Sponge-lamellar instability of fluctuating membranes

P. Pieruschka
Department of Applied Mathematics, Australian National University, Canberra 0200, Australia and Physical Chemistry 1, Chemical Center, University of Lund, Lund 22100, Sweden
(Received 6 March 1995)

We consider the instability of amphiphilic sponge phases with respect to a fluctuating lamellar phase in a consistent random interface model based on the curvature-elastic Hamiltonian of the membranes. The phase behavior is investigated in terms of bending moduli and surfactant concentration. First-order transitions are found upon changes in surfactant concentration, bending modulus, or saddle-splay modulus in agreement with experimental observation.

PACS number(s): 68.15.+e, 05.40.+j, 02.40.−k

INTRODUCTION

Experimentally, it is well established that in self-assembling amphiphilic systems of both binary and ternary types (where the amphiphile is dissolved in water or/and oil, respectively) the appearance of the isotropic sponge phase is intimately related to a nearby lamellar phase where the observed transition from sponge to lamellae can be triggered by increasing surfactant concentration or chain length or by decreasing alcohol content [1,2].

The theoretical literature on the relative stability of sponge and lamellar phases evolves mainly around microscopic (Ising-type) models, phenomenological Ginzburg-Landau (GL) theories [3–5], and the effective interface (membrane) model [2,6–9]. While microscopic and GL theories yield phase diagrams which are in principle difficult to relate to experiment because they are cast in phenomenological parameters without obvious physical meaning [5], the coarse-grained membrane model of Andelman *et al.* consistently predicted phase diagrams for both microemulsions [6] and L_3 phases [7] which could be expressed in terms of observable parameters and which qualitatively resemble measurement. However, the free energy of the lamellar phase considered there was heuristically taken as Helfrich's free of steric repulsion [10,11] and is therefore not consistent with the free energy of the sponge phase derived in [6,7]. An extension of the coarse-grained lattice model by Golubović and Lubensky remedied this inconsistency, but at the expense of an extended parameter space [8]. Finally, Porte *et al.*'s work [2] is based on general stability properties of the bending Hamiltonian [cf. Eq. (1)], leads to very useful insights into the role of the saddle-splay curvature and compares well to experiment, but remains semiquantitative because it does not take entropic terms into account.

In general, a consistent and quantitative theoretical approach to the structure and thermodynamics of the sponge (asymmetric or symmetric) and fluctuating lamellar phases in terms of parameters which can be related to experiment remains a challenge. An up-to-date account of experimental phenomena and the (mostly open) theoretical problems they pose has recently been given by Strey [12], who lists the relative stability of the sponge and lamellar phases, the typical shape of the lamellar region of the phase diagram (in ternary systems), and the vanishing of the one-phase microemulsion region upon change in surfactant chain length as outstanding problems. Furthermore, both experimentalists and theorists have often pointed out that no current approach can do justice to the fact that topological changes are a crucial factor for the sponge-lamellar (S-L) transition, so that the Gaussian curvature of the surfactant layer (cf. below) should by no means be dropped in an approach to the S-L transition [2,13–16]. This has led to renewed interest in the role of topology in the most recent literature [17,18]. Another startling point is the stability of L_3 toward L_α phases up to a relatively high surfactant concentration $\phi_s \approx 30\%$ [1], which has also been related to the effect of saddle-splay curvature [2,13].

In this paper we will treat the instability of the sponge phase which leads to a fluctuating lamellar phase within the framework of a random interface model which allows for a systematic and consistent approach to the structure and thermodynamics of fluctuating membranes with variable topology. Detailed attention will be given to the role of Gaussian elasticity (Euler characteristic) [19] and surfactant concentration. Unlike most previous approaches we will *not* work in the limit of membranes with high bending stiffness [20,17,18,11], but will take effects of configurational (topological) entropy quantitatively into account. Free energies of both fluctuating sponge and anisotropic phases will be consistently derived in one theoretical framework.

MODEL

We build on a variational model of random self-avoiding interfaces which has recently been successfully applied to consistently describe both structure and thermodynamics of bicontinuous microemulsions and L_3 sponge phases [21–23]. This approach is based on the description of the surfactant film as an ensemble of flexible interfaces which are governed by the bending Hamiltonian $\mathcal{H}$ of an elastic bilayer [24]

$$\mathcal{H}=\int_S dS[2\kappa H^2+\bar{\kappa}K] , \tag{1}$$

where H^2 and K denote the local mean square and saddle-splay curvatures of the film, respectively. The parameters which characterize Eq. (1) are the surfactant volume fraction ϕ_s (which is proportional to the surface to volume ratio $\phi_s=r_c S/V$ [20], where r_c is the layer thickness) and the bending and saddle-play moduli κ and $\bar{\kappa}$ of the flexible interface. The ratio of the bulk partitions on either side of the interface (or of inside and outside [26] in binary systems) ϕ is fixed by the oil and water volume fractions in ternary systems, but is in principle a free variable in binary systems. The variational model of fluctuating membrane systems is discussed (for the isotropic case) in detail in [22,23]. It introduces surfaces that are implicitly defined by a smoothly varying scalar field, $s(\mathbf{r})$, whose level cuts $s(\mathbf{r})=\text{const}=\alpha$ [25] delineate the position of the surfactant film separating the bulk components in ternary systems and the inside-outside partitions in binary systems. The spectral density (structure factor) of the field $s(\mathbf{r})$ can be systematically derived, if it is assumed to be Gaussian, by using the variational Feynman-Hellman theorem [27,28] which relates the free energies of the real and model (Gaussian) systems $\underline{F}$ and $\underline{F}_0$ by

$$\underline{F}\le F=\underline{F}_0+\langle\mathcal{H}-\mathcal{H}_0\rangle_0 , \tag{2}$$

where $\langle\ \rangle_0$ denotes Gaussian ensemble averages, and $\mathcal{H}_0$ is the Gaussian model Hamiltonian

$$\mathcal{H}_0\sim\sum_{\mathbf{k}}\nu^{-1}(\mathbf{k})|s(\mathbf{k})|^2 \tag{3}$$

characterized by its structure factor $\nu(\mathbf{k})$. One can write the free energy per unit volume $f=F/V$ in units of k_BT (neglecting constant terms) explicitly as

$$f[\nu(\mathbf{k})]=2\kappa\langle H^2\rangle_0+\bar{\kappa}\langle K\rangle_0-\tfrac{1}{2}\sum_{\mathbf{k}}\ln\nu(\mathbf{k}) , \tag{4}$$

where the (surface) average of a physical quantity O is defined here as $\langle O\rangle_0/V=\langle\delta(s-\alpha)\sqrt{(\nabla s)^2}O\rangle_0$. In membrane models with a bending Hamiltonian it is common to assume further that the surfactant film is incompressible [20], so that the free energy density $f=f[\nu(\mathbf{k});\kappa,\bar{\kappa},\phi_s,\alpha]$ has to be functionally minimized with respect to $\nu(\mathbf{k})$ under the constraint of fixed total surfactant volume fraction ϕ_s. Moreover, a mean-spherical condition [22] has to be applied to contain the overcounting of the entropy of the random field $s(\mathbf{r})$. These physical constraints can again be expressed solely in terms of $\nu(\mathbf{k})$ and α, the asymmetry parameter which is related to the inside-outside ratio by $\phi=\frac{1}{2}[1-\text{erf}\,(\alpha/\sqrt{2})]$ [29]. The mean curvature of the interface $\langle H\rangle_0$ is proportional to α (cf. the Appendix), and hence we deal with symmetric structures for $\langle H\rangle_0\sim\alpha=0$ and with asymmetric structures for $\alpha\neq 0$. For a given physical situation, i.e., at fixed values of κ, $\bar{\kappa}$, ϕ_s, and ϕ, the physical state of the system can therefore be determined by variationally minimizing the free energy density f with respect to $\nu(\mathbf{k})$ (and, possibly, by a subsequent second minimization with respect to α in binary systems). All structural and thermodynamic results of the theory are then described by the parameters κ, $\bar{\kappa}$, and ϕ_s only, with no further adjustable parameters.

The simplest way of consistently generalizing the random interface formalism beyond isotropic sponge phases is by going to anisotropic phases with $D_{\infty h}$ type symmetry. One can then use a probability distribution of the form

$$\sim\exp\left[-\sum_{k_\rho,k_z}\frac{|s(k_\rho,k_z)|^2}{2\langle|s(k_\rho,k_z)|^2\rangle_0}\right] ,$$

where $s(k_\rho,k_z)$ is the Fourier transform of the random field $s(\rho,z)$, and ρ and z now denote in-plane and normal coordinates. Isotropic and anisotropic structures can be described using a (uniaxial, nonchiral) nematic order parameter which can be expressed as $m_{ij}=\langle s_is_j-\frac{1}{3}\delta_{ij}(\nabla s)^2\rangle_0$, where the s_i are first derivatives of s, analogous to the order parameter introduced by Maier and Saupe [30–33]. If we—without loss of generality—do the usual simplification to align the z axis of the coordinate system with the direction of lamellar ordering [32,33], m_{ij} becomes diagonal, and a more convenient, scalar quantity can be used as the order parameter. For our purposes it is most convenient to define the dimensionless quantity m by

$$m=1-\frac{\sigma_\rho}{\sigma_z},\quad \sigma_\rho=\tfrac{1}{2}\langle s_x^2+s_y^2\rangle_0,\quad \sigma_z=\langle s_z^2\rangle_0 . \tag{5}$$

Values of the order parameter $m\approx 1$ describe an ensemble of nearly flat layers; for $m=0$ we regain the sponge phase and for $m<0$ a fluctuating columnar phase is described (which we found to be always unstable and which we will not pursue here).

The nematic lamellar phase was first postulated by Huse and Leibler [34]. Unlike smectic lamellar phases which show long range orientational and quasi-long-range positional order, nematic phases are characterized by long range orientational order but only short range positional order. The ground state of nematic phases is highly degenerate, and can be imagined as an ensemble of freely moving flat layers, so that an infinite number of zero temperature configurations is possible (a paramagnet with a molecular lattice constant in one dimension). For all these configurations the bending energy is zero. The smectic phase, in contrast, has a periodic ground state. On the other hand, Morse and Milner's Brazovskii (GL) model predicts that the nematic phase is always unstable with respect to the smectic phase [33]. We cannot join the discussion concerning the nematic-smectic instability here [35], but note that our treatment will certainly provide an *upper boundary* of the stability of the sponge phase (within the limits of accuracy of the first-order Feynman-Hellman approximation) [40]. As this upper limit can be predicted within a model that is capable of consistently and quantitatively treating structure and thermodynamics of fluctuating membranes with variable topology beyond the limit of high bending stiffness and under rigorous conservation of membrane area, it will in

any case contribute to the understanding of the isotropic-anisotropic transition in amphiphilic systems.

RESULTS

We can proceed by establishing the statistical quantities needed to evaluate Eq. (4) for uniaxial nematic lamellar phases [41]. With the definition

$$\langle k_\rho^n k_z^m\rangle=(4\pi^2)^{-1}\int\int dk_\rho dk_z k_\rho^{n+1}k_z^m \nu(k_\rho,k_z) \tag{6}$$

of the moments of the structure factor $\nu(k_\rho,k_z)$, we find the surface average of the mean square curvature to read (cf. the Appendix for details concerning the calculation of statistical averages)

$$\langle H^2\rangle_0=H_1(\sigma_\rho,\sigma_z)\langle k_\rho^4\rangle+H_2(\sigma_\rho,\sigma_z)\langle k_\rho^2 k_z^2\rangle + H_3(\sigma_\rho,\sigma_z)\langle k_z^4\rangle+H_4(\sigma_\rho,\sigma_z)\ , \tag{7}$$

with

$$H_1(\sigma_\rho,\sigma_z)=(4\pi)^{-1}\sigma_z^{-1/2}e^{-\alpha^2/2}m^{-2}[-\tfrac{3}{8}-\tfrac{3}{8}m+(\tfrac{3}{8}+\tfrac{1}{4}m+\tfrac{3}{8}m^2)m^{-1/2}\operatorname{arctanh}(m^{1/2})]\ ,$$

$$H_2(\sigma_\rho,\sigma_z)=(4\pi)^{-1}\sigma_z^{-1/2}e^{-\alpha^2/2}m^{-2}[3-m+(-3+2m+m^2)m^{-1/2}\arctan(m^{1/2})]\ ,$$

$$H_3(\sigma_\rho,\sigma_z)=(4\pi)^{-1}\sigma_z^{-1/2}e^{-\alpha^2/2}m^{-2}[-1+\tfrac{5}{3}m+(1-m)^2m^{-1/2}\operatorname{arctanh}(m^{1/2})]\ ,$$

$$H_4(\sigma_\rho,\sigma_z)=(12\pi)^{-1}\sigma_z^{3/2}e^{-\alpha^2/2}(\alpha^2-1)m^{-2}[9m^2-7m^3+3m^2(1-m)^2m^{-1/2}\operatorname{arctanh}(m^{1/2})]\ .$$

For $m\to 0$, Eq. (7) converges towards its isotropic form $(2/\pi)e^{-\alpha^2/2}\sqrt{\langle k^2\rangle/3}\,[\frac{1}{6}(\alpha^2-1)\langle k^2\rangle+\frac{1}{5}\langle k^4\rangle/\langle k^2\rangle]$ (which was derived by Teubner in [29]) as it should, with $\sigma_z=\frac{1}{2}\sigma_\rho\to\frac{1}{3}\langle k^2\rangle$, $\langle k_\rho^4\rangle\to\frac{8}{15}\langle k^4\rangle$, $\langle k_\rho^2 k_z^2\rangle\to\frac{2}{15}\langle k^4\rangle$, and $\langle k_z^4\rangle\to\frac{1}{5}\langle k^4\rangle$.

The saddle-splay curvature reads

$$\langle K\rangle_0=\pi^{-1}e^{-\alpha^2/2}(\alpha^2-1)\sigma_z^{3/2}(1-m)\ , \tag{8}$$

where the isotropic limit

$$\langle K\rangle_0\to 2/\pi e^{-\alpha^2/2}\sqrt{\langle k^2\rangle/3}\,\tfrac{1}{6}(\alpha^2-1)\langle k^2\rangle$$

[29] can be taken without problem. We see that, in the absence of in-plane fluctuations, $m\to 1$ and $\langle K\rangle_0\to 0$, corresponding to essentially parallel interfaces without saddlelike connections.

Finally, the surface to volume ratio which is proportional to ϕ_s reads

$$S/V=\pi^{-1}e^{-\alpha^2/2}(\sigma_z)^{1/2} \times[1+(1-m)m^{-1/2}\operatorname{arctanh}(m^{1/2})]\ . \tag{9}$$

This expression converges toward the proper isotropic limit for $m\to 0$ (cf. [29]) and remains well defined for maximal anisotropy $m\to 1$.

We can now write the free energy per unit volume more explicitly:

$$f[\nu(k_\rho,k_z)]=2\kappa[H_1\langle k_\rho^4\rangle+H_2\langle k_\rho^2k_z^2\rangle +H_3\langle k_z^4\rangle+H_4]+\bar\kappa\langle K\rangle_0 -\frac{1}{8\pi^2}\int\int dk_\rho dk_z k_\rho \ln\nu(k_\rho,k_z)\ . \tag{10}$$

Analogous to our work on isotropic systems [22], we can functionally minimize $\partial\bar f[\nu]/\partial\nu=0$ (where $\bar f=f+\lambda_1 S/V+\lambda_2\langle s^2(\mathbf{r})\rangle_0$ is the free energy per unit volume including the physical constraints coupled by Lagrange multipliers) to gain the optimal structure factor which, after simple calculation [42], reads

$$\nu(k_\rho,k_z)=[ak_\rho^4+bk_\rho^2k_z^2+ck_z^4-dk_\rho^2-ek_z^2+g]^{-1}\ . \tag{11}$$

The coefficients $a,\ldots,g$ have to be determined by minimization. In the case of a, b, and c this can be done immediately due to the simple form of Eq. (10), in which H_1, H_2, and H_3 are only dependent on σ_ρ and σ_z, and are thus given by

$$a(\kappa,\phi_s,\phi)=4\kappa H_1,\quad b(\kappa,\phi_s,\phi)=4\kappa H_2,\quad c(\kappa,\phi_s,\phi)=4\kappa H_3\ , \tag{12}$$

while the remaining coefficients d, e, and g can be determined by the two constraints $\langle s^2(\mathbf{r})\rangle_0=\langle 1\rangle=1$ and $\phi_s=\text{const}$ and the definition of the order parameter $m=1-\sigma_\rho/\sigma_z$ which form the nonlinear equation system

$$\begin{aligned}&(4\pi^2)^{-1}\int\int dk_\rho dk_z k_\rho \nu(k_\rho,k_z)=1\ ,\\ &(4\pi^2)^{-1}\int\int dk_\rho dk_z k_\rho^3\nu(k_\rho,k_z)\\ &\quad=2(1-m)\pi^2e^{\alpha^2}\phi_s^2\\ &\qquad\times[1+(1-m)m^{-1/2}\operatorname{arctanh}(m^{1/2})]^{-2}\\ &(4\pi^2)^{-1}\int\int dk_\rho dk_z k_\rho k_z^2\nu(k_\rho,k_z)\\ &\quad=\pi^2e^{\alpha^2}\phi_s^2[1+(1-m)m^{-1/2}\operatorname{arctanh}(m^{1/2})]^{-2}\ .\end{aligned} \tag{13}$$

Equation system (13) can be solved numerically or perturbatively for small values of m in the spirit of a Landau expansion. In the latter case we write all relevant quantities up to fourth order:

$$x\approx x_0+x_1m+x_2m^2+x_3m^3+x_4m^4\ , \tag{14}$$

with $x=a$, b, c, d, e, g, σ_ρ, σ_z, and ν, and where the indices i refer to orders in m. The series for σ_ρ, σ_z, a, b, and c are readily known. To calculate the remaining coefficients and the structure factor, we can write

$$\nu_i=w_i-n_0^{-2}n_i\ , \tag{15}$$

with the recursion sequence $w_1=0$, $w_2=n_0^{-3}n_1^2$, $w_3=n_0^{-4}[-n_1^3+2n_0n_1n_2]$, and $w_4=n_0^{-5}[n_1^4-3n_0n_1^2n_2+n_0^2n_2^2+2n_0^2n_1n_3]$, where

$$n_i = a_i k_\rho^4 + b_i k_\rho^2 k_z^2 + c_i k_z^4 - d_i k_\rho^2 - e_i k_z^2 + g_i \ ,$$

and the indices i again denote orders in m. The particularly simple form of the coefficients of the structure factor can be fully exploited by performing the integrations on the left-hand side of Eqs. (13) in spherical coordinates with appropriate integration limits in cylindrical coordinates $\int_0^{\sqrt{k_c^2-k_z^2}} \int_{-k_c}^{k_c} \ldots dk_\rho dk_z$. k_c is an integration limit chosen as a small multiple of the inverse molecular size; therefore thermal fluctuations (which do *not* necessarily have to leave the topology unchanged; the membrane is, for example, allowed to disintegrate into small aggregates for small values of κ [22,23], cf. also the S-A transition below) at all length scales down to some $2\pi/k_c$ are naturally included, and we do not have to make use of renormalized bending moduli. Equation (15) also shows that the 3×3 equation systems which determine the successive sets of coefficients $d_1, e_1, g_1, \ldots, d_4, e_4, g_4$ are inhomogeneous linear equation systems. The calculation of the coefficients is therefore reduced to the evaluation of (solvable) radial integrals and a set of linear equation systems

$$\begin{bmatrix} -\frac{2}{3}V_{24} & -\frac{1}{3}V_{24} & V_{22} \\ -\frac{8}{15}V_{26} & -\frac{2}{15}V_{26} & \frac{2}{3}V_{24} \\ -\frac{2}{15}V_{26} & -\frac{1}{5}V_{26} & \frac{1}{3}V_{24} \end{bmatrix} \begin{bmatrix} d_i \\ e_i \\ g_i \end{bmatrix} = \begin{bmatrix} L_{i1} \\ L_{i2} \\ L_{i3} \end{bmatrix} , \qquad (16)$$

where $V_{mn} = (2\pi^2)^{-1} \int_0^{k_c} dk\, n_0^{-m} k^n$, $L_{i1} = W_i - \lambda_{i1}$, $L_{i2} = -2\sigma_{\rho i} + W_i - \lambda_{i2}$, $L_{i3} = -\sigma_{zi} + W_i - \lambda_{i3}$, $W_i = (2\pi^2)^{-1} \int\int dk_\rho dk_z k_\rho w_i$, $\lambda_{i1} = V_{26}/15[8a_i + 2b_i + 3c_i]$, $\lambda_{i2} = V_{28}/105[48a_i + 8b_i + 6c_i]$, and $\lambda_{i3} = V_{28}/105[8a_i + 6b_i + 15c_i]$. The missing expansion coefficients of the structure factor, d_i, e_i, and g_i, can finally be given as

$$d_i(\kappa,\phi_s,\phi) = 4^{-1} V^{-1} V_{26}^{-1} [4L_{i1} V_{24} V_{26} + L_{i2}(5V_{24}^2 - 9V_{22}V_{26}) + L_{i3}(6V_{22}V_{26} - 10V_{24}^2)] \ ,$$

$$e_i(\kappa,\phi_s,\phi) = -2^{-1} V^{-1} V_{26}^{-1} [-2L_{i1} V_{24} V_{26} + L_{i2}(5V_{24}^2 - 3V_{22}V_{26}) + L_{i3}(12V_{22}V_{26} - 10V_{24}^2)] \ ,$$

$$g_i(\kappa,\phi_s,\phi) = V^{-1}[L_{i1} V_{26} - L_{i2} V_{24} - L_{i3} V_{24}]$$

for $i = 1, \ldots, 4$ and with $V = -V_{24}^2 + V_{22} V_{26}$. Together with the already known expressions for a_i, b_i, and c_i, we have thus determined the coefficients of the structure factor as functions of κ, ϕ_s, and ϕ up to fourth order in m, where the most complicated terms appearing in the expansion coefficients are given as one-dimensional radial integrals which are exactly solvable.

In order to check the perturbative results, we have compared with independently calculated numerical solutions (to all orders in m) of equation system (13) for a number of choices of κ and ϕ_s. Agreement was found to be satisfactory but deteriorates—as expected—for increasing values of m [43].

Before we proceed with stability and phase transitions, it is instructive to consider briefly examples of nematic lamellar structure. In Fig. 1 we show angle averaged structure factors for $\kappa = 5$, $\phi_s = 0.1$, and $\alpha = 0$ for order parameter values of $m = 0$ and 0.9. Corresponding real-space representations for different values of the order parameters are given in the next figure, Fig. 2. The image for $m = 0.9$ resembles the freeze fracture electron microscopy (FFEM) images in [14,39] (particularly when looking at more detailed zooms into the images given in [14,39]) [44]. Uniaxial order is clearly discernible, but there are still many topological defects. These become progressively fewer for higher values of the order parameter $m \to 1$ when the structure factor approaches the form expected for lamellar structure ($\sigma_\rho \to 0$)

$$\nu^{-1}(k_\rho, k_z) = c \left[k_z^2 - \frac{1}{2c}(e - bk_\rho^2) \right]^2 - \frac{1}{4c}(e - bk_\rho^2)^2 + ak_\rho^4 - dk_\rho^2 + g \ .$$

For small $k_\rho \to 0$ we find that for $e^2/(4c) - g \approx 0$ a sharp peak at $k_z^2 \approx e/(2c)$ emerges, while at the same time due to $be/(2c) - d \approx 0$ the fluctuation in the k_ρ direction converges for $k_z^2 \to e/(2c)$ toward a sharp peak centered at $k_\rho \approx 0$.

Having determined the structure factor, we can insert $\nu(k_\rho, k_z; \kappa, \phi_s, \alpha; m)$ into the free energy per unit volume [Eq. (10)] and integrate over k_ρ and k_z to find the Landau free energy per unit volume up to fourth order:

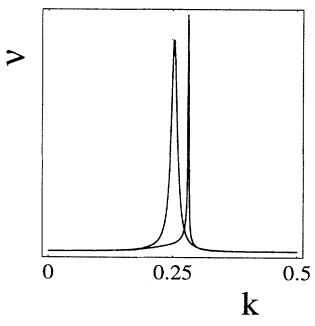

FIG. 1. Angle averaged structure factors $\nu(k)$ for the isotropic case ($m = 0$, left curve) and a nematic state ($m = 0.9$, right curve) evaluated numerically for $\kappa = 5$, $\phi_s = 0.1$, and $\alpha = 0$. The expected difference of the swelling factor β which relates the domain size λ_0 to the surfactant concentration $\lambda_0 \sim \beta \phi_s^{-1}$ is well known in experiment, e.g. [51], and is clearly visible from the shift of peak positions of the above curves. Note that while the nematic peak appears very sharp, it is not a quasi-Bragg peak, as expected from a smectic lamellar phase. ν is plotted in units of k_c^{-3} and k in units of k_c.

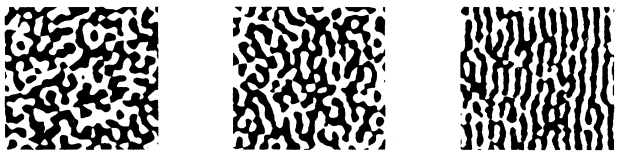

FIG. 2. Two-dimensional cuts through the real-space structures gained from structure factors for $\kappa=5$, $\phi_s=0.1$, and $\alpha=0$ for various values of m. The Euler characteristic of the structure at $m=0.9$ is about half that of the isotropic sponge case, $m=0$. All images were generated from variationally determined structure factors $v(\kappa,\phi_s,\alpha;m)$ using cylindrical coordinates (in **k** space). (Note that the structures for $m=0.5$ and 0.9 are not stable in this case, and are only given here for illustrative purposes.)

$$f(\kappa,\bar{\kappa},\alpha,\phi_s)\approx f_0(\kappa,\bar{\kappa},\alpha,\phi_s)+f_2(\kappa,\bar{\kappa},\alpha,\phi_s)m^2 + f_3(\kappa,\bar{\kappa},\alpha,\phi_s)m^3+f_4(\kappa,\bar{\kappa},\alpha,\phi_s)m^4 . \tag{17}$$

The linear term vanishes as usual [32,45]. For the other terms we find

$$f_2(\kappa,\bar{\kappa},\alpha,\phi_s)=-\frac{\pi^2}{60}\phi_s^3 e^{\alpha^2}(\alpha^2-1)\bar{\kappa}+f_2'(\kappa,\alpha,\phi_s) ,$$

$$f_3(\kappa,\bar{\kappa},\alpha,\phi_s) = \frac{\pi^2}{975}\phi_s^3 e^{\alpha^2}(\alpha^2-1)[2\kappa-17\bar{\kappa}]+f_3'(\kappa,\alpha,\phi_s) , \tag{18}$$

$$f_4(\kappa,\bar{\kappa},\alpha,\phi_s)=\frac{\pi^2}{37800}\phi_s^3 e^{\alpha^2}(\alpha^2-1) \times[134\kappa-599\bar{\kappa}]+f_4'(\kappa,\alpha,\phi_s) ,$$

where f_i' symbolizes terms comprising straightforward multiple integrals which are, however, too lengthy to be given here. Nevertheless, Eq. (18) explicitly contains all $\bar{\kappa}$ dependent terms, and shows that negative values of $\bar{\kappa}$ destabilize the sponge, as expected. Quantitatively we find that at constant ϕ_s the stability of the sponge depends sensitively on the value of $\bar{\kappa}$. In our model it is straightforward to distinguish the (bending) energetic and entropic contributions to the free energy per unit volume. As expected, for a rising value of the order parameter we observe a decrease in bending energy, while the entropic contribution to the free energy per unit volume increases. The sum of the two contributions leads to transitions which turn out to be strongly first order in all investigated cases (m is close to saturation for the stable nematic systems). Strongly negative values of $\bar{\kappa}$ destroy the sponge even for soft membranes $\kappa\approx 1$, while in a narrow region of only slightly negative $\bar{\kappa}$ sponges appear to exist up to quite large values of $\kappa\approx 10$. In Fig. 3 we show a κ-$\bar{\kappa}$ phase diagram for $\phi_s=0.1$ and $\alpha=0$.

To calculate phase diagrams in representations containing ϕ_s or ϕ is more complicated. Upon an increase in ϕ_s we again observe a strongly first-order transition (accompanied by phase coexistence). To determine the concentrations of the coexisting phases, accurate knowledge of the free energy per unit volume is needed which is beyond the scope of the Landau expansion, while numerical techniques require a very complex computational effort in order to work with a spherical integration region and to surmount the current numerical limit of $m\approx 0.95$. We will not tackle this technically involved task here, but will be content with presenting the respective stability lines (where the free energy densities of the respective phases are minimal) which suffice in providing the general shape of the phase diagram. In Fig. 4 we show a ϕ_s-κ stability diagram for a value of $\bar{\kappa}=0$. Alternatively in Fig. 4, we could have plotted ϕ_s vs the "temperature" $\kappa^{-1}=T$ as, e.g., in [6]. Then we would see that the phase sequence asymmetric sponge [26]—symmetric sponge—lamellar phase resembles qualitatively experimental ϕ_s-T phase diagrams, e.g., the one for $C_{12}E_5$ in [1]. However, a change in temperature also affects the saddle-splay curvature, so that in a genuine ϕ_s-T phase diagram the detailed shape of the L_3 region could be different from that predicted by a ϕ_s-κ^{-1} plot. Nevertheless, even as the stability plot (Fig. 4) stands, it is clear that the region of sponge phase stability is rather narrow, in qualitative agreement with experiment.

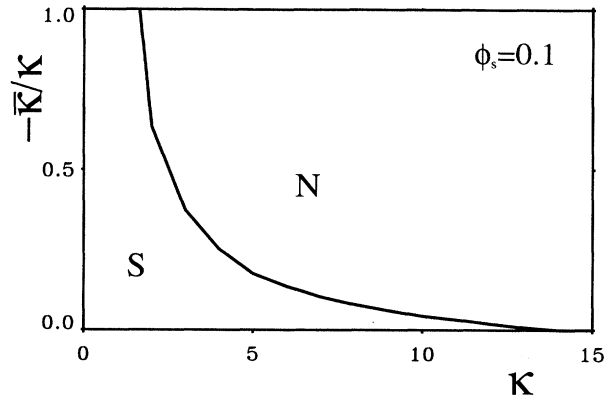

FIG. 3. κ-$\bar{\kappa}$ phase diagram at $\phi_s=0.1$ and $\alpha=0$. S and N denote the sponge and (nematic) lamellar phase. As in any of the investigated cases the transition was strongly first order, and it was necessary to check the results obtained from Landau theory by a few points which were determined numerically. Agreement is satisfactory, and lies for values of $\kappa=2$ and 5 within a few percent of the Landau values. The maximum of sponge existence $\kappa\approx 13$ in the plot should, however, actually be $\kappa\approx 10$. (κ is given in units of $k_B T$ as throughout the text.)

However, it is safer to relate changes in κ to changes in the surfactant chain length as investigated by Schubert and Strey and by Strey in [46,12]. Figure 4 is plotted for $\bar{\kappa}=0$, where the sponge region is maximal. Qualitatively, we see that upon increase in κ the L_3 region shrinks visibly in extent. This agrees with the result of Strey, who found (in microemulsions) that the difference in surfactant concentration between the middle phase and the S-L transition decreased for longer chain length [47]. Although we could not deal with bending moduli $\kappa>20$ be-

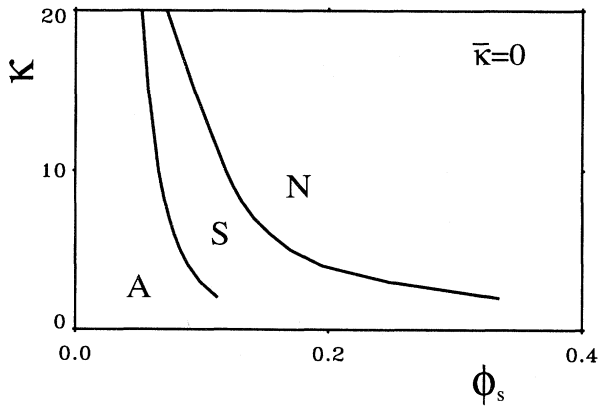

FIG. 4. ϕ_s-κ stability diagram for $\bar{\kappa}=0$, where A, S, and N denote the asymmetric sponge, symmetric sponge, and (nematic) lamellar phases, respectively. The A phase region was determined on the basis of our previous work in [22,23]. The S-A transition is in this case first order with phase coexistence (tie lines were omitted). The results for the S-N instability line are based on Landau expansion (accurate S-N or A-N tie lines cannot be given due to the technical difficulty of accurately determining the N free energy). Two cases at $\kappa=5$ and 10 were cross-checked with exact numerical solutions with satisfactory success.

cause of strong numerical instability, it is clear that for some $\kappa > 20$ the L_3 phase will have entirely vanished. In the same way—as we know from our above results—the L_3 phase can be eradicated by decreasing $\bar{\kappa}$. At high κ the asymmetric and lamellar regions collide, and we expect a direct asymmetric sponge to lamellar transition (as mentioned in passing in [13]). In microemulsions this situation would mean that we would predict a very dilute lamellar phase to be in equilibrium with oil- and water-rich phases. This has been observed, e.g., by Strey upon further increase of the surfactant chain length to $C_{14}E_5$ [12].

Finally, in all investigated systems we never found an indication for a stable asymmetric lamellar phase ($\alpha \neq 0, m \neq 0$). This was suggested by Cates in [4], and finds quantitative support here.

CONCLUSIONS

We have presented a consistent structural and thermodynamic random interface theory of sponge and (nematic) lamellar phases. The model is based on a canonical ensemble of fluctuating interfaces which is appropriate in a picture of membrane phases as incompressible two-dimensional fluid objects. The major virtues of our description are that it goes beyond flat interface approximations (high κ models) and remains well defined for low values of the bending stiffness. Furthermore, the interfaces are described in a truly continuous fashion, their structure [quantified by $\nu(\mathbf{k})$] and thermodynamics consistently derived (unlike [6–8,18], where coarse graining and renormalization lead to similar phase diagrams but do not provide consistently structural information), and the conservation of the membrane area is rigorously implemented. The theory allows for a quantitative and consistent approach to the complex topological changes that take place when a sponge undergoes a transition to a lamellar structure without leaving the simple description and parameter space given by the bending Hamiltonian. Both energy and configurational entropy could be quantified for the fluctuating membranes under investigation, and lead upon changes in the saddle-splay modulus or surfactant concentration to first-order transitions. The respective stability diagrams show a sequence of phases which agrees with experiments. The extension of the theory toward a consistent structural and thermodynamic treatment of smectic lamellar phases with random topological defects is clearly significant but very demand-

ACKNOWLEDGMENTS

We are grateful to S. A. Safran, B. W. Ninham, S. Marčelja, and H. Wennerström for critical comments, and are indebted to M. Teubner for helpful discussions.

APPENDIX

Because $s(\mathbf{r})$ is a Gaussian process in real space [48], statistical averages can be derived from the multivariate Gaussian distribution [49]

$$p=\frac{1}{\sqrt{(2\pi)^n|A|}}\exp[-\tfrac{1}{2}A^{-1}\mathbf{x}^T],$$

where $\mathbf{x}$ contains the whole set of random variables comprising s and its first and second derivatives. The matrix elements of the positive definite correlation matrix A contain all possible autocorrelations and cross-correlations between the random variables. As in the isotropic case—cf. [29]—the symmetry of the problem ($D_{\infty h}$) leads to a decoupling of the first derivatives and the mixed second derivatives from the rest. We can write the operators in differential form,

$$H=\tfrac{1}{2}\mathrm{div}\mathbf{n},\quad K=\sum_{i,j,k\,\mathrm{cycl}}\frac{\mathbf{x}_i}{|\mathbf{x}_i|}\left[\frac{\partial\mathbf{n}}{\partial x_j}\times\frac{\partial\mathbf{n}}{\partial x_k}\right],$$

$$\mathbf{n}=\frac{\nabla s}{|\nabla s|}.$$

Because of the cylindrical and mirror symmetry of the system the only parts which do not vanish during the averaging of the operator for the mean square curvature read, for example,

$$\sqrt{(\nabla s)^2}H^2=\frac{1}{4\sqrt{(\nabla s)^2}^5}[s_{xx}^2(s_y^2+s_z^2)^2+s_{yy}^2(s_x^2+s_z^2)^2+s_{zz}^2(s_x^2+s_y^2)^2+4s_{xy}^2s_x^2s_y^2+4s_{xz}^2s_x^2s_z^2+4s_{yz}^2s_y^2s_z^2$$
$$+2(s_x^2s_y^2+s_x^2s_z^2+s_y^2s_z^2)(s_{xx}s_{yy}+s_{xx}s_{zz}+s_{yy}s_{zz})+2(s_x^4s_{yy}s_{zz}+s_y^4s_{xx}s_{zz}+s_z^4s_{xx}s_{yy})],$$

so that the ensemble average explicitly reads

$$\langle \delta(s-\alpha)\sqrt{(\nabla s)^2}H^2\rangle_0=\left\langle\frac{s_z^4}{\sqrt{(\nabla s)^2}^5}\right\rangle_0[\tfrac{1}{2}\langle\delta(s-\alpha)s_{xx}^2\rangle_0+\tfrac{1}{2}\langle\delta(s-\alpha)s_{xx}s_{yy}\rangle_0]$$
$$+\left\langle\frac{s_x^2s_z^2}{\sqrt{(\nabla s)^2}^5}\right\rangle_0[\langle\delta(s-\alpha)s_{xx}^2\rangle_0+\langle\delta(s-\alpha)s_{xx}s_{yy}\rangle_0+2\langle\delta(s-\alpha)s_{xx}s_{zz}\rangle_0+2\langle\delta(s-\alpha)s_{xz}^2\rangle_0]$$
$$+\left\langle\frac{s_x^4}{\sqrt{(\nabla s)^2}^5}\right\rangle_0[\tfrac{1}{2}\langle\delta(s-\alpha)s_{xx}^2\rangle_0+\tfrac{1}{6}\langle\delta(s-\alpha)s_{xx}s_{yy}\rangle_0$$
$$+\tfrac{1}{3}\langle\delta(s-\alpha)s_{xy}^2\rangle_0+\tfrac{4}{3}\langle\delta(s-\alpha)s_{xx}s_{zz}\rangle_0+\tfrac{2}{3}\langle\delta(s-\alpha)s_{zz}^2\rangle_0] .$$

The averages over the zeroth and second derivatives are not difficult, because the respective arguments of the multivariate Gaussian are essentially quadratic. In the case $\alpha=0$ they can be evaluated using Wick's theorem [50]. The averages over the first derivatives are more complicated. A set of successive transformations, $\rho=s_x^2+s_y^2$, $s_z^2=y$, and $y=\rho x$, is required and leads to solvable integrals. Other differential operators, including Gaussian curvature and the surface to volume ratio, can be treated analogously. For the mean curvature $\langle H\rangle_0$ we find that for $\alpha=0$ the surface is a zero mean curvature surface for all values of m, as it should be. Finally, to obtain formulas (7) and (9), the definition of the order parameter m has to be applied [note that Eqs. (7)–(9) have been derived for $\langle 1\rangle=1$; generalization is trivial].

[1] R. Strey, R. Schomäcker, and D. Roux *et al.*, J. Chem. Soc. Faraday Trans. **86**, 2253 (1990).

[2] G. Porte, J. Appell, and P. Bassereau *et al.*, J. Phys. (Paris) **50**, 1335 (1989).

[3] S. A. Brazovskii, Zh. Eksp. Teor. Fiz. **68**, 175 (1975) [Sov. Phys. JETP **41**, 85 (1975).

[4] M. E. Cates, Physica A **176**, 187 (1991).

[5] For review of Ising and GL theories of amphihilic systems, e.g., G. Gompper and G. Schick, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebovitz (Academic, London, 1994).

[6] S. A. Safran, D. Roux, and M. E. Cates *et al.*, Phys. Rev. Lett. **57**, 2718 (1986); D. Andelman, M. E. Cates, and D. Roux *et al.*, J. Chem. Phys. **87**, 7229 (1987).

[7] M. E. Cates, D. Roux, and D. Andelman *et al.*, Europhys. Lett. **5**, 733 (1988); P. Chandra and S. A. Safran, *ibid.* **17**, 691 (1992).

[8] L. Golubović and T. C. Lubensky, Europhys. Lett. **10**, 513 (1989); Phys. Rev. A **41**, 4343 (1990).

[9] J. Daicic, U. Olsson, and H. Wennerström *et al.*, J. Phys. (France) II **5**, 199 (1995); J. Daicic, U. Olsson, and H. Wennerström, Langmuir **11**, 2451 (1995).

[10] W. Helfrich, Z. Naturforsch **33a**, 305 (1978).

[11] We note that Helrich's free energy of smectic lamellar phases is derived in the limit of high bending stiffness. Similarly, the renormalization corrections to the bending moduli are usually only used in leading order.

[12] R. Strey, Ber. Bunsenges. Phys. Chem. **97**, 742 (1993).

[13] M. E. Cates, J. Phys. (Paris) Colloq. **51**, C7-73 (1990).

[14] R. Strey, W. Jahn, and G. Porte *et al.*, Langmuir **6**, 1635 (1990).

[15] D. Anderson, H. Wennerström, and U. Olsson, J. Phys. Chem. **50**, 1335 (1989).

[16] H. Wennerström and U. Olsson, Langmuir **9**, 365 (1993).

[17] D. C. Morse, Phys. Rev. E **50**, R2423 (1994).

[18] L. Golubović, Phys. Rev. E **50**, R2419 (1994).

[19] Golubović has recently discussed topological changes in lamellar fluid membrane phases in a thermodynamic model [18] which is also based on the bending Hamiltonian, but analyzes the problem in a rather different way. Both our random interface model and the ideas in [18] (a grand-canonical description using renormalization of the bending constants and the notion of persistence length) eventually lead to reasonable phase diagrams.

[20] S. Leibler, R. Lipowsky, and L. Peliti, in *Physics of Amphiphilic Layers,* edited by J. Meunier, D. Langevin, and N. Boccara (Springer, Berlin, 1987).

[21] P. Pieruschka and S. Marčelja, J. Phys. (France) II **2**, 235 (1992).

[22] P. Pieruschka and S. A. Safran, Europhys. Lett. **22**, 625 (1993).

[23] P. Pieruschka and S. A. Safran, Europhys. Lett. **31**, 207 (1995).

[24] P. B. Canham, J. Theor. Biol. **26**, 61 (1970); W. Helfrich, Z. Naturforsch. **28c**, 693 (1973).

[25] D. Roux, M. E. Cates, and U. Olsson *et al.*, Europhys. Lett. **11**, 229 (1990); C. Coulon, D. Roux, and A. M. Bellocq, Phys. Rev. Lett. **66**, 1709 (1991); C. Coulon, D. Roux, and M. E. Cates, *ibid.* **67**, 3194 (1991); R. Granek and M. E. Cates, Phys. Rev. A **46**, 3319 (1992); D. Roux, C. Coulon, and M. E. Cates, J. Phys. Chem. **96**, 4174 (1992).

[26] N. F. Berk, Phys. Rev. Lett. **58**, 2718 (1987).

[27] R. P. Feynman, *Statistical Mechanics* (Addison-Wesley, Reading, MA, 1972).

[28] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA 1994).

[29] M. Teubner, Europhys. Lett. **14**, 403 (1991).

[30] W. Maier and A. Saupe, Z. Naturforsch. Teil A **14**, 882 (1959); **15**, 287 (1960).

[31] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[32] M. Plischke and B. Bergersen, *Equilibrium Statistical*

Physics (Prentice-Hall, Englewood Cliffs, NJ, 1989).

[33] D. C. Morse and S. T. Milner, Phys. Rev. E **47**, 1119 (1993).

[34] D. A. Huse and S. Leibler, J. Phys. (Paris) **49**, 605 (1988).

[35] On the experimental side we note the existence of extremely swollen lamellar systems where the usual experimental indicators of smectic order, a true quasi-Bragg divergence and focal conics texture, cannot be confirmed [36–38]. Moreover, freeze fracture microscopic images by Strey *et al.* [14] and Boltenhagen, Kléman, and Laurentovich [39], which focused specifically on the transition from L_3 to dilute L_α phases in binary systems, suggested the existence of disordered lamellar systems with many topological defects and short-range positional order. While this might even encourage investigation of the nematic lamellar phase in its own right, it is not the prime objective of this paper, which stresses the instability of the sponge phase. In principle, however, both bulk and film structure factors of the uniaxial nematic lamellar phase are readily determined where the film structure factor can be derived from the bulk structure factor by a multiple Gaussian integral, $v_{\text{film}} \sim \mathcal{F}\{\langle \delta[s(\mathbf{r}) - \alpha]\sqrt{(\nabla s(\mathbf{r}))^2}\,\delta[s(\mathbf{r}') - \alpha]\sqrt{(\nabla s(\mathbf{r}'))^2}\rangle_0\}$, where $\mathcal{F}$ is the Fourier transform.

[36] F. C. Larche, J. Appell, and G. Porte *et al.*, Phys. Rev. Lett. **56**, 1700 (1986).

[37] G. Porte, J. Marignan, and P. Bassereau *et al.*, Europhys. Lett. **7**, 713 (1988).

[38] G. Porte (private communication).

[39] P. Boltenhagen, M. Kléman, and O. D. Lavrentovich, J. Phys. (France) II **4**, 1439 (1994).

[40] Although the sponge-nematic transition can possibly be preempted by a sponge-smectic transition, the sponge phase can under no circumstances exist beyond the limits predicted by the sponge-nematic instability.

[41] The statistical averages [Eqs. (7)–(9)] have also been evaluated for more exotic nematic phases; M. Teubner (unpublished). The specialization to uniaxial symmetry leads to identical results for Eqs. (7)–(9); M. Teubner (private communication).

[42] For $m = 0$ this structure factor turns into the isotropic Teubner-Strey inverse polynomial ubiquitous in bulk scattering from isotropic systems; M. Teubner and R. Strey, J. Chem. Phys. **87**, 3195 (1987).

[43] An exact numerical solution (to all orders in m) of Eq. (13) vs the simpler perturbation theory is a choice which neither option can fully satisfy. The former turns out to be a demanding computational task. Even with the simplification of taking constant integration limits—i.e., integrating over a cylindrical volume—when one of the integrations can be carried out analytically the remaining numerical integration suffers at large order parameters from an emerging very sharp peak in the structure factor which can flip into a divergence for small changes in the parameters. Only a relatively complex algorithm (Powell hybrid method) could be used to solve Eq. (13) and yet showed increasingly bad convergence properties for m approaching saturation, $m \to 1$; in fact we never succeeded in surpassing some $m \approx 0.95$. The perturbation expansion, on the other hand, retains the spherical integration region and is computationally far less complicated. However, it is well known that the Landau expansion of the free energy density is, strictly speaking, invalid for cases of strongly first-order transitions, so that results gained from the perturbation analysis might then not be reliable. Nevertheless, for most of the remainder of this paper it was a necessity to use perturbative results; these were checked for some selected cases by exact calculations with good success.

[44] A comparison to FFEM pictures is encouraging, but of course not a proof of the existence of nematic lamellar phases.

[45] We have checked explicitly that the linear term vanishes.

[46] K. V. Schubert and R. Strey, J. Chem. Phys. **95**, 8532 (1991).

[47] In [12] the respective concentration ranges for $C_{10}E_5$ and $C_{12}E_4$ were 12% and 2%.

[48] E. Wong and B. Hajek, *Stochastic Processes in Engineering Systems* (Springer, New York, 1971).

[49] D. Middleton, *An Introduction to Statistical Communication Theory* (McGraw-Hill, New York, 1960).

[50] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley, Reading, MA, 1992).

[51] P. Bassereau, J. Marignan, and G. Porte, J. Phys. (Paris) **48**, 673 (1987).