(z')}{E_{n\mathbf{q}_\|}} \tag{81}$$

terms other than the undulation modes can be essentially neglected. However, *all* undulation modes contribute appreciably to the scattering intensity; the negative coefficients γ_n of the spectrum of these modes leads to additional peaks in the intensity at wave vector $q_{\max} = \sqrt{-\gamma_n(d)/2c}$. In the range of wall separa-

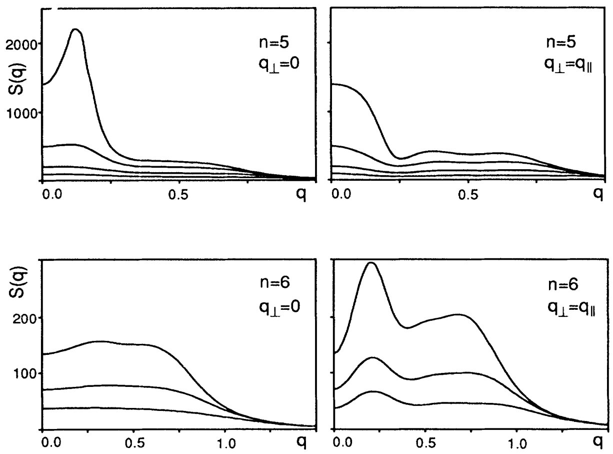

FIG. 8. Scattering intensities $S(q)$ for five and six monolayers between walls, with wave vector $\mathbf{q}$ parallel to the walls, as well as with an angle of 45°. Parameters are the same as in Fig. 3. For five layers, the wall separations $d = 18, 20, 22, 24$ are used; for six layers $d = 20, 22, 24$ (from bottom to top).

tions studied in Fig. 8, the peak position decreases with d; however, the expected exponential behavior could not be observed, since the $\gamma_n(d)$ have not yet reached their asymptotic exponential regime for large d.

VI. SUMMARY AND CONCLUSIONS

The fluctuations of interfaces in ternary oil-water-surfactant mixtures have been studied for a simple Ginzburg-Landau model. On the level of Gaussian fluctuation theory, we find that the bending rigidity κ, which controls the fluctuations of the oil-water interface, agrees very well with the rigidity obtained from the free energy of cylinders and spheres. Furthermore, we confirm that the modification of the intrinsic interfacial profile due to curvature can be neglected for the calculation of κ for saturated monolayers. On the other hand, the bending rigidity of the water-microemulsion interface is dominated by the curvature-induced distortion of the intrinsic profile. We have also shown that the interfacial tension term in the spectrum of the translational mode in the lamellar phase vanishes identically. Thus, we have shown that our Ginzburg-Landau model correctly reproduces the spectrum expected from general symmetry arguments.

The Ginzburg-Landau model has then been used to study fluctuations of several interfaces between two parallel walls. This geometry is accessible to experiments, and has already been investigated in some detail experimentally. We find that the interfacial tension is now a function of the distance between the walls, and thus a function of the distance between interfaces. When the interfaces are pulled apart, the tension becomes negative, signaling the system's desire to increase its interfacial area, whereas the tension becomes positive under compression. The negative tension leads to a peak in the scattering intensity, which should be possible to detect in x-ray or neutron-scattering experiments. By following the peak position as a function of the wall separation d, the d dependence of the interfacial tension could be measured.

Gaussian fluctuation theory is limited to the investigation of small fluctuations. This condition is fulfilled in the lamellar phase between walls, as long as the number of interfaces is small, and the distance between the interfaces is not too large. Thus, it cannot be used, for example, to calculate the scattering intensity for a large stack near the Bragg positions, where an algebraic singularity appears [14, 4, 24]. It also cannot be used to calculate the structure and fluctuations of microemulsions with strong amphiphiles. Therefore, we use Monte Carlo simulations to investigate large fluctuations in ternary amphiphilic systems in the second paper of this series [25].

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APPENDIX: CALCULATIONS IN THE PIECEWISE PARABOLIC MODEL

In the piecewise parabolic model, the Euler-Lagrange equation (5) reduces to a piecewise linear equation [5, 7]. The amplitudes of the resulting exponential functions are determined by matching conditions at the points $z = z_0$ where $\Phi = \Phi_0$. The matching conditions at $\Phi = \Phi_0$ are the continuity of the profile, its first two derivatives, and of the first integral (6).

The eigenvalue equation (17) for the Gaussian fluctuations also reduces to a piecewise linear equation,

$$(c\Delta^2 - b\Delta + \omega - E)\eta = 0\,. \tag{A1}$$

This equation can be solved by the ansatz

$$\begin{aligned} \eta(z) &= \sum_{i=1}^{4} L_i e^{\lambda_i z}\ , \quad c\lambda^4 - b_2\lambda^2 + \omega_2 - E = 0\ , \\ &\qquad\qquad\qquad\qquad\qquad\qquad |\Phi| > \Phi_0\ , \\ \eta(z) &= \sum_{i=1}^{4} M_i e^{\mu_i z}\ , \quad c\mu^4 - b_0\mu^2 + \omega_0 - E = 0\ , \\ &\qquad\qquad\qquad\qquad\qquad\qquad |\Phi| < \Phi_0\,. \end{aligned} \tag{A2}$$

At the points $z = z_0$ with $\Phi(z_0) = \Phi_0$, we again need matching conditions, from which we can determine the amplitudes L_i and M_i. Because of the discontinuity of $g(\Phi)$, $\hat{D}$ contains terms proportional to $\delta'(z - z_0)$ and $\delta''(z - z_0)$. These singular contributions have to be compensated by similar terms in the highest derivative of η,

$$\nabla^4\eta = A\ \delta'(z - z_0) + B\ \delta(z - z_0) + \cdots\ . \tag{A3}$$

To solve Eq. (17) at $z = z_0$, we demand

$$\lim_{\epsilon\to 0} \int_{z_0-\epsilon}^{z_0+\epsilon} [(\hat{D} - E)\eta(z)]h(z)\ dz = 0 \tag{A4}$$

for an arbitrary test function h. After partial integration and with the use of the fact that $h(z_0)$ and $h'(z_0)$ should be independent, we arrive at

$$A = \frac{b_2 - b_0}{2c}\ \eta(z_0), \tag{A5}$$

$$\begin{aligned} B = {} & \frac{b_2 - b_0}{2c} \left(\frac{\overline{\Phi}''(z_0)}{\overline{\Phi}'(z_0)}\eta(z_0) + \eta'(z_0) \right) \\ & + \frac{\omega_2 - \omega_0}{c} \frac{\overline{\Phi}(z_0)}{\overline{\Phi}'(z_0)}\eta(z_0). \end{aligned} \tag{A6}$$

We conclude that at the matching points $\eta(z_0)$ and $\eta'(z_0)$ must be continuous, and

$$\eta''_{me}(z_0) = \eta''_{o/w}(z_0) + A, \tag{A7}$$

$$\eta'''_{me}(z_0) = \eta'''_{o/w}(z_0) + B\,, \tag{A8}$$

where the subscripts "me" and "o/w" denote the phase in which the functions are evaluated. Since A and B are linear functions of η and η', respectively, we have to solve a system of homogeneous linear equations in the amplitudes L_i and M_i. This determines the energy eigenvalues E_n.

After a Fourier transform parallel to the interface, (A2) can be generalized to modes with wave vectors $q \neq 0$,

$$\eta(\mathbf{q}, z)e^{i\mathbf{q}\cdot\mathbf{x}} = \sum_{j=1}^{4} L_j e^{\lambda_j z} e^{i\mathbf{q}\cdot\mathbf{x}} \ , \tag{A9}$$

$$\lambda^4 + \left(-\frac{b}{c} - 2q^2\right)\lambda^2 + \left(q^4 + \frac{b}{c}q^2 + \frac{\omega - E}{c}\right) = 0 \ . \tag{A10}$$

The matching conditions remain unchanged. The full spectrum can be calculated numerically.

The correlation function $G(q_{\|}, z, z')$ can be obtained using the same ansatz. The δ function in Eq. (65) becomes an additional matching point at $z = z'$, where $A = 0$ and $B = 1$.

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