Description of the geometrical and topological structure in amphiphilic systems

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A unified description of internal interfaces in oil-water-surfactant mixtures is proposed. Surfactant degrees of freedom are explicitly taken into account in the form of a vector field. A general definition of average curvatures in terms of the vector field is given. They are averages of the mean and Gaussian curvatures and characterize globally the geometrical and topological structure of the internal interface. It is argued that this definition can be applied to both sharp and diffuse oil-water interfaces, in ordered phases and in disordered microemulsions. A few examples concerning ordered phases are considered, and the results for the average curvatures are compared with the standard approach, in which the interface is modeled by an infinitely thin mathematical surface. It is also shown that the approach reduces to the standard one in the case of well-defined surfactant monolayers. Finally, the definition of average curvatures is extended to the case of microscopic Hamiltonians.

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Experimental results [1,2] show that in oil-water-surfactant mixtures the surfactant particles form monolayers in various ordered phases (lamellar, hexogonal, cubic, etc.) and in microemulsions. The microemulsion and the homogeneous mixture cannot be distinguished thermodynamically. However, they have different structures on a mesoscopic length scale (~ 100 Å). This structure can be observed in scattering experiments [1,2]. It consists of oil- and water-rich regions separated by a thin surfactant film (monolayer). The water-water structure factor is well described by the Teubner-Strey expression [2,3] $S_{ww}(k) = (k^4 + bk^2 + c)^{-1}$. In the real space the correlation function exhibits exponentially damped oscillations. Thus, the structure is characterized by two lengths: the period of oscillations λ, related to the size of water- or oil-rich regions, and the correlation length ξ. In the microemulsion $S_{ww}(k)$ assumes the maximum at $k = k_{max} \neq 0$. This corresponds to $\xi > \lambda$, i.e., to correlated water and oil domains. When the concentration of the surfactant decreases, k_{max} moves towards zero and eventually at the Lifshitz line $k_{max} = 0$, which corresponds to $\xi = \lambda$. When the surfactant concentration is further decreased, the ratio ξ/λ decreases. The water-water correlation function still oscillates, but the amplitude decreases rapidly, and the water- and oil-rich regions become uncorrelated. eventually $\xi/\lambda = 0$ at the disorder line. Beyond the disorder line the correlation function decays monotonically.

Since surfactant monolayers existing in ordered phases and in microemulsions with $k_{max} \neq 0$ form well-defined surfaces, it is natural to consider them as idealized, infinitely thin mathematical surfaces [4,5]. Then one can study geometrical and topological properties of such surfaces to obtain more information about the mesoscopic structure of the system. This is basically the approach used for membranes, which are described by two local invariants: the mean curvature H and the Gaussian curvature K [6]. It is well known that the total curvature, defined as the integral of K over the surface A, is a topo-

logical invariant related to the number of holes in the surface. This relation is given by the Gauss-Bonnett theorem

$$\frac{1}{2\pi} \int_A K(\mathbf{r}) d\sigma = \chi_E = 2(1-p) , \qquad (1)$$

where χ_E is the Euler characteristic and p denotes the number of holes. Various ordered phases formed by oil-water-surfactant mixtures can be classified in terms of H and K. For example, the micellar and reverse micellar phases have $H > 0$ and $H < 0$, respectively, and $K > 0$. In phases with hexagonal symmetry, $K = 0$ and $H > 0$ or $H < 0$. The bicontinuous phases have $K < 0$, which indicates existence of holes in the structure and, in the case of oil-water symmetry, $H = 0$.

The microemulsion does not exhibit long-range or quasi-long-range order characteristic for ordered phases. Nevertheless, it does have an interesting and complex mesoscopic structure observed in experiment. Topologically this structure is similar to that observed in ordered bicontinuous phases. This means that the internal interface should have $K < 0$ and hence, $\chi_E < 0$. To describe this interface in terms of a mathematical surface we have to assume that almost all surfactant molecules form a monolayer separating oil- and water-rich regions. However, close to the disorder line this picture may not be correct. Then one rather deals with diffuse interface and possibly with surfactant patches in oil- and water-rich regions [7]. In that case it is no longer justified to model the interface, thickness of which can be comparable to the characteristic length of the structure, by a single mathematical surface. It would be more appropriate to consider a continuous set of mathematical surfaces reflecting in some way the distribution of surfactant molecules.

In this paper we propose a new approach to the problem of the internal interface in oil-water-surfactant mixtures. Since we do not make any particular assumptions about the nature of the interface, this approach can be

applied both to ordered phases and to the microemulsion, even if the latter is between the Lifschitz line and the disorder line. Using this new approach we would like to obtain more information about the geometrical and topological structure of the microemulsion. We show below how the definitions of H and K for a single mathematical surface can be extended to be applicable to both well-defined surfactant monolayers and diffuse interfaces.

There are many models of oil-water-surfactant mixtures, both microscopic and using a mesoscopic level of description. The latter are referred to as Landau-Ginzburg models. An excellent review is presented in Ref. [1]. For our present purpose it is sufficient to note that usually one takes into account only translational degrees of freedom of oil and water molecules, while for surfactant molecules also their orientations are specified. Thus, using a mesoscopic level of description one considers a scalar field $\phi(\mathbf{r})$ for the concentration difference between oil and water and a vector field $\mathbf{u}(\mathbf{r})$ describing surfactant degrees of freedom. In principle, a second scalar field specifying the surfactant concentration $\rho_s(\mathbf{r})$ should also be considered. However, simplified models with two order parameters $\phi(\mathbf{r})$ and $\mathbf{u}(\mathbf{r})$ have also been used [8]. Our model, defined below, is based on these two order parameters. Although $\mathbf{u}(\mathbf{r})$ does not contain full information about the surfactant concentration, in the case of surfactant molecules aligned along some common local direction $\hat{\mathbf{n}}(\mathbf{r})$ one has

$$\mathbf{u}(\mathbf{r}) = \rho_s(\mathbf{r})\hat{\mathbf{n}}(\mathbf{r}) . \tag{2}$$

For a well-defined surfactant monolayer $\rho_s(\mathbf{r}) = 0$ beyond the monolayer and $\hat{\mathbf{n}}(\mathbf{r})$ is normal to the surface formed by surfactant. However, in real systems orientations of surfactant molecules fluctuate around their local average orientation $\hat{\mathbf{n}}(\mathbf{r})$ and therefore (2) does not hold in general. To take into account these fluctuations we split $\mathbf{u}(\mathbf{r})$ as follows:

$$\mathbf{u}(\mathbf{r}) = \mathbf{s}(\mathbf{r}) + \mathbf{t}(\mathbf{r}) \tag{3}$$

where the fields $\mathbf{s}$ and $\mathbf{t}$ satisfy conditions $\nabla \times \mathbf{s} = 0$ and $\nabla \cdot \mathbf{t} = 0$. Because of the first condition there exists a potential field $\psi(\mathbf{r})$, such that $\mathbf{s} = \nabla \psi$. Thus, at each point

$\mathbf{s}(\mathbf{r})$ is normal to the surface $\psi(\mathbf{r}) = $ const and we can define $\hat{\mathbf{n}}(\mathbf{r}) = \mathbf{s}(\mathbf{r})/s(\mathbf{r})$, where $s = |\mathbf{s}|$. The fluctuations around the normal direction are described by the field $\mathbf{t}(\mathbf{r})$. Since the potential field has been defined, it is possible to calculate at each point $\mathbf{r}$ the mean and Gaussian curvatures corresponding to the surface $\psi(\mathbf{r}) = $ const. We expect $s(\mathbf{r})$ to be large in the region of the interface and to decay to zero away from it. We note that to define H and K it is not necessary to make any assumptions about the thickness of the interface. In the coordinate frame in which $\hat{\mathbf{n}} = (0, 0, 1)$, H and K are given by

$$H = \tfrac{1}{2}(\nabla_x \hat{\mathbf{n}}_x + \nabla_y \hat{\mathbf{n}}_y) , \tag{4}$$

$$K = \nabla_x \hat{\mathbf{n}}_x \nabla_y \hat{\mathbf{n}}_y - \nabla_y \hat{\mathbf{n}}_x \nabla_x \hat{\mathbf{n}}_y . \tag{5}$$

Using the definition of $\hat{\mathbf{n}}$ we can expresses the local mean and Gaussian curvatures in the invariant form as follows:

$$s^3(\mathbf{r})H_s(\mathbf{r}) = \tfrac{1}{2}(s^2 \nabla \cdot \mathbf{s} - \tfrac{1}{2}\mathbf{s} \cdot \nabla s^2) \tag{6}$$

and

$$s^4(\mathbf{r})K_s(\mathbf{r}) = \tfrac{1}{2}s_i s_l \epsilon_{ijk} \epsilon_{lmn} \nabla_m s_j \nabla_n s_k , \tag{7}$$

where the index s has been used to indicate that the curvatures depend on the field $\mathbf{s}(\mathbf{r})$. When the Hamiltonian of the system is specified, the averages $\langle s^3 H_s \rangle$ and $\langle s^4 K_s \rangle$ can, in principle, be calculated without any additional assumptions about formation of thin surfactant films. To characterize global geometrical and topological properties of the internal interface we introduce average curvatures defined as follows:

$$\overline{H} = \frac{\int_V d\mathbf{r} \langle s^3 H_s \rangle}{\int_V d\mathbf{r} \langle s^3 \rangle} \tag{8}$$

and

$$\overline{K} = \frac{\int_V d\mathbf{r} \langle {}^4 K_s \rangle}{\int_V d\mathbf{r} \langle s^4 \rangle} \tag{9}$$

where V is the volume of the system. It is often more convenient to use the Fourier representation of $\mathbf{s}$ in expressions (8) and (9). We find that

$$\langle s^3 H_s \rangle = -\frac{3}{4} \int \frac{d\mathbf{k}_1}{(2\pi)^d} \cdots \int \frac{d\mathbf{k}_3}{(2\pi)^d} (2\pi)^d \delta\left[\sum_i^3 \mathbf{k}_i\right] \hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2 k_3 G_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \tag{10}$$

and

$$\langle s^4 K_s \rangle = \frac{1}{2} \int \frac{d\mathbf{k}_1}{(2\pi)^d} \cdots \int \frac{d\mathbf{k}_4}{(2\pi)^d} (2\pi)^d \delta\left[\sum_i^4 \mathbf{k}_i\right] \frac{|\mathbf{k}_3 \cdot (\mathbf{k}_1 \times \mathbf{k}_2)|^2}{k_1 k_2 k_3 k_4} G_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) , \tag{11}$$

where the n-body correlation function is defined as

$$G_n(\mathbf{k}_1, \ldots, \mathbf{k}_n) = \langle s_\parallel(\mathbf{k}_1) \ldots s_\parallel(\mathbf{k}_n) \rangle . \tag{12a}$$

and the field $s_\parallel$ is related to the Fourier transform of $\mathbf{s}$ by

$$\tilde{\mathbf{s}}(\mathbf{k}) = i\hat{\mathbf{k}} s_\parallel(\mathbf{k}) . \tag{12b}$$

The above follows from the condition $\nabla \times \mathbf{s} = 0$.

First we consider the case of ordered phases. The average distribution $\langle s(\mathbf{r}) \rangle$ is then periodic in space. If the fluctuations around $\langle s(\mathbf{r}) \rangle$ are neglected then $\overline{H}$ and $\overline{K}$ can be approximated by

$$\overline{H} \approx \frac{\int_V d\mathbf{r} \langle s \rangle^3 H_{\langle s \rangle}}{\int_V d\mathbf{r} \langle s \rangle^3} , \tag{13}$$

$$\bar{K} \approx \frac{\int_V d\mathbf{r}\langle s\rangle^4 K_{\langle s\rangle}}{\int_V d\mathbf{r}\langle s\rangle^4} \ . \tag{14}$$

For thin surfactant films the integrals in (13) and (14) are restricted to the region of the film and if $\langle s(\mathbf{r})\rangle \approx$ const across the film then

$$\bar{H} \approx \bar{H}_m = \frac{1}{|A|} \int_A d\sigma H_{\langle s\rangle} \ , \tag{15}$$

$$\bar{K} \approx \bar{K}_m = \frac{1}{|A|} \int_A d\sigma K_{\langle s\rangle} \ , \tag{16}$$

where A denotes the mathematical surface of area $|A|$ modeling the surfactant film. It results from Eqs. (15) and (16) that in this case we recover the standard definition of the average curvatures of a single mathematical surface, denoted here by $\bar{H}_m$ and $\bar{K}_m$. Combination of Eqs. (1) and (16) gives $\bar{K}_m = 2\pi\chi_E/|A|$. For periodic structures it is conventional to consider a part of the total surface A_0 of area $|A_0|$, contained in the unit cell and define $\chi_0 = \chi_E |A_0|/|A|$. It results from (1) that in the limit $V \to \infty$, $\chi_0 = -2p_0$ where p_0 is the number of holes per unit cell. Different structures are usually characterized by the ratio $\chi_0/\tilde{A}_0$ where $\tilde{A}_0 = |A_0|L_0^{-2}$ and L_0 is the linear size of the unit cell. Finally we obtain

$$\frac{L_0^2}{2\pi}\bar{K}_m = \frac{\chi_0}{\tilde{A}_0} \ . \tag{17}$$

It is interesting to compare $\bar{H}_m$ and $\bar{K}_m$ for various ordered phases with their counterparts $\bar{H}$ and $\bar{K}$ obtained for a diffuse interface. We present a few examples further on in this paper.

In order to calculate the average curvatures $\bar{H}$ and $\bar{K}$ for ordered structures, we consider a Landau-Ginzburg model of oil-water-surfactant mixtures, assuming symmetry between oil and water. The free-energy functional depends on two order-parameter fields: $\phi(\mathbf{r})$ describing the concentration difference between oil and water and a vector field $\mathbf{u}(\mathbf{r})$, representing surfactant degrees of freedom [1,8]. Direction of $\mathbf{u}(\mathbf{r})$ describes local orientation of surfactant molecules in elementary volume d^3r; the larger $|\mathbf{u}(\mathbf{r})|$ is, the higher the surfactant density, and the more surfactant molecules in d^3r are oriented along common direction $\hat{\mathbf{u}}(\mathbf{r})$. In a disordered phase average values of both fields vanish. The free-energy density can be approximated by polynomials in $\phi, \mathbf{u}$ and their derivatives. We assume the following form for F:

$$F = \int d\mathbf{r}[\tfrac{1}{2}\zeta(\nabla\phi)^2 + f(\phi) + \tfrac{1}{2}r_0 u^2 + \tfrac{1}{2}K_1(\nabla\cdot\mathbf{u})^2$$
$$+ \tfrac{1}{2}K_2(\nabla\times\mathbf{u})^2 + \frac{r_2}{4!}\phi^2 u^2 - J\mathbf{u}\cdot\nabla\phi] \ , \tag{18}$$

where $f(\phi) = \sum_i^3 a_{2i}\phi^{2i}$. A similar model (with similar notation) was considered in Ref. [8]. As in Ref. [8], we do not consider ordering of pure surfactant, therefore only the second power of $\mathbf{u}$ is included. In Ref. [8] the term $\sim[\nabla\times\mathbf{u}(\mathbf{r})]^2$ is absent. We include this term, because it is of the same order as the term $\sim(\nabla\cdot\mathbf{u})^2$. Contrary to the model of Ref. [8] and to the models with only one order parameter ϕ (Refs. [9,1]), F given by (18) does not

contain a term $\sim(\nabla^2\phi)^2$, which appears in continuum approximation to the lattice models with competing first- and second-neighbor interactions [10,1]. However, there exists a class of lattice models in which only nearest-neighbor interactions are assumed [11,1]. In these models the orientational degrees of freedom of surfactant particles are explicitly taken into account and the interactions strongly depend on the orientation. Therefore in continuum approximation to this class of lattice models, the higher-order derivatives can be neglected, $\zeta > 0$, and the microemulsion structure should result from the amphiphilic interactions. In continuum approximation such interactions are represented by the term $\sim -\mathbf{u}\nabla\phi$ (surfactant is preferentially located at the oil-water interface). Indeed, one can easily calculate the structure factor $S_{\phi\phi}(k)$ and obtain a form similar to the Teubner-Strey expression. Even though $\zeta > 0$, the $S_{\phi\phi}(k)$ assumes maximum at $k \neq 0$ if J is sufficiently large. After integration over the field $\mathbf{u}(\mathbf{r})$, the Laplacian term and $\zeta < 0$ would appear [8]. We also assume that in the presence of surfactant $a_2 > 0$ in the disordered phase, and $a_2 < 0$ corresponds to oil- and water-rich phase coexistence. The form of $f(\phi)$ allows for water-rich, oil-rich, and microemulsion phase coexistence. The term $\sim \phi^2 u^2$ describes the solubility of surfactant in oil and water. We shall present more detail concerning this model in the next paper [12]. Here we concentrate only on the average curvatures $\bar{H}$ and $\bar{K}$. After integration over the field $\mathbf{t}$ ($\nabla\cdot\mathbf{t}=0$) we obtain an effective free-energy functional of fields $\phi(\mathbf{r})$ and $s(\mathbf{r})$:

$$F_{\text{eff}} = \int d\mathbf{r} \left[\frac{1}{2}\zeta(\nabla\phi)^2 + f_r(\phi) + \frac{1}{2}r_0 s^2 + \frac{1}{2}K_1(\nabla\cdot s)^2 \right.$$
$$\left. + \frac{r_2}{4!}\phi^2 s^2 - Js\cdot\nabla\phi + \frac{g_2}{4!}\phi^2(\nabla\phi)^2 \right] \ , \tag{19}$$

where the index r means "renormalized." After rescaling of the order parameters and F_{eff} we have $\zeta = r_0 = K_1 = 1$. We do not study here the phase diagram in detail, but consider only various ordered phases in the proximity of the stability limit of the disordered phase. This corresponds to extremely diffuse interface, of thickness comparable to the size of water and oil domains.

In order to find the boundary of stability of the uniform phase, we introduce a field

$$\tilde{\psi}(\mathbf{k}) = \tilde{s}_\parallel(\mathbf{k}) + \frac{J|\mathbf{k}|}{1+k^2}\tilde{\phi}(\mathbf{k}) \ .$$

The Gaussian part of F_{eff} takes the form

$$F_0[\tilde{\psi}(\mathbf{k}), \tilde{\phi}(\mathbf{k})] = \frac{1}{2} \int \frac{d\mathbf{k}}{(2\pi)^3}[(1+k^2)|\tilde{\psi}(\mathbf{k})|^2$$
$$+ A(k)|\tilde{\phi}(\mathbf{k})|^2] \ ,$$

where

$$A(k) = (1+k^2)^{-1}[(k^2-\alpha^2)^2 + a_2 - \alpha^4]$$

and

$$\alpha^2 = \frac{J^2 - 1 - a_2}{2} \ .$$

The bifurcation takes place when $A(k)$ changes sign, thus $\alpha^2 = \sqrt{a_2}$ or $\tau = 2\sqrt{a_2} + a_2 + 1 - J^2 = 0$, and the wave number corresponding to bifurcation $k_b = \alpha$. Minimization of $F_{\rm eff}$ just below the bifurcation (small and

$$F_{\rm eff}/V \simeq \frac{1}{2} \sum_{|\mathbf{k}|=k_b} \frac{k_b^2 \tau}{1+k_b^2} |\tilde{\phi}(\mathbf{k})|^2 + \sum_{|\mathbf{k}_i|=k_b} \delta\left[\sum_i^4 \mathbf{k}_i\right] [a_4 - k_b^2(g_2 + r_2)\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2] \prod_i^4 \tilde{\phi}(\mathbf{k}_i) \ , \tag{20b}$$

where $|\tilde{\phi}(\mathbf{k})|^2 = O(|\tau|)$. We find that the disordered phase becomes unstable with respect to fluctuations of the lamellar, hexagonal, or double-diamond symmetry. It turns out that the global minimum of $F_{\rm eff}$ corresponds to the lamellar phase, at least when the bifurcation analysis predicts a continuous transition, and the other two phases are metastable. Nevertheless, it is instructive to calculate $\bar{H}$ and $\bar{K}$ for all three phases. The instability occurs for one of the following forms of $\langle \tilde{\phi}(\mathbf{k}) \rangle$:

(i) lamellar symmetry

$$\langle \tilde{\phi}(\mathbf{k}) \rangle = \phi_l [\delta^{Kr}(\mathbf{k} - k_b \hat{\mathbf{p}}) + \delta^{Kr}(\mathbf{k} + k_b \hat{\mathbf{p}})] \ , \tag{21}$$

where $\hat{\mathbf{p}}$ defines the direction normal to the layers,

(ii) hexagonal symmetry (water cylinders in oil or *vice versa*)

$$\langle \tilde{\phi}(\mathbf{k}) \rangle = \pm \phi_h \sum_i^3 [\delta^{Kr}(\mathbf{k} - k_b \hat{\mathbf{p}}_i) + \delta^{Kr}(\mathbf{k} + k_b \hat{\mathbf{p}}_i)] \ , \tag{22}$$

where $\hat{\mathbf{p}}_i$ ($i = 1,2,3$) form an equilateral triangle, and

(iii) double-diamond symmetry (intertwined oil and water tunnels)

$$\langle \tilde{\phi}(\mathbf{k}) \rangle = \phi_{dds} \left[(1+i) \sum_i^4 \delta^{Kr}(\mathbf{k} - k_b \hat{\mathbf{p}}_i) \right.$$

$$\left. + (1-i) \sum_i^4 \delta^{Kr}(\mathbf{k} + k_b \hat{\mathbf{p}}_i) \right] \ , \tag{23}$$

where in this case $\hat{\mathbf{p}}_i$ ($i = 1,2,3,4$) form tetrahedron. For comparison we also consider a cubic crystal of oil and water droplets arranged in two fcc lattices shifted with respect to each other by half a period, i.e.,

(iv) cubic crystal (oil and water droplets)

$$\langle \tilde{\phi}(\mathbf{k}) \rangle = \phi_c \sum_i^4 [\delta^{Kr}(\mathbf{k} + k_b \hat{\mathbf{p}}_i) + \delta^{Kr}(\mathbf{k} + k_b \hat{\mathbf{p}}_i)] \ , \tag{24}$$

where $\hat{\mathbf{p}}_i$ are the same as in the previous case.

To calculate $\bar{H}$ and $\bar{K}$ we approximate the n-body correlation function by

$$G_n(\mathbf{k}_1, \ldots, \mathbf{k}_n) \approx \langle s_\parallel(\mathbf{k}_1) \rangle, \ldots, \langle s_\parallel(\mathbf{k}_n) \rangle \ . \tag{25}$$

Then Eqs. (10) and (11) simplify to

$$\langle s^3 H \rangle = -\frac{3}{4} J^3 \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} \sum_{\mathbf{k}_3} \delta^{Kr}\left[\sum_i^3 \mathbf{k}_i\right] \mathbf{k}_1 \cdot \mathbf{k}_2 k_3^2 \prod_i^3 \frac{\tilde{\phi}^b(\mathbf{k}_i)}{1+k_i^2} \ . \tag{26a}$$

and

negative τ) gives, to second order in bifurcation analysis,

$$\langle s_\parallel(\mathbf{k}) \rangle \simeq -J \frac{k_b}{1+k_b^2} \langle \tilde{\phi}(\mathbf{k}) \rangle \ , \tag{20a}$$

where $s_\parallel$ is defined in (12b) and

$$\langle s^4 K \rangle = \frac{J^4}{2} \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} \sum_{\mathbf{k}_3} \sum_{\mathbf{k}_4} \delta^{Kr}\left[\sum_i^4 \mathbf{k}_i\right] |\mathbf{k}_3 \cdot (\mathbf{k}_1 \times \mathbf{k}_2)|^2$$

$$\times \prod_i^4 \frac{\tilde{\phi}^b(\mathbf{k}_i)}{1+k_i^2} \ . \tag{26b}$$

Using the above together with Eqs. (20)–(24) we are able to calculate $\bar{H}$ and $\bar{K}$ for the given ordered phase. For the lamellar phase one easily sees that both $\bar{H}$ and $\bar{K}$ vanish, as expected. In the case of the two hexagonal phases there are 12 contributions to the sum in Eq. (26a), for which $\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2 = -\frac{1}{2}$. We thus have

$$\langle s^3 H \rangle = \mp \frac{9}{2} J^3 \left[\frac{k_b}{1+k_b^2}\right]^3 \phi_h^3 k_b \ .$$

The denominator in (8) is computed with the help of Eqs. (12b), (20a), and (22). To find $\langle s^4 K \rangle$ we note that $|\mathbf{k}_3 \cdot (\mathbf{k}_1 \times \mathbf{k}_2)|^2 \prod_i^4 \tilde{\phi}(\mathbf{k}_i) = 0$, since $\tilde{\phi}(\mathbf{k}_i) \neq 0$ for vectors within one plane [see (22)], for which, on the other hand, $|\mathbf{k}_3 \cdot (\mathbf{k}_1 \times \mathbf{k}_2)|^2 = 0$. The results for the hexagonal phases are thus

$$\bar{H} L_0 = \mp 1.02\pi \ ,$$

$$\bar{K} \frac{L_0^2}{2\pi} = 0 \ . \tag{27}$$

The results are presented in a dimensionless form, i.e., $\bar{K} L_0^2 / 2\pi$ [see Eq. (17)] and $\bar{H} L_0$ are calculated, where the linear size of the unit cell, L_0, is related to k_b by $L_0 = 4\pi/k_b$ in the case of the hexagonal phases.

This should be compared with the mathematical surface $\langle \phi(\mathbf{r}) \rangle = 0$, obtained from the Fourier transform (22), which is approximately cylindrical with the curvature $\bar{H}_m$. The ratio of the mean curvatures is

$$\frac{\bar{H}}{\bar{H}_m} \approx 0.6 \ . \tag{28}$$

Next we consider the double-diamond and fcc phases, for which $L_0 = 2\pi\sqrt{3}/k_b$. Because of the oil-water symmetry $\bar{H}$ should vanish. Indeed, for $\mathbf{k}_i = \pm k_b \hat{\mathbf{p}}_j$, where $\hat{\mathbf{p}}_j$ form tetrahedron, we obtain $\prod_i^3 \tilde{\phi}(\mathbf{k}_i) \delta^{Kr}(\sum_i^3 \mathbf{k}_i) = 0$, thus from (26a) it follows that $\bar{H} = 0$. To find $\langle s^4 K \rangle$ we first note that $|\hat{\mathbf{p}}_i \cdot (\hat{\mathbf{p}}_j \times \hat{\mathbf{p}}_k)|^2 = \frac{16}{27}$ for $i \neq j \neq k$. There are 4! contributions to the sum in (26b) from all $\mathbf{k}_{i_n} = \hat{\mathbf{p}}_{j_n}$ and 4! contributions from all $\mathbf{k}_{i_n} = -\hat{\mathbf{p}}_{j_n}$ where $\mathbf{k}_{i_1} \neq \mathbf{k}_{i_2} \neq \mathbf{k}_{i_3} \neq \mathbf{k}_{i_4}$. For such vectors $\prod_i^4 \tilde{\phi}(\mathbf{k}_i) = -4\phi_{dds}^4$ for the

dds structure and $\prod_i^4 \widetilde{\phi}(\mathbf{k}_i) = \phi_c^4$ for the fcc structure. The denominator in (9) is computed in a similar way. The results are as follows. For the *dds* phase we have

$$\overline{H}L_0 = 0 \,,$$
$$\overline{K}\frac{L_0^2}{2\pi} = -\frac{32}{45}\pi \,.$$ (29)

Again we compare this result with the one for the mathematical surface $\langle\phi(\mathbf{r})\rangle = 0$ obtained from (23). That surface has eight holes in the unit cell, hence $\chi_0 = -16$, and $\widetilde{A}_0 \approx 3.8$ [1]. Using (17) we find the ratio

$$\frac{\overline{K}}{\overline{K}_m} \approx 0.53 \,.$$ (30)

Finally, for the cubic crystal of oil and water droplets

$$\overline{H}L_0 = 0 \,,$$
$$\overline{K}\frac{L_0^2}{2\pi} = \frac{32}{81}\pi \,,$$ (31)
$$\frac{\overline{K}}{\overline{K}_m} \approx 0.49 \,.$$

To obtain $\overline{K}_m$ we used the fact that in this structure there are four spheres of radius $L_0/4$ in the unit cell.

Note that in all cases the ratios $\overline{H}/\overline{H}_m$ and $\overline{K}/\overline{K}_m$ are positive and less than 1. This means that even though the oil-water interfaces considered above are diffuse, they have average curvatures of the same sign as those modeled by the mathematical surface $\langle\phi(\mathbf{r})\rangle = 0$ or $\langle s(\mathbf{r})\rangle = \max\langle s\rangle$. The values less than 1 result from the fact that the integrals in (13) and (14) are over a continuous set of surfaces and the contribution of each surface to $\overline{H}$ and $\overline{K}$ is weighted, respectively, by $\langle s(\mathbf{r})\rangle^3$ and $\langle s(\mathbf{r})\rangle^4$, while $\overline{H}_m$ and $\overline{K}_m$ are calculated for a single surface. When the oil-water interface becomes increasingly sharp the ratios $\overline{H}/\overline{H}_m$ and $\overline{K}/\overline{K}_m$ tend to unity. Thus, in the case of thin surfactant films our prescription for calculation of $\overline{H}$ and $\overline{K}$ reduces to the standard one, based on a single mathematical surface $\langle\phi(\mathbf{r})\rangle = 0$.

Although we have concentrated on the mesoscopic level of description, formulas (10) and (11) could, in principle, be applied to microscopic Hamiltonians. This, however, requires a microscopic definition of the field $\mathbf{s}(\mathbf{r})$. We proceed as follows. First the field $\mathbf{u}(\mathbf{r})$ is defined:

$$\mathbf{u}(\mathbf{r}) = \int d\widehat{\omega}\rho_s(\mathbf{r}, \widehat{\omega})\widehat{\omega} \,,$$ (32)

where $\rho_s(\mathbf{r}, \omega) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\omega - \omega_i)$ is the microscopic density distribution of the position $\mathbf{r}$ and orientation $\widehat{\omega}$ of the surfactant molecule. Next, to obtain $\mathbf{s}(\mathbf{r})$ we have to extract the curlless part of $\mathbf{u}(\mathbf{r})$. However, the microscopic $\mathbf{s}(\mathbf{r})$ obtained in this way cannot be automatically applied in Eqs. (6)–(11) to calculate $\overline{H}$ and $\overline{K}$ because all the field components and their derivatives are taken at the same point [see Eqs. (6) and (7)]. To avoid this difficulty we introduce a microscopic cutoff Λ in the Fourier representation of the δ function, i.e.,

$$\delta_\Lambda(\mathbf{r} - \mathbf{r}_i) = \frac{1}{(2\pi)^d}\int^\Lambda d\mathbf{k}\, e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}_i)}$$ (33)

hence

$$\mathbf{u}_\Lambda(\mathbf{r}) = \sum_i \delta_\Lambda(\mathbf{r} - \mathbf{r}_i)\omega_i \,.$$ (34)

Then $s_\|(\mathbf{k})$ is defined as the projection of $\widehat{\mathbf{u}}_\Lambda(\mathbf{k})$ onto the direction $\widehat{\mathbf{k}}$. We think that the microscopic expressions for $\overline{H}$ and $\overline{K}$ obtained from the procedure outlined above, could be used in Monte-Carlo simulations.

To summarize, we have proposed a statistical-mechanical generalization of the mean and Gaussian curvatures of the internal interface in oil-water-surfactant mixtures. In our approach no *a priori* assumption about formation of a surfactant monolayer separating oil from water is necessary. We only assume that the surfactant degrees of freedom are described by a curlless vector field $\mathbf{s}(\mathbf{r})$. The system is characterized by the average curvatures $\overline{H}$ and $\overline{K}$ and the process of averaging is both with respect to $\mathbf{s}$ and over the space. As a test we have calculated $\overline{H}$ and $\overline{K}$ for a few ordered phases using a Landau-Ginzburg model and compared their values with $\overline{H}_m$ and $\overline{K}_m$ obtained for a single mathematical surface $\langle\phi(\mathbf{r})\rangle = 0$. In all cases we have found qualitative agreement between the description based on $\overline{H}, \overline{K}$ and $\overline{H}_m, \overline{K}_m$. Moreover, the ratios $\overline{H}/\overline{H}_m$ and $\overline{K}/\overline{K}_m$ tend to unity for the structures with well-defined surfactant monolayers. For a diffuse interface these ratios are less than 1. In general, the absolute values of $\overline{H}$ and $\overline{K}$ are related to the strength of surfactant fluctuations. These fluctuations should be particularly important in the case of the microemulsion when $\langle\phi(\mathbf{r})\rangle = 0$ and $\langle\mathbf{s}(\mathbf{r})\rangle = 0$ in the whole space.

Even though the microemulsion is disordered, it does not mean that $\overline{H}$ and $\overline{K}$ vanish. If the symmetry between oil and water is assumed, $\overline{H} = 0$ but $\overline{K} \neq 0$. Because of the Gauss-Bonnet theorem $\overline{K}$ provides information about the topological structure of the microemulsion. Even in the case of a system close to the disorder line the description based on $\overline{H}$ and $\overline{K}$ can be useful. The standard description of the microemulsion using the concept of a mathematical surface defined by $\phi(\mathbf{r}) = 0$ is also possible and has been applied in Monte Carlo simulations [13]. However, it does not distinguish between sharp and diffuse interfaces, while our approach allows for a unified description of both sharp and diffuse interfaces, in ordered and disordered phases. It is worth noting that the same formalism can also be used in the case of a one order-parameter model [9]. Then one simply defines $\mathbf{s}(\mathbf{r}) = \nabla\phi(\mathbf{r})$.

In a future paper [12] we shall present studies of $\overline{H}$ and $\overline{K}$ in the microemulsion. In particular, it would be interesting to study the behavior of the average curvatures when the disorder line is approached from the Lifshitz line. It would be reasonable to expect that they eventually vanish when the mixture becomes homogeneous. However, we do not know at present how this could occur. We defer this problem to a future work.

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