Four-point correlation functions and average Gaussian curvature in microemulsions

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The structure of microemulsions is studied in the Landau-Ginzburg model [A. Ciach, J. Chem. Phys. **104**, 2376 (1996)], in which all the coupling constants are expressed in terms of temperature T, surfactant volume fraction ρ_s, and amphiphilicity. The *extension* of surface-averaged Gaussian curvature, K [A. Ciach and A. Poniewierski, Phys. Rev. E **52**, 596 (1995)], is calculated in the Landau-Ginzburg approximation. In the neighborhood of the liquid-crystal phases $K<0$. Thermal fluctuations destroy the bicontinuous structure and cause a transition to $K>0$. A dimensionless average radius of curvature $R=|K|^{-1/2}/\lambda$, where λ is a period of damped oscillations of the two-point correlation function, is calculated. Comparison with a corresponding quantity for periodic minimal surfaces shows that microemulsions have (for $K<0$) a structure resembling different periodic minimal surfaces with low genus for different T and ρ_s. [S1063-651X(97)11008-X]

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I. INTRODUCTION

Systems exhibiting structure on a mesoscopic length scale, for example, amphiphilic mixtures, biological systems, etc., have been extensively studied in recent years [1–3]. The structure on the mesoscopic length scale results from self-assembling of amphiphiles or lipids which form internal interfaces (films). In standard approaches to systems in which monolayers or bilayers are formed, one assumes that the width of the film is much smaller than the length characterizing the structure (oil or water domain size, for example). In such a case it is justified to represent the film by a mathematical surface and the structure can be described by the local invariants of the surface, i.e., the mean H and the Gaussian K curvatures [1,3] and by the global (topological) invariant, the Euler characteristic χ_E [1,3]. Such an approach has been very successful in phenomenological models, such as Helfrich-type [3] models of membranes and level-surfaces [4] or Landau-Ginzburg (LG) [5,1] models for microemulsions. In the above mentioned approaches the surfactant films are represented by the mathematical surfaces by definition. Therefore, within such models the structure can obviously be defined in terms of the properties of those surfaces.

In real microemulsions, however, especially close to the disorder line [1], the crucial assumption that the surfactant films are very thin, compared to the characteristic length of the structure, may not be satisfied. The internal interfaces may be diffused but a structure may still exist. Thermodynamically microemulsions and homogeneous mixtures are indistinguishable. It is only the structure in the mesoscopic length scale which distinguishes between them [1,6], a well defined borderline, however, does not exist. The structure changes gradually. Thus the region in the phase space, in which an assumption justifying description of the structure of the system by invariants of mathematical surfaces, is not well defined. Moreover, recent works [7] show that the width of the interface in microemulsions can be large, even comparable to the oil and water domain sizes. For diffuse and delocalized interfaces one can still define a mathematical surface which in some way describes the film. For example, in LG models with order parameter $\phi(\mathbf{r})$ describing the oil-water concentration difference, the internal surfaces are defined by $\phi(\mathbf{r})=0$. Such a choice is, however, not unique. While for well localized thin films it is fully justified to describe the structure of the system in terms of invariants of corresponding surfaces, for delocalized interfaces such a description is *a priori* no longer obvious, or at least not complete. In order to overcome this problem, the finite width of the film is taken into account [8].

Recently an alternative approach for the description of the structure in systems with self-assembling particles has been proposed in Ref. [9]. In this approach no particular assumption about the nature of the internal interfaces is necessary, therefore within the same formalism both localized, well defined thin films, as well as diffuse interfaces can be described. In Ref. [9] one assumes that surfactant degrees of freedom can be described by a vector field. For example, in LG models the vector field describes local orientational ordering of amphiphiles. In terms of three- and four-point correlation functions for this vector field, structure parameters H and K are defined. It is next shown in Ref. [9] that for ordered phases and very (infinitely) thin surfactant film, H and K reduce to the mean and the Gaussian curvatures of a surface A describing the film, averaged over this surface. Strictly speaking $H\rightarrow H_m=(1/|A|)\int_A d\sigma H$ and $K\rightarrow K_m=(1/|A|)\int_A d\sigma K$, where $|A|$ is the area of the surface A and H and K are the corresponding local curvatures. By virtue of the Gauss theorem K_m is related to the Euler characteristic by $K_m=2\pi\chi_E/|A|$. Since H and K, in the case of thin films in ordered phases, *reduce to the usual geometrical invariants averaged over the surface*, they may be considered as *extensions of average mean and Gaussian curvatures* to the case of diffuse films, which cannot be represented by just a single surface. Also, since K reduces to $K_m=2\pi\chi_E/|A|$, it may be considered as an extension of the topological invariant per unit surface area.

Different structures can be classified by the signs of the mean and the Gaussian curvatures. For example, $H_m>0$, $K_m>0$ ($H_m<0$, $K_m>0$) for micelles (reverse micelles),

$\bar{H}_m > 0$, $\bar{K}_m = 0$ ($\bar{H}_m < 0$, $\bar{K}_m = 0$) for cylinders of oil (water), and $\bar{H}_m = 0$, $\bar{K}_m < 0$ for bicontinuous structures. Extensions of H_m and K_m should allow for similar classification of structures, where the signs of H and K are crucial.

In Ref. [9] the parameters H and K are calculated for several ordered phases (micellar, hexagonal, and double diamond) with diffuse surfactant film, of a thickness comparable to the period of the structure. They are next compared to H_m and K_m, respectively, calculated for surfaces $\langle \phi(\mathbf{r}) \rangle = 0$, describing the center of the film. In all cases H and K have the same sign as H_m and K_m, respectively, and smaller (by about one half) absolute values. Smaller values of H and K reflect the diffuse nature of the film. The same signs of the parameters defined in a different way suggest that either way of defining the structure leads to *the same classification of its type*.

For diffuse and strongly fluctuating interfaces the quantities defined in Eqs. (3) loose the simple geometrical interpretation. Still, their signs are the same as the signs of the corresponding geometrical quantities calculated for the ''central'' surface $[\phi(\mathbf{r}) = 0]$ of the film [9]. Therefore they can be used for the classification of the structure instead of the usual geometrical quantities. Strictly speaking, it has not been generally proven that the quantities defined in Eqs. (3) have the same sign as the corresponding geometrical quantities related to the ''central'' surface. However, no example which would contradict this observation has been found, although for several structures the signs of these parameters have been compared [9]. At the same time the quantities (3) are defined in terms of the correlation functions, without any additional assumptions about the nature of the surfactant films, and are thus applicable within the whole region of stability of the uniform phase, a part of which is a microemulsion.

The above observations suggest that this new method can be applied to investigation of the structure of a microemulsion. Experimentally the structure of a microemulsion is studied by different techniques [2,6]. Theoretically, beyond the two-particle correlation functions, it has been studied in Ref. [10] by methods developed for percolation phenomena, in Refs. [4] and [11] by considering the level surfaces, and in Ref. [11] by calculation of χ_E in Monte Carlo (MC) simulations for a LG model [5] with one order parameter. In the case of oil-water symmetry, for equal volume fractions, χ_E was found to be negative. These results suggest the bicontinuous structure of microemulsions.

In real systems, however, one expects that very high temperature destroys the bicontinuous structure. Also, if the volume fraction of the surfactant is too low or too high, the bicontinuous structure may not appear. Thermodynamically, the microemulsion is not distinguished from a structureless mixture, which is stable beyond the disorder line [1]. The disorder line is located in a region with a low surfactant volume fraction [12,13]. We do not expect a bicontinuous structure for a structureless fluid. Here by bicontinuous structure we mean a structure which is water, oil, and also surfactant continuous, with the latter component located at the internal interfaces separating oil and water channels of mesoscopic thickness. Close to the disorder line, where the surfactant volume fraction is low, the system should no longer be bicontinuous in the above sense. The oil- and water-percolation channels, however, may still exist as in ordinary mixtures (i.e., on a microscopic length scale). Also, for a very large surfactant volume fraction, essentially larger from the oil and water volume fractions, one can imagine that oil and water form closed droplets in a surfactant sea. Formation of such a disordered structure can be preempted by a phase transition to some ordered, cubic phase, but *a priori* one cannot exclude that within the disordered phase the system is only surfacant continuous. It means that in real systems χ_E may not be negative at some part of the phase space, at least beyond the disorder line, where the system is homogeneous. Percolation phenomena [10] observed in such systems also indicate that the bicontinuous structure is stable in a limited part of the phase space. In the models studied so far a transition between positive and negative Euler characteristics within microemulsions has not been observed for balanced systems. In the case of broken oil-water symmetry a transition to $\chi_E > 0$ is found in Ref. [11b] for a model introduced in Ref. [5].

While many properties of mixtures with weak surfactants are well described by the elegant Gompper-Schick (GS) model [5], in the case of strong surfactants a more extended description is probably necessary. Cubic phases, present in such mixtures are stable only in LG models in which an additional order parameter, describing orientational ordering of surfactant particles, is considered. In the case of binary mixtures such a model was introduced in Ref. [14], whereas for ternary mixtures a model in which cubic phases are stable was introduced in Ref. [13]. In addition, in this model all the coupling constants are expressed in terms of the surfactant volume fraction ρ_s, temperature, and a single parameter γ describing the amphiphilicity of surfactant. Small γ corresponds to weak, and large γ to strong surfactants. No parameters in this model are fitted. All the calculated quantities are expressed in terms of directly measurable parameters and a single parameter specifying the system. It is thus interesting to study the structure of microemulsions within this model. It is a purpose of this work.

In order to describe the structure of microemulsions, in this paper we calculate the structure parameters H and K, introduced in Ref. [9] in the model introduced in Ref. [13]. We limit ourselves to the symmetric case in which $H = H_m = 0$ by symmetry. We thus only calculate K. The calculations are performed within the LG approximation. Strictly speaking, we calculate K up to first order term in the standard perturbation expansion [15].

The new quantity K has been calculated so far only for several ordered, periodic structures [9]. Therefore, here we calculate K in the GS model also, for which the corresponding $K_m = 2\pi\chi_E/|A|$ has been calculated for microemulsions by the MC method [11]. We find that in microemulsions, as in ordered phases, K_m and K have the same sign. Thus both parameters provide the same classification for the structure. The magnitude of K is $K \approx K_m/2$, as in ordered phases with interfaces of large width [9]. This result is consistent with the observation that the width of the interface in microemulsions is large in this model [7a].

The surface-averaged Gaussian curvature $\bar{K}_m$, introduces a length scale, $|\overline{K_m}|^{-1/2}$, describing an average radius of curvature of the single, ''central'' surface of the film. The extension of $\overline{K_m}$ for systems with thick surfactant films $\overline{K}$, similarly introduces a length scale $|\overline{K}|^{-1/2}$, which represents the average radius of curvature of the collection of surfaces modeling the film.

For ordered periodic structures of period λ a dimensionless ratio between the two lengths $R_m=|\overline{K_m}|^{-1/2}/\lambda$ provides additional characterization of the structure. Based on the results of Ref. [16b], we can estimate this ratio for periodic minimal surfaces. For simple minimal surfaces, P, D, or G [16] we find, respectively, $R_m=0.306$, $R_m=0.195$, and $R_m=0.248$. For more complicated periodic structures [16] its value can be even smaller than 0.1, for example, for the surface labeled GX5 $R_m=0.073$.

In microemulsions the role of λ is played by a period of damped oscillations of the correlation functions. We calculate here $R=|\overline{K}|^{-1/2}/\lambda$. Since $\overline{K}$ differs for diffuse films from corresponding $\overline{K_m}$ related to the ''central'' surface of the film by about 1/2, the above ratio also has a different value than R_m, with $R_m\approx|R|/\sqrt{2}$. It is interesting to compare the ratio between the two characteristic lengths in microemulsions and in ordered periodic structures.

The paper is arranged as follows. In Sec. II we present the definitions of the structure parameters $\overline{H}$ and $\overline{K}$. The model is defined in Sec. III. Section IV contains an outline of the calculation of the structure parameters in microemulsions within the model described in the preceding section; some details are described in the Appendix. The results are described in Sec. V. The last section contains the summary.

II. EXPLICIT EXPRESSIONS FOR CURVATURE PARAMETERS

Because of the amphiphilic nature of surfactant particles one can define a vector field $\mathbf{u}(\mathbf{r})$ describing their local orientational ordering. We split the field $\mathbf{u}$ into two fields $\mathbf{s}$ and $\mathbf{t}$

$$\mathbf{u}=\mathbf{s}+\mathbf{t}, \tag{1}$$

where $\nabla\times\mathbf{s}=\mathbf{0}$ and $\nabla\cdot\mathbf{t}=0$. For a description of the structure the curless part of $\mathbf{u}$, i.e., $\mathbf{s}$, is relevant. It defines a collection of surfaces $\psi(\mathbf{r})=\text{const}$, the normal vector of which is $\hat{\mathbf{n}}=\mathbf{s}/s$. The other part of $\mathbf{u}$ describes fluctuations of amphiphiles around common direction $\hat{\mathbf{n}}(\mathbf{r})$. For a particular field $\mathbf{s}(\mathbf{r})$ we can calculate at every point $\mathbf{r}$ the mean and the Gaussian curvatures of a corresponding surface passing through $\mathbf{r}$. Using the standard geometrical definitions based on $\hat{\mathbf{n}}$ and its derivatives, we obtain

$$s^3(\mathbf{r})H_s(\mathbf{r})=\tfrac{1}{2}\left(s^2\nabla\cdot\mathbf{s}-\tfrac{1}{2}\mathbf{s}\cdot\nabla s^2\right), \tag{2a}$$

$$s^4(\mathbf{r})K_s(\mathbf{r})=\tfrac{1}{2}\mathbf{s}_i\mathbf{s}_l\epsilon_{ijk}\epsilon_{lmn}\nabla_m s_j\nabla_n s_k\,, \tag{2b}$$

where the subscript s means that the related quantity refers to the particular field $\mathbf{s}$. For the system characterized by some probability distribution for $\mathbf{s}$, average values for the above defined quantities can be calculated.

In Ref. [9] the structure parameters $\overline{H}$ and $\overline{K}$ are introduced in the following way:

$$\overline{H}=\frac{\int_V d\mathbf{r}\langle s^3H_s\rangle}{\int_V d\mathbf{r}\langle s^3\rangle}, \tag{3a}$$

and

$$\overline{K}=\frac{\int_V d\mathbf{r}\langle s^4K_s\rangle}{\int_V d\mathbf{r}\langle s^4\rangle}. \tag{3b}$$

where in the numerator average values of the quantities (2) are calculated and integrated over the unit cell in case of ordered structures. The denominator plays a role of a normalization with respect to the field $\mathbf{s}$. In Ref. [9] ordered phases in which $\langle\mathbf{s}(\mathbf{r})\rangle=\mathbf{0}$ beyond very thin films are considered. It is shown that in such a case, in the limit of infinitely thin films, approximated by a surface A, $\overline{H}\to\overline{H}_m=(1/|A|)\int_A d\sigma H$ and $\overline{K}\to\overline{K}_m=(1/|A|)\int_A d\sigma K$. In the above $|A|$ is the area of the surface A and H and K are the corresponding local curvatures. Thus the structure parameters (3) reduce to the usual geometrical characteristics of the structure for very (infinitely) thin surfactant films. Therefore one may consider them as extensions of surface-averaged curvatures. The advantage of the above defined extensions of $\overline{H}_m$ and $\overline{K}_m$ is that these quantities can be expressed just in terms of many-body correlation functions.

Because of the condition $\nabla\times\mathbf{s}=\mathbf{0}$, the Fourier transform of $\mathbf{s}(\mathbf{r})$ can be represented by a scalar field $s_\parallel(\mathbf{k})$, $\tilde{\mathbf{s}}(\mathbf{k})=i\hat{\mathbf{k}}s_\parallel(\mathbf{k})$. Then the numerators in the definitions (3) in the Fourier representation assume for the uniform phase the forms

$$\langle s^3H_s\rangle=-\frac{3}{4}\int\frac{d\mathbf{k}_1}{(2\pi)^d}\cdots\int\frac{d\mathbf{k}_3}{(2\pi)^d}\,\hat{\mathbf{k}}_1\cdot\hat{\mathbf{k}}_2k_3\times G_{3S}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3), \tag{4a}$$

and

$$\langle s^4K_s\rangle=\frac{1}{2}\int\frac{d\mathbf{k}_1}{(2\pi)^d}\cdots\int\frac{d\mathbf{k}_4}{(2\pi)^d}\frac{|\mathbf{k}_3\cdot(\mathbf{k}_1\times\mathbf{k}_2)|^2}{k_1k_2k_3k_4}\times G_{4s}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4), \tag{4b}$$

where the n-body correlation function is defined as

$$G_{ns}(\mathbf{k}_1,\ldots,\mathbf{k}_n)=\langle s_\parallel(\mathbf{k}_1),\ldots,s_\parallel(\mathbf{k}_n)\rangle. \tag{4c}$$

The numerical values of $\overline{H}$ and $\overline{K}$ clearly depend on the length unit. In the considered mixtures the natural length is the length of the surfactant molecules, or the bare thickness of the monolayer $\xi_s\approx 20$ Å.

In Eqs. (3) and (4) the many-body correlation functions are formally calculated at one point. It results from the relation between curvatures and derivatives of the normal vector for continuous mathematical surfaces. In physical systems, however, a continuous Landau-Ginzburg description is not correct when the distances become smaller than the size of molecules. Rather, for such distances a molecular description is appropriate. Let us adopt, for a while, a molecular picture, in which a surfactant monolayer is represented by an assembly of amphiphiles. An average tendency for bending (or a shape) of such an object should be determined by correlations between *different* particles being close neighbors. Therefore in a microscopic description the correlation functions in Eqs. (3) should be calculated at points whose distances from one another are comparable to the size of molecules. Distances smaller than the size of molecules correspond to correlation functions calculated for the same molecule, and are not relevant for determination of the geometrical structure of the surfactant assembly. According to the above discussion, in the LG approximation we regularize the integrals in Eqs. (3) and (4) by calculating the corresponding correlation functions at points whose distances from one another are comparable to the size of molecules, i.e., using a real-space cutoff, instead of the upper cutoff in the Fourier space, as is usually done. Such regularization seems to be more appropriate in this case. In addition, particularly in the case of the multidimensional integrals (4b), it is much simpler to reduce them to a one-dimensional one in the case of the real-space cutoff.

III. THE MODEL

Instead of introducing the LG model on symmetry grounds, in Ref. [13] the free-energy functional is derived from a lattice microscopic model [17], therefore all the coupling constants are expressed in terms of parameters of the lattice model. In the lattice Ciach, Høye, and Stell (CHS) model only nearest neighbors interact. The interactions between amphiphiles in the simplest version of the model are neglected. In case of oil-water symmetry only two parameters characterize the interactions in this model. One b, is the strength of the water-water (oil-oil) interaction, the other one c, describes the interaction between water (oil) and an amphiphile. The interaction between amphiphiles and ordinary molecules is proportional to a scalar product between the orientation of the amphiphile and the distance between the particles.

The LG functional is derived in the following way. We consider the grand-thermodynamical potential in the mean-field approximation. The potential is expanded in a power series of fluctuations around the average values of the fields $\phi(\mathbf{r})$, $\rho_s(\mathbf{r})$, and $\rho_s(\mathbf{r},\hat{\boldsymbol{\omega}})$, where $\phi(\mathbf{r})$ describes the concentration difference between oil and water, $\rho_s(\mathbf{r})$ the total surfactant concentration, and $\rho_s(\mathbf{r},\hat{\boldsymbol{\omega}})$ the density of the surfactant in orientation $\hat{\boldsymbol{\omega}}$. The fluctuation of $\rho_s(\mathbf{r},\hat{\boldsymbol{\omega}})$ consists of two parts. The first one is the uniform fluctuation, the same in all directions, related to the fluctuation of the total concentration of surfactant which is denoted by $\rho(\mathbf{r})$. The second part is related to the orientational ordering and can be represented by a vector field $\mathbf{u}(\mathbf{r})$. In Ref. [13] we introduce $\mathbf{u}$ in the following way:

$$\delta\rho_s(\mathbf{r},\hat{\boldsymbol{\omega}})=\rho_s(\mathbf{r},\hat{\boldsymbol{\omega}})-\frac{\rho_s}{4\pi}=\frac{1}{4\pi}\,\rho(\mathbf{r})+\frac{\rho_s}{4\pi}\,\hat{\boldsymbol{\omega}}\cdot\mathbf{u}(\mathbf{r}). \tag{5}$$

We assume that the fluctuations are small and approximate the free energy by a polynomial in fields ϕ, ρ, and $\mathbf{u}$. Next we assume that the fields vary slowly on the length scale of the lattice constant (size of molecules) and introduce continuous approximation for the thermodynamical-potential density. The resulting functional assumes the form

$$\Omega_{\text{eff}}=(\Omega_2+\Omega_{\text{int}})b, \tag{6a}$$

with

$$\Omega_2=\int d\mathbf{r}\big(\tfrac{1}{2}a_2\phi^2+\tfrac{1}{2}(\nabla\phi)^2+\tfrac{1}{2}\alpha_2\rho^2+\tfrac{1}{2}(\nabla\rho)^2 +\tfrac{1}{2}[|\mathbf{u}|^2+(\nabla\cdot\mathbf{u})^2+(\nabla\times\mathbf{u})^2]-J\mathbf{u}\cdot\nabla\phi\big), \tag{6b}$$

and

$$\Omega_{\text{int}}=\int d\mathbf{r}\left[\frac{1}{3!}\,(\alpha_3\rho^3+b_3\phi^2\rho+c_3|\mathbf{u}|^2\rho)+\frac{1}{4!}\,(a_4\phi^4 +\alpha_4\rho^4+b_4\phi^2\rho^2+c_4\rho^2|\mathbf{u}|^2+A_4|\mathbf{u}|^4)\right]. \tag{6c}$$

All the coupling constants in the model related to the CHS model can be expressed in terms of an average surfactant volume fraction ρ_s, temperature $\tau=kT/b$, and a parameter describing the amphiphilicity $\gamma=(2c/b)^2$. The grand-thermodynamical potential is calculated in units of b. Macroscopically b is related to the critical temperature of oil-water separation by $kT_c=3(1-\rho_s)b$. In a model so constructed the length of the amphiphile ξ_s, should be equal to the lattice constant a of the original model. In derivation of Eqs. (6) we assumed that $a=1$, thus the distance is measured in units of the length of the amphiphiles.

The coupling constants, which are used here for calculation of $\bar{K}$, have the forms:

$$a_2=2\left(\frac{\tau}{1-\rho_s}-d\right), \tag{6d}$$

$$J=\left(\frac{2\rho_s\gamma}{3\tau}\right)^{1/2}, \tag{6e}$$

$$a_4=\frac{8\tau}{(1-\rho_s)^3}, \tag{6f}$$

$$A_4=\frac{18}{5\tau\rho_s}. \tag{6g}$$

We briefly summarize the results of Ref. [13], which we need in the present calculation. The Gaussian correlation functions have the following forms:

$$G_{\phi\phi}(\mathbf{k})=\frac{1+k^2}{k^4+Bk^2+a_2}\,\tau, \tag{7a}$$

$$G_{\phi s}(\mathbf{k})=-\frac{Jk}{k^4+Bk^2+a_2}\,\tau, \tag{7b}$$

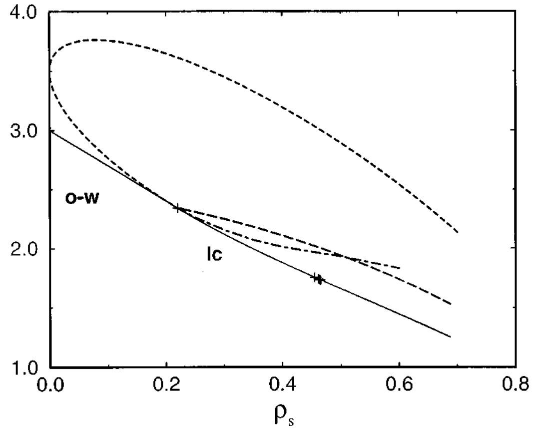

FIG. 1. Bifurcation (solid), Lifshitz (dashed), disorder (dotted), and $K=0$ (dashed-dotted) lines for $\gamma=16$; ρ_s is a surfactant volume fraction and τ a dimensionless temperature defined below Eq. (6c). Regions of stability of coexisting oil- and water-rich phases and liquid crystals are denoted by ''o-w'' and ''lc'', respectively. The Lifshitz point is marked by a cross. The crosses to the right of the Lifshitz point separate different lc phases (Ref. [13]).

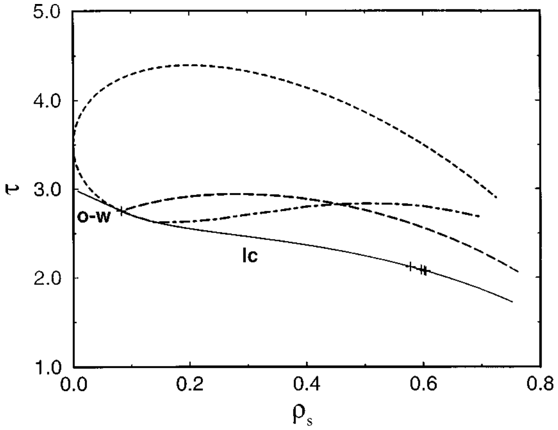

FIG. 2. Bifurcation (solid), Lifshitz (dashed), disorder (dotted), and $K=0$ (dashed-dotted) lines for $\gamma=50$; ρ_s is a surfactant volume fraction and τ a dimensionless temperature defined below Eq. (6c). Regions of stability of coexisting oil- and water-rich phases and liquid crystals are denoted by ''o-w'' and ''lc'', respectively. The Lifshitz point is marked by a cross. The crosses to the right of the Lifshitz point separate different lc phases (Ref. [13]).

$$G_{ss}(\mathbf{k})=\frac{a_2+k^2}{k^4+Bk^2+a_2}\,\tau, \tag{7c}$$

where

$$B=1+a_2-J^2. \tag{7d}$$

The form of $G_{\phi\phi}$ is different from the Teubner-Strey (TS) [6c] form. However, we are interested in a structure on the length scale larger (about one order of magnitude) from molecular size ξ_s. Since the length unit is chosen such that $\xi_s=1$, the relevant range of k in our units is $k<1$. For such k (strictly speaking for $k\ll 1$) the two formulas are similar.

The Lifshitz line [1] can be defined as a line at which $k_{\max}$ starts to be different from zero, or as a line at which the water- (or oil-) domain size $\lambda/2\pi$ becomes equal to the correlation length ξ. For the TS form both definitions give the same line, namely, $B=0$. For our expression the line at which $\lambda/2\pi=\xi$ is $B=0$, and it is the line shown in Figs. 1 and 2. The line at which $k_{\max}$ starts to be different from zero is $J=1$, i.e., $B=a_2$. We should also stress that in the model introduced in Ref. [13] the interactions between amphiphiles are neglected. Therefore, the pure surfactant system does not undergo the ordering phase transition and for very high surfactant concentration the results obtained in this model are not expected to agree with experiments.

In Ref. [13] the bifurcation line, the tricritical and the Lifshitz points, and the Lifshitz and the disorder lines are presented in variables (ρ_s,τ) in Figs. 1 and 2, for systems specified by parameters $\gamma=16$ and $\gamma=50$, respectively. Below the bifurcation line $\tau_b(\rho_s)$ a free energy of several ordered phases has been calculated to order $O(\epsilon^4)$, with the bifurcation parameter $\epsilon\sim\sqrt{|\tau-\tau_b|/\tau_b}$. The following ordered phases have the lowest free energy for increasing surfactant volume fraction: lamellar, simple cubic (P surface of Schwarz), double diamond (D surface), and double fcc phase, consisting of closed oil and water droplets arranged in two fcc lattices shifted with respect to each other by half a period. Thus, at least close to the bifurcation, the cubic phases are stable in this model. The stability region of the lamellar phase is much larger than the stability regions of the cubic phases. Other cubic phases, like G or I-WP, can also be stable in this model, but it has not been verified by calculations yet. In Sec. IV, we calculate the structure parameters within the region of stability of microemulsion.

IV. CALCULATION OF THE STRUCTURE PARAMETER K

In case of oil-water symmetry three-point correlation functions vanish and $H=0$. In order to calculate K we need explicit expressions for the four-point correlation functions. As already noted in the Sec. II, the correlation functions in definitions (3) and (4) should be calculated at points $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$, such that the distances from one another are comparable to a (the size of molecules). For shorter distances the correlation functions are calculated for the same molecule in the molecular description, and are irrelevant for determination of the geometrical structure of the film. One could regularize the integrals in Eqs. (3b) and (4b) with the help of the upper cutoff in the Fourier space, and avoid the arbitrariness in the choice of the four points. However, since the integrals strongly depend on the cutoff, it is impossible to avoid the arbitrariness, which in this case consists in choosing the actual value of the cutoff. Moreover, the calculations of Eq. (4b) are simpler in the case of the real-space cutoff. We thus consistently regularize both the numerator and the denominator in Eq. (3b) with the help of the real-space cutoff.

We calculate K in the perturbation expansion about the Gaussian part of the thermodynamical potential $\Omega_{\rm eff}$ [Eq. (6)], to a first order term in the coupling constants of $\Omega_{\rm int}$ [Eq. (6c)]. First consider the Gaussian part of $\Omega_{\rm eff}$, i.e., Ω_2 [Eq. (6b)]. Because in the Gaussian approximation [15]

$$(2\pi)^{-2d}\left\langle \prod_i^4 s_{\parallel}(k_i)\right\rangle = G_{ss}(\mathbf{k}_1)\,\delta(\mathbf{k}_1+\mathbf{k}_2)G_{ss}(\mathbf{k}_3)\,\delta(\mathbf{k}_3 + \mathbf{k}_4) + G_{ss}(\mathbf{k}_1)\,\delta(\mathbf{k}_1+\mathbf{k}_3)G_{ss}(\mathbf{k}_2) \times\delta(\mathbf{k}_2+\mathbf{k}_4)+G_{ss}(\mathbf{k}_1)\,\delta(\mathbf{k}_1+\mathbf{k}_4) \times G_{ss}(\mathbf{k}_2)\,\delta(\mathbf{k}_2+\mathbf{k}_3), \tag{8}$$

we find that $\mathbf{k}_1\cdot(\mathbf{k}_2\times\mathbf{k}_3)=0$ for nonvanishing $\langle\Pi_i^4 s_{\parallel}(\mathbf{k}_i)\rangle$, thus from Eq. (4b) we see that in the Gaussian approximation $\overline{K}$ vanishes. Consider now the perturbation expansion for $\overline{K}$ in the coupling constants of $\Omega_{\rm int}$ about the Gaussian solution. We truncate the expansion at the first order term. Consistently, the numerator in Eq. (3b) is truncated at the first order term and the denominator at the zeroth order term.

The denominator in definition (3b), i.e., the function

$$\langle \mathbf{s}(\mathbf{r}_1)\cdot\mathbf{s}(\mathbf{r}_2)\mathbf{s}(\mathbf{r}_3)\cdot\mathbf{s}(\mathbf{r}_4)\rangle = \int \frac{d\mathbf{k}_1}{(2\pi)^d}\int \frac{d\mathbf{k}_2}{(2\pi)^d}\int \frac{d\mathbf{k}_3}{(2\pi)^d}\int \frac{d\mathbf{k}_4}{(2\pi)^d} \times\exp\left(-\sum_i^4 \mathbf{k}_i\cdot\mathbf{r}_i\right)\left\langle(\hat{\mathbf{k}}_1\cdot\hat{\mathbf{k}}_2\hat{\mathbf{k}}_3\cdot\hat{\mathbf{k}}_4)\prod_i^4 s_{\parallel}(\mathbf{k}_i)\right\rangle \tag{9}$$

has in Gaussian approximation [see Eq. (8)] the explicit form

$$\begin{aligned}\langle \mathbf{s}(\mathbf{r}_1)\cdot\mathbf{s}(\mathbf{r}_2)\mathbf{s}(\mathbf{r}_3)\cdot\mathbf{s}(\mathbf{r}_4)\rangle &= \int \frac{d\mathbf{k}_1}{(2\pi)^d}\,G_{ss}(\mathbf{k}_1)e^{-i\mathbf{k}_1(\mathbf{r}_1-\mathbf{r}_2)} \\ &\times\int \frac{d\mathbf{k}_3}{(2\pi)^d}\,G_{ss}(\mathbf{k}_3)e^{-\mathbf{k}_3(\mathbf{r}_3-\mathbf{r}_4)} \\ &+\int \frac{d\mathbf{k}_1}{(2\pi)^d}\,e^{-i\mathbf{k}_1(\mathbf{r}_1-\mathbf{r}_3)}\int \frac{d\mathbf{k}_2}{(2\pi)^d}\,e^{-i\mathbf{k}_2(\mathbf{r}_2-\mathbf{r}_4)} \\ &\times(\mathbf{k}_1\cdot\mathbf{k}_2)^2\,\frac{G_{ss}(k_1)}{k_1^2}\,\frac{G_s(k_2)}{k_2^2}+\int \frac{d\mathbf{k}_1}{(2\pi)^d}\,e^{-i\mathbf{k}_1(\mathbf{r}_1-\mathbf{r}_4)} \\ &\times\int \frac{d\mathbf{k}_2}{(2\pi)^d}\,e^{-i\mathbf{k}_2(\mathbf{r}_2-\mathbf{r}_3)}(\mathbf{k}_1\cdot\mathbf{k}_2)^2\,\frac{G_{ss}(k_1)}{k_1^2}\,\frac{G_s(k_2)}{k_2^2},\end{aligned} \tag{10}$$

where the distances between the points $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$ should be close to a. We assume that $|\mathbf{r}_1-\mathbf{r}_2|=|\mathbf{r}_3-\mathbf{r}_4| = a\kappa$ and that $\mathbf{r}_1-\mathbf{r}_3=-(\mathbf{r}_2-\mathbf{r}_4)=\mathbf{a}_1$ and $\mathbf{r}_1-\mathbf{r}_4=-(\mathbf{r}_2-\mathbf{r}_3)=\mathbf{a}_2$, $|\mathbf{a}_1|=|\mathbf{a}_2|=a$. For $\kappa=\sqrt{2}$ the points form a square. In our calculation we just choose $\kappa=1$. The numerical values for $\overline{K}$ would be slightly different for different regularization.

In perturbation expansion [15] the first order contribution to G_{4s} consists of two terms which read

$$-(2\pi)^d\,\frac{a_4}{\tau}\,\delta\left(\sum_i^4 \mathbf{k}_i\right)\prod_i^4 G_{\phi s}(\mathbf{k}_i) \tag{11a}$$

$$-(2\pi)^d\,\frac{A_4}{3\tau}\,\delta\left(\sum_i^4 k_i\right)\prod_i^4 G_{ss}(\mathbf{k}_i)(\hat{\mathbf{k}}_1\cdot\hat{\mathbf{k}}_2\hat{\mathbf{k}}_3\cdot\hat{\mathbf{k}}_4 +\hat{\mathbf{k}}_1\cdot\hat{\mathbf{k}}_3\hat{\mathbf{k}}_2\cdot\hat{\mathbf{k}}_4+\hat{\mathbf{k}}_1\cdot\hat{\mathbf{k}}_4\hat{\mathbf{k}}_2\cdot\hat{\mathbf{k}}_3) \tag{11b}$$

The multidimensional integrals in the definition of $\overline{K}$ can be calculated for the denominator [Eq. (10)] or reduced to a one-dimensional integral for the numerator [Eq. (4b) with Eq. (11)] with the help of the Fourier-transform method. A description of the calculation and rather lengthy explicit expressions for the results are given in the Appendix.

The Gompper-Schick model

In this extensively studied model the free-energy functional depends only on one order parameter, namely, the oil-water concentration difference $\phi(\mathbf{r})$ and has a form [5,11]

$$\beta F[\phi]=\int d_3\mathbf{r}[(\Delta\phi)^2+g_0(\nabla\phi)^2+(1-2f_0)\phi^2 +(f_0-2)\phi^4+\phi^6+g_2\phi^2(\nabla\phi)^2]. \tag{12}$$

We assume, as in Ref. [11] that $g_2=4\sqrt{1+f_0}-g_0+0.01$.

We assume that for this model the vector field describing orientational ordering of amphiphiles is given by

$$\mathbf{s}(\mathbf{r})=\nabla\phi(\mathbf{r}). \tag{13}$$

In Fourier representation we have $\tilde{\mathbf{s}}(\mathbf{k})=i\mathbf{k}\tilde{\phi}(\mathbf{k})$. Recall that previously the scalar field was introduced by $\tilde{\mathbf{s}}(\mathbf{k}) = i\hat{\mathbf{k}}s_{\parallel}(\mathbf{k})$, therefore in this case

$$s_{\parallel}(\mathbf{k})=k\tilde{\phi}(\mathbf{k}). \tag{14}$$

For the normalization factor and for the numerator in Eq. (3b) we thus obtain, respectively, the expressions

$$\langle\nabla\phi(r_1)\cdot\nabla\phi(r_2)\nabla\phi(r_3)\cdot\nabla\phi(r_4)\rangle = \int \frac{d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3 d\mathbf{k}_4}{(2\pi)^{4d}}\exp\left(-\sum_i^4 \mathbf{k}_i\cdot\mathbf{r}_i\right) \times\left\langle(\mathbf{k}_1\cdot\mathbf{k}_2\mathbf{k}_3\cdot\mathbf{k}_4)\prod_i^4 \phi(k_i)\right\rangle \tag{15}$$

and

$$\langle s^4 K_s\rangle=\frac{1}{2}\int \frac{d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3}{(2\pi)^{3d}}\,|\mathbf{k}_3\cdot(\mathbf{k}_1\times\mathbf{k}_2)|^2\left\langle\prod_i^4 \phi(\mathbf{k}_i)\right\rangle. \tag{16}$$

We proceed in the same way as in the previously considered model. We calculate $\overline{K}$ to a first order term in perturbation expansion about the Gaussian solution and regularize the corresponding integrals with the help of the real-space cutoff. The real-space cutoff a is identified with the characteristic (molecular) length l of Ref. [11], assumed to be equal to [11], thus $a=1$.

There are two contributions to $\langle\Pi_i^4\phi(k_i)\rangle$ in the first order in perturbation expansion [15], namely,

$$-(2\pi)^d\delta\left(\sum_i^4 \mathbf{k}_i\right)a_4^r\prod_i^4 f(\mathbf{k}_i), \tag{17a}$$

and

$$(2\pi)^d\delta\left(\sum_i^4 \mathbf{k}_i\right)4g_2\sum_{i<j}\mathbf{k}_i\cdot\mathbf{k}_j\prod_i^4 f(\mathbf{k}_i). \tag{17b}$$

In the above a_4^r is given by

$$a_4^r=4!(f_0-2)+\frac{6!}{2}\int\frac{d\mathbf{k}}{(2\pi)^d}f(k)=4!(f_0-2)+\frac{45\xi}{2\pi}, \tag{18}$$

where the first term is a contribution coming from the term proportional to ϕ^4 in Eq. (12) and the second term comes from the term proportional to ϕ^6. The correlation length is [11] $\xi=2(2\sqrt{(1-2f_0)}+g_0)^{-1/2}$.

Again, as in the previously considered model, we use the Fourier-transform method. The explicit expression for K is given in the Appendix. From its form it follows immediately that K is always negative for a uniform phase in this model.

V. RESULTS

The numerical values of the parameter $\overline{K}$ are calculated for $\gamma=16$ and $\gamma=50$. The lines at which K changes sign are shown as the dashed-dotted lines at the phase diagrams, at which also the Lifshitz and the disorder lines are included (Figs. 1 and 2). The lines $K=0$ start at the Lifshitz point, like the Lifshitz and the disorder lines. Near the transition to the liquid-crystal phases K in microemulsions is thus always negative. For surfactant densities $\rho_s<\rho_s^L+0.1$, where ρ_s^L corresponds to the Lifshitz point, the line $K=0$ lies in the vicinity of the bifurcation line. For higher densities the region of negative K grows, and at $\rho_s\sim0.5$ the $K=0$ line crosses the Lifshitz line. Thus for strong surfactants ($\gamma=16$ or $\gamma=50$) the region of the negative Gaussian curvature is smaller than the region in which oil and water domains are correlated $[\xi\geq\lambda/(2\pi)]$ for $\rho_s<0.5$, whereas for $\rho_s>0.5$ the situation is reversed. By increasing the temperature in this model we cause a transition from $K<0$ to $K>0$. The bicontinuous structure is thus destroyed in this model by thermal fluctuations, as expected for real systems.

The examples of numerical values for $\overline{K}$ are shown in Figs. 3 and 4 for $\gamma=16$ and for $\gamma=50$, respectively. In the first case we plot K for the constant surfactant density $\rho_s=0.4$, in the second case for the constant temperature $\tau=2.7$. In both cases we cross the line of vanishing K. We also plot $1/\sqrt{|K|}$ and λ in Figs. 5 and 6 for $\gamma=16$ and $\gamma=50$, respectively. We approximately obtain the ratio $R=|K|^{-1/2}/\lambda\sim0.25-0.5$ for $\gamma=16$, $\rho_s=0.4$ in the temperature range $\tau\sim1.96-2.0$, and $R\sim0.33-0.5$ for $\gamma=50$, $\tau=2.7$ for surfactant concentrations $\rho_s\sim0.3-0.6$.

The results for $R\approx R_m\sqrt{2}$ show that in the region of negative K, not too close to the line $K=0$ nor to the bifurcation line, the structure of microemulsions has features resembling the corresponding features of simple minimal surfaces. For example, for surfaces D, G, and P $\overline{R_m}\approx0.2$, 0.25, and 0.3, respectively. In case of diffuse interface $R=0.267$ for the D structure [9]. For other cubic structures R was not calculated in the case of thick films. The above results show that the structure of microemulsions changes gradually, and for different temperatures and surfactant volume fractions, is similar to the structure of different periodic minimal surfaces with low genus.

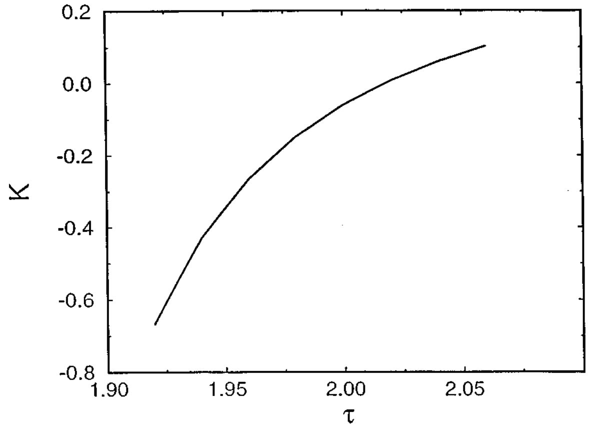

FIG. 3. Average Gaussian curvature for $\gamma=16$ at fixed surfactant volume fraction $\rho_s=0.4$. τ is a dimensionless temperature defined below Eq. (6c). A length unit is a size of surfactant molecule (a bare thickness of the monolayer).

A microemulsion contrary to systems which can be represented by periodic minimal surfaces is a disordered phase. The surface averaged Gaussian curvature $K_m=2\pi\chi_E/|A|$ is a *topological* invariant per surface area. Therefore, comparison between $R_m=|K_m|^{-1/2}/\lambda$ in disordered and in ordered phases is justified.

For positive K the lines λ and $1/\sqrt{|K|}$ are completely different. The common property is the fact that R decreases when the system becomes less ordered. R changes from infinity down to molecular distances when the disorder line is approached. We also calculated K in the region of structureless fluid, i.e., in the region of monotonically decaying correlation functions, in which surfactant density is very low.

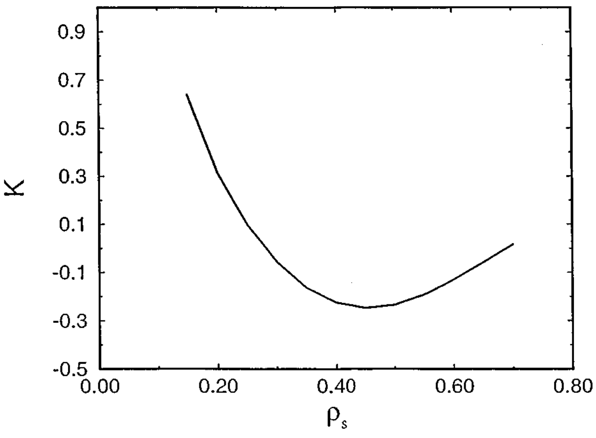

FIG. 4. Average Gaussian curvature for $\gamma=50$ at fixed temperature $\tau=2.7$. ρ_s is a surfactant volume fraction and a length unit is a size of surfactant molecule (a bare thickness of the monolayer).

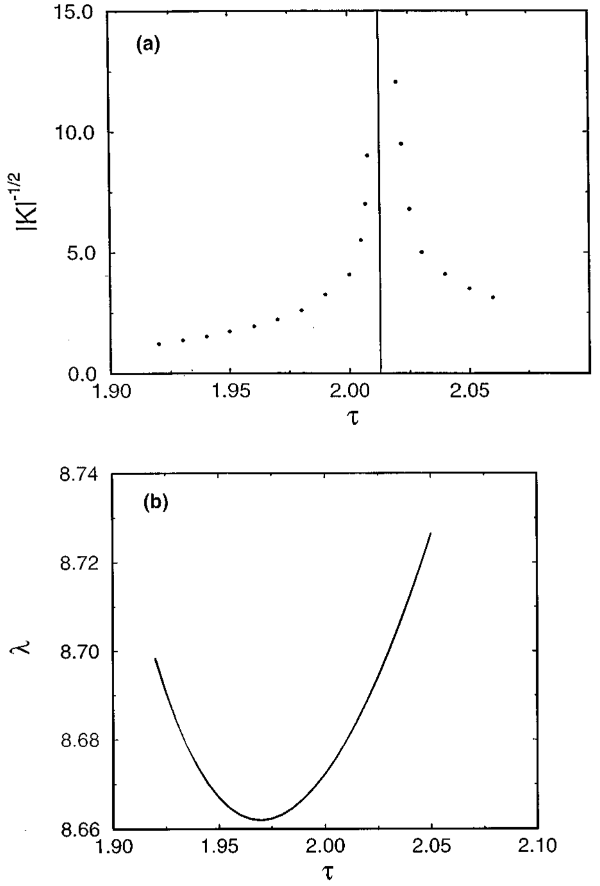

FIG. 5. (a) $|\overline{K}|^{-1/2}$ for $\gamma=16$ at fixed surfactant density $\rho_s=0.4$. τ is a dimensionless temperature defined below Eq. (6c); a length unit is a size of surfactant molecule (a bare thickness of the monolayer). (b) λ for $\gamma=16$ at fixed surfactant density $\rho_s=0.4$. τ is a dimensionless temperature defined below Eq. (6c); a length unit is a size of surfactant molecule (a bare thickness of the monolayer).

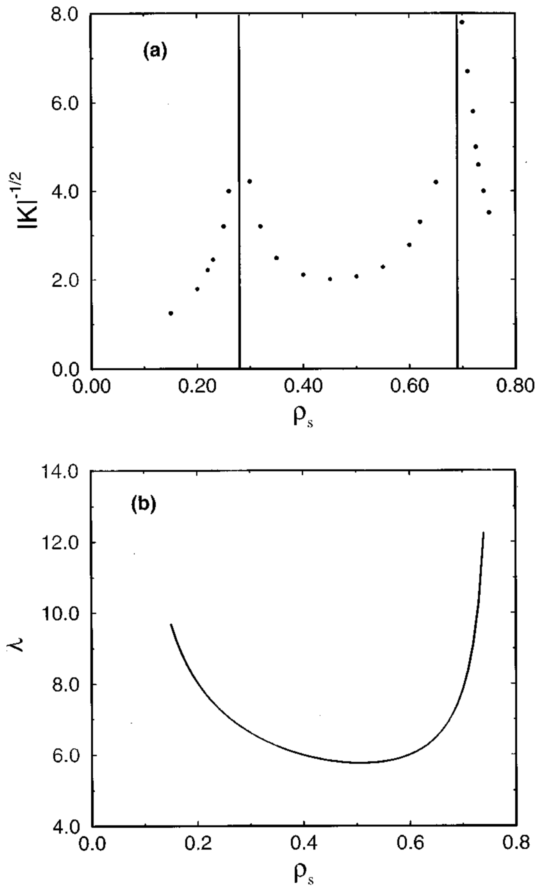

FIG. 6. (a) $|\overline{K}|^{-1/2}$ for $\gamma=50$ at fixed temperature $\tau=2.7$. ρ_s is a surfactant volume fraction; a length unit is a size of surfactant molecule (a bare thickness of the monolayer). (b) λ for $\gamma=50$ at fixed temperature $\tau=2.7$. ρ_s is a surfactant volume fraction; a length unit is a size of surfactant molecule (a bare thickness of the monolayer).

We obtain for $\overline{K}$ positive values larger than one. It indicates that surfactant molecules are correlated in such a way that preferred orientations and positions of four molecules at distances $\sim a$ from one another is such that they form vectors normal to a sphere with a radius comparable to the size of molecules.

The Gompper-Schick model

The results for $\overline{K}$ are shown in Fig. 7 for $f_0=-0.4$ as a function of g_0. By comparing $\overline{K}$ with the results of MC simulations [11] for $2\pi\chi_E/|A|$, we find $\overline{K}\approx\overline{K}_m/2$, as for interfaces of large width in ordered phases [9]. Since in microemulsions the interfaces have large width in this model [7a], we can conclude that the diffuse nature of the internal interfaces leads to lower values of $\overline{K}$ compared to $\overline{K}_m$, with the ratio ≈ 2, both in ordered structures and in microemulsions. Also, since the model considered in Ref. [9] is different, it is plausible that this property is not limited to a particular model.

In Fig. 8 λ and $1/\sqrt{|\overline{K}|}$ are compared. The lines are almost parallel, and $\lambda\sqrt{|\overline{K}|}\sim 2-3$, as in the previously described model. The same arguments as before lead us to the conclusion that the relation between $\overline{K}_m$ calculated for the central surface of the film and λ is similar to the corresponding relation for the minimal surfaces P, D, or G.

VI. SUMMARY

We calculated in microemulsions, in the LG approximation, a structure parameter $\overline{K}$, which can be considered as an

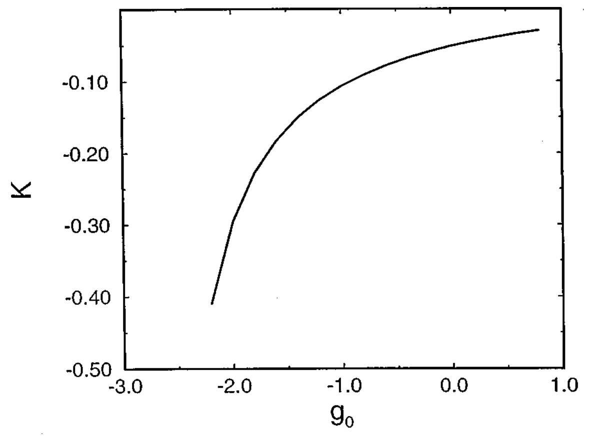

FIG. 7. Average Gaussian curvature in the GS model for $f_0=0.4$.

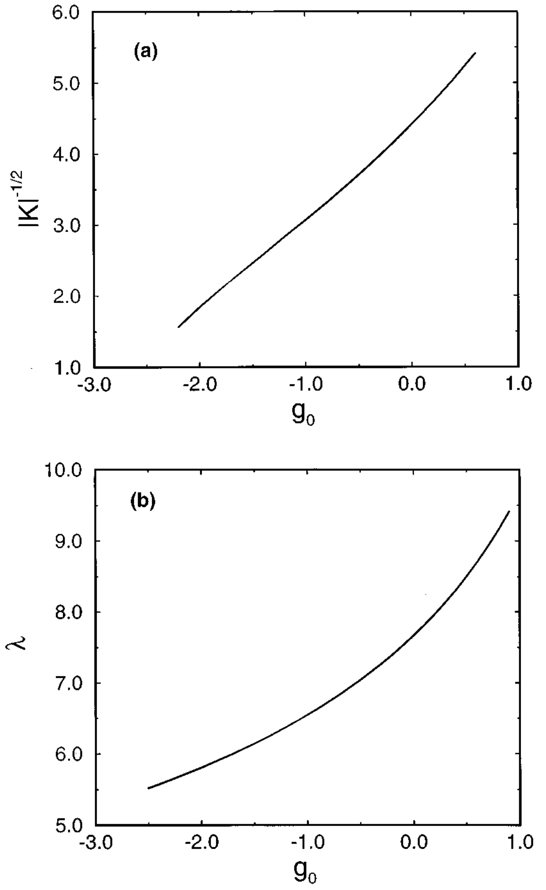

FIG. 8. (a) $|K|^{-1/2}$ in the GS model for $f_0=0.4$. (b) λ in GS model for $f_0=0.4$.

extension of the average Gaussian curvature. A definition for K is based on four-point correlation functions for oriented amphiphiles. For Landau-Ginzburg models the final results can be expressed in terms of single integrals. We should note that the results are obtained within LG approximations, and thus the exact value of K may be somewhat different, especially close to the bifurcation line.

In the case of the GS model the results obtained within the method introduced in Ref. [9] agree with the results of simulations; both K found here and K_m found in MC simulations [11] are negative. Also, their ratio is ~1/2 indicating diffuse nature of interfaces in microemulsions, in agreement with MC simulations [7a].

In the case of the three order-parameter model [13], K is negative only in the neighborhood of the liquid-crystal phases, i.e., in the part of the stability region of microemulsions. We find the line of $K=0$ in the phase space (ρ_s,τ). Beyond this line, temperatures are too high and/or surfactant volume fractions are too low or too high and the bicontinuous structure cannot be formed in this model.

Within the region of $K<0$, not too close to its boundary, the structure of microemulsions has properties resembling properties of simple minimal surfaces. We draw this conclusion by comparing the two important typical lengths for this system, the period of damped oscillations λ and the average radius of curvature $1/\sqrt{|K_m|}$ of the "central" surface of the film. Actually we calculate $1/\sqrt{|K|}$ which is an average radius of curvature for a collection of surfaces modeling the film whose thickness is comparable to λ. We thus calculate quantitatively, to first order in perturbation expansion, the ratio R, find $R\approx 0.25-0.5$ and *estimate* the ratio R_m. We find for R_m in microemulsion values close to R_m in different periodic minimal surfaces with low genus for different temperatures and surfactant volume fractions. Thus the structure of microemulsions is quite sensitive to the physical conditions, and resembles *different* ordered periodic structures.

Quantitative results for R_m in microemulsions would depend on the choice of the "central" surface, which is not unique, especially for interfaces of large width. The parameter R does not depend on the choice of the surface representing the film. At the same time it allows for *qualitative* comparison between the structure of microemulsions and structures represented by different surfaces, including periodic minimal surfaces. One can also calculate the structure parameters considered in this paper for different ordered structures with interfaces of large width. R in microemulsions is close to $R=0.267$ in the D structure with thick interfaces [9] only in some part of the stability region of microemulsions. For different structures with thick films R has not been calculated.

For $K>0$ the structure is more complicated. The ratio between the typical lengths λ and $|K|^{-1/2}$ depends strongly on ρ_s and τ. R decreases on approaching the disorder line, either by dilution or by heating the system.

The definition (3b) shows that the structure of a system with molecules self-assembled into internal films is determined by their correlation functions. Unlike in the case of simple fluids, the four-point correlation functions are as important, as the two-point functions for description of the structure in this case. The oil- or water-domain size is related to the period of oscillations λ of the two-point functions. The *connectivity* of oil and water domains, related to the sign of K *is determined by the way four molecules at distances comparable to their sizes are correlated*. For $K>0$ surfactant molecules are correlated in such a way that preferred orientations and positions of four molecules at distances $\sim a$ from one another is such that they form vectors normal to a sphere (or an elypsoid). For $K<0$, four molecules at distances close to a from one another are correlated in such a way that their preferred positions and orientations fit a saddle. Moreover, the four-point correlation function determines another important length $|K|^{-1/2}$, related to an average radius of curvature of the internal film. We propose consideration of a dimensionless ratio between the two lengths, λ and $|K|^{-1/2}$, as a convenient parameter which allows for comparison between microemulsions and different ordered structures.

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APPENDIX

1. The vector model

Let us first consider the denominator in definition (3b), given by Eq. (10). The integrals in Eq. (10) can be calculated with the help of the inverse Fourier transform of the function

$$p(k)=\frac{G_{ss}(k)}{k^2}, \tag{A1}$$

and the final result reads

$$\langle s^4\rangle=\widetilde{G}_{ss}^2(a)+2(\widetilde{p}_2^2(a)a^2+3\widetilde{p}_1^2(a)+2\widetilde{p}_1(a)\widetilde{p}_2(a)a), \tag{A2}$$

where the functions $\widetilde{p}_i$ are defined by

$$\widetilde{p}_{n+1}=\frac{1}{r}\frac{d}{dr}\widetilde{p}_n(r) \quad \text{and} \quad \widetilde{p}_0=\widetilde{p}, \tag{A3}$$

with $\widetilde{p}(r)$ being an inverse Fourier transform of $p(k)$,

$$\widetilde{p}(r)=\int \frac{d\mathbf{k}}{(2\pi)^d}\, e^{-i\mathbf{kr}}\, p(k). \tag{A4}$$

The numerator in definition (3b) is given by $\langle s^4K_s\rangle=K^a+K^A$, with

$$K^a=-\frac{a_4J^4}{2\tau}\int \frac{d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3}{(2\pi)^{3d}}\,|\mathbf{k}_3\cdot(\mathbf{k}_1\times\mathbf{k}_2)|^2\prod_i^4 f(k_i), \tag{A5a}$$

$$K^A=K_1^A+K_2^A, \tag{A5b}$$

$$K_1^A=\frac{A_4}{2\tau}\int \frac{d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3}{(2\pi)^{3d}}\,|\mathbf{k}_3\cdot(\mathbf{k}_1\times\mathbf{k}_2)|^2\mathbf{k}_1\cdot\mathbf{k}_2 g(k_3) \times\prod_{i\neq 3}^4 p(k_i), \tag{A5c}$$

$$K_2^A=\frac{A_4}{\tau}\int \frac{d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3}{(2\pi)^{3d}}\,|\mathbf{k}_3\cdot(\mathbf{k}_1\times\mathbf{k}_2)|^2(\mathbf{k}_1\cdot\mathbf{k}_2)(\mathbf{k}_1\cdot\mathbf{k}_3) \times\prod_i^4 p(k_i), \tag{A5d}$$

where $\mathbf{k}_4=-(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)$, $p(k)$ is defined in Eq. (A1) and we introduced a notation

$$f(k)=-\frac{G_{\phi s}(k)}{Jk}=\frac{\tau}{k^4+Bk^2+a_2}, \tag{A6a}$$

$$g(k)=G_{ss}(k)=f(k)(a_2+k^2). \tag{A6b}$$

In the expressions (A5) the correlation functions are formally calculated at one point. As in the case of the denominator, however, the correlations have to be calculated for distances comparable to the size of particles. We proceed in the following way. The two-point functions obtained in the model are in real space multiplied by a unit step function $\theta(r-a)$, i.e., only distances larger than the size of particles (lattice constant) are considered. Then in Eqs. (A5) the functions f, g, and p are replaced by the Fourier transforms of the corresponding real-space functions, multiplied by $\theta(r-a)$, however. Again, as in the case of denominator, the method of Fourier transform leads to one-dimensional integrals, with lower cutoff $a=1$ in this case, of the form:

$$K^a=-\frac{12\pi a_4J^4}{\tau}\int_1^\infty dr\ r^2\widetilde{f}(r)\widetilde{f}_1^2(r)(\overline{f_1}(r)+r^2\widetilde{f}_2(r)) \tag{A7a}$$

$$K_1^A=-\frac{4\pi A_4}{\tau}\int_1^\infty dr\ r^4\widetilde{p}(r)\widetilde{p}_2(r)(5\widetilde{g}_1(r)p_2(r) +r^2\widetilde{g}_2(r)\widetilde{p}_2(r)+2r^2\widetilde{g}_1(r)\widetilde{p}_3(r)), \tag{A7b}$$

and

$$K_2^A=\frac{8\pi A_4}{\tau}\int_1^\infty dr\ r^4\widetilde{p}(r)\widetilde{p}_2(r)(11\widetilde{p}_2^2(r)+10r^2\widetilde{p}_2(r)\widetilde{p}_3(r) +2r^4\widetilde{p}_3^2(r)+r^4\widetilde{p}_2(r)\widetilde{p}_4(r)), \tag{A7c}$$

where the functions $\widetilde{f}(r)$ and $\widetilde{g}(r)$ are inverse Fourier transforms of the functions $f(k)$ and $g(k)$, respectively, and the functions $\widetilde{f}_n$ and $\widetilde{g}_n$ are defined in the same way as $\widetilde{p}_n$ [see Eq. (A3)].

2. The Gompper-Schick model

The final expression for the denominator in Eq. (3b) [Eq. (15)], obtained with the help of the Fourier-transform method reads

$$\langle s^4\rangle=\widetilde{F}(a)^2+2[\widetilde{f}_2(a)^2a^2+3\widetilde{f}_1^2(a)+2\widetilde{f}_2(a)\widetilde{f}_1(a)a], \tag{A8}$$

where $\widetilde{f}_n$ are defined in the same way as in Eq. (A3) $\widetilde{f}(r)$ is an inverse Fourier transform of the structure factor

$$f(k)=\frac{1}{2}\frac{1}{k^4+g_0k^2+1-2f_0}, \tag{A9a}$$

and where $\widetilde{F}(r)$ is an inverse Fourier transform of

$$F(k)=f(k)k^2. \tag{A9b}$$

The numerator in Eq. (3b) for this model is calculated in the same way as before. Using Eq. (17) we find $\langle s^4K_s\rangle=K_1+K_2$ where the first contribution is of the form

$$K_1=-12\pi a_4^r\int_1^\infty dr\ r^2\widetilde{f}(r)\widetilde{f}_1^2(r)(\widetilde{f}_1(r)+r^2\widetilde{f}_2(r)) \tag{A10a}$$

and the second one is of the form

$$K_2=-96\pi g_2\int_1^\infty dr\ r^4\widetilde{f}(r)\widetilde{f}_2(r)(5\widetilde{f}_1(r)f_2(r) +r^2\widetilde{f}_2(r)\widetilde{f}_2(r)+2r^2\widetilde{f}_1(r)\widetilde{f}_3(r)). \tag{A10b}$$

One can see immediately that $\widetilde{K}$ is always negative in this model.

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