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Landau model for self-assembly and liquid crystal formation in surfactant solutions

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A new universal approach to the description of the formation of supramolecular structures in surfactant solutions based on the Landau theory of phase transitions with coupled order parameters is proposed. It is shown that the specific interaction of amphiphiles with random inhomogeneities of a solvent (in water/oil/surfactant mixtures) may lead to a particular type of phase transition: formation of the locally inhomogeneous isotropic phase (microemulsion) or lyotropic liquid-crystalline phases. The topology of the phase diagram is discussed.

It is well-known that surfactant solutions display a great variety of exotic liquid-crystalline and isotropic phases which are of considerable scientific and practical interest [1]. However, in spite of the apparently endless flow of theoretical and experimental work on this subject, a universal approach, able to explain the entire succession of phase transitions in such a system, is still lacking. We introduce here a new semi-phenomenological approach, which, as we expect, will provide considerable progress towards a greater understanding of the processes of supramolecular structure formation in surfactant solutions. We start from the following definition. Let us distinguish between surfactant molecules from both, roughly-speaking, sphere-like molecules which form isotropic liquids, and rod-like molecules constituting thermotropic liquid crystalline phases. The presence of a small parameter $a/\xi \ll 1$ (where a is the thickness of an amphiphillic molecule, ξ is its length) relates these molecules to rod-like ones, but the hydrophobic tails and hydrophillic heads of surfactant molecules are not equivalent with respect to the solvent. This leads to the specific interaction of such molecules with density inhomogeneities, either induced by spontaneous fluctuations, or connected with interfaces (for example water–air or water–oil surfaces). Turning to the mathematical formulation of the model, we note that in order to account for the non-equivalence of the head and tail of a surfactant molecule, we can introduce a unit vector $\mathbf{p}_i$ corresponding to a molecule, which defines its orientation. Let us consider this vector as being directed from the hydrophobic tail to the polar head of the molecule. Taking a volume, which is small, as compared to the volume of the system, but containing a considerable number of surfactant molecules ΔN, we define the mean value of $\mathbf{p}_i$ by

$$\mathbf{p} \equiv \langle \mathbf{p}_i \rangle = (1/\Delta N) \sum_i \mathbf{p}_i.$$

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The idea of using the vector order parameter for the description of surfactant solutions was reported by us in [2] and independently by Chen *et al.* [3]. The difference between these two similar approaches will be discussed later.

For definitiveness we consider a ternary water/oil/surfactant system. We suggest the following form of the excess Gibbs free energy $\Delta\Phi$ which accounts for the appearance of density inhomogeneities

$$\Delta\Phi = \Delta\Phi_1 + \Delta\Phi_2 + \Delta\Phi_{\text{int}}, \tag{1}$$

$$\Delta\Phi_1 = (T/r_0^3)\int d\mathbf{r}[\tfrac{1}{2}\tau\varphi^2 + \tfrac{1}{6}v\varphi^3 + \tfrac{1}{24}\gamma\varphi^4 + \tfrac{1}{2}b_1 r_0^2(\nabla\varphi)^2 + \tfrac{1}{2}b_2 r_0^4(\nabla^2\varphi)^2], \tag{2}$$

$$\Delta\Phi_2 = (T/r_0^3)\int d\mathbf{r}\{f[c(\mathbf{r})] - f(c_0) - [\partial f(c_0)/\partial c_0][c(\mathbf{r}) - c_0]\}, \tag{3}$$

$$\Delta\Phi_{\text{int}} = (T/r_0^3)\int d\mathbf{r}\,c(\mathbf{r})[\tfrac{1}{2}A\mathbf{p}^2 + \lambda\xi\mathbf{p}\nabla\varphi + \tfrac{1}{2}\beta\xi^2\sum_j(\nabla p_j)^2] \tag{4}$$

and

$$f(c) = c\ln\frac{c}{e} + (1-c)\ln\frac{1-c}{e}. \tag{5}$$

Where $\Delta\Phi_1$ is the usual Landau expansion for the free energy of a fluid binary mixture near the critical consolute point together with a higher order gradient term (cf.[4]), $\Delta\Phi_2$ is that part of the free energy, related to deviations of the surfactant local concentration $c(\mathbf{r})$ from its mean value c_0, $\Delta\Phi_{\text{int}}$ is that part of the free energy associated with the interaction of the surfactant molecules with density inhomogeneities, $\tau = (T - T_c)/T_c$ is the deviation of temperature T from the critical temperature T_c, φ is the density difference between oil and water phases, r_0 is the average distance between molecules, which is much less than the length of an amphiphillic molecule ξ, p_j is the jth component of the vector $\mathbf{p}$; v, γ, b_1, b_2, A, λ, and β are system-dependent constants.

We can obtain the equilibrium distributions $c(\mathbf{r})$, $\mathbf{p}(\mathbf{r})$, and $\varphi(\mathbf{r})$ from the minimization conditions for the free energy $\Delta\Phi$

$$\delta\Delta\Phi/\delta c(\mathbf{r}) = 0, \tag{6}$$

$$\delta\Delta\Phi/\delta\mathbf{p}(\mathbf{r}) = 0 \tag{7}$$

and

$$\delta\Delta\Phi/\delta\varphi(\mathbf{r}) = 0. \tag{8}$$

The first of these equations leads to the relation

$$c(\mathbf{r}) = c_0\{c_0 + (1-c_0)\exp[E(\mathbf{p},\varphi)]\}^{-1}, \tag{9}$$

between the local concentration $c(\mathbf{r})$ and mean concentration c_0 where the function $E(\mathbf{p},\varphi)$ is defined by

$$E(\mathbf{p},\varphi) = \tfrac{1}{2}A\mathbf{p}^2 + \lambda\xi\mathbf{p}\nabla\varphi + \tfrac{1}{2}\beta\xi^2\sum_j(\nabla p_j)^2. \tag{10}$$

Equation (7) may be solved easily in momentum space and yields

$$\mathbf{p}(\mathbf{r}) = -i\lambda/(\beta\xi)\sum_{k}\mathbf{k}\varphi(\mathbf{k})[\kappa^2+k^2]^{-1}\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{11}$$

where $\mathbf{k}$ is the wavevector, and $\kappa=(A/\beta)^{1/2}\xi^{-1}$ is the inverse correlation length of fluctuations of the order parameter $\mathbf{p}$.

Incidentally, neglecting the term proportional to $\Sigma(\nabla p_j)^2$ in equation (4), we can solve equation (7) even in real space, and this yields $\mathbf{p} = -(\lambda\xi/A)\nabla\varphi$. Thus, the coupling $c(\frac{1}{2}A\mathbf{p}^2+\lambda\xi\mathbf{p}\nabla\varphi)$ reduces to the term $\alpha - c(\nabla\varphi)^2$. Such coupling, to our mind, is one of the main features of amphiphiles. In general, it seems plausible to use the interaction term of the form

$$cg(\nabla\varphi, \nabla^2\varphi, \nabla(\nabla^2\varphi), \ldots).$$

For instance, we can take $g=\lambda_1(\nabla\varphi)^2+\lambda_2(\nabla^2\varphi)^2+\lambda_3[\nabla(\nabla^2\varphi)]^2+\ldots$. We argue that this specific coupling of the surfactant concentration c with gradients of density of the dissolvent is responsible for the self-assembly processes in lyotropic systems.

Substituting the calculated values of $c(\mathbf{r})$ and $\mathbf{p}(\mathbf{r})$ (equation (9) and (11)) into equations (1)–(5), we obtain, in momentum space, up to the fourth order term

$$\Delta\Phi \simeq (TV/r_0^3)\Bigg[\sum_{k}\tfrac{1}{2}\chi(k)^{-1}\varphi(\mathbf{k})\varphi(-\mathbf{k})+\tfrac{1}{6}v\sum_{k_i}\varphi(\mathbf{k}_1)\varphi(\mathbf{k}_2)\varphi(\mathbf{k}_3)\delta_{k_1+k_2+k_3,0}$$
$$+\tfrac{1}{24}\sum_{k_i}\tilde{\gamma}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)\varphi(\mathbf{k}_1)\varphi(\mathbf{k}_2)\varphi(\mathbf{k}_3)\varphi(\mathbf{k}_4)\delta_{k_1+k_2+k_3+k_4,0}\Bigg] \tag{12}$$

where

$$\chi(k)^{-1}=\tau+b(k)r_0^2k^2+b_2r_0^4k^4, \tag{13}$$

$$b(k)=b_1-\lambda^2/(\beta r_0^2)c_0[\kappa^2+k^2]^{-1}, \tag{14}$$

$$\tilde{\gamma}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)=\gamma-(3\lambda^4c_0/\beta^2)F(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4), \tag{15}$$

$$F(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)=\frac{(\mathbf{k}_1\mathbf{k}_2)(\mathbf{k}_3\mathbf{k}_4)[\kappa^2+2k_2^2+\mathbf{k}_1\mathbf{k}_2][\kappa^2+2k_4^2+\mathbf{k}_3\mathbf{k}_4]}{(\kappa^2+k_1^2)(\kappa^2+k_2^2)(\kappa^2+k_3^2)(\kappa^2+k_4^2)}$$

$\chi(k)^{-1}$ is the inverse susceptibility with respect to the order parameter $\varphi(\mathbf{k})$, V is the volume of the system and δ is the Kronecker delta function.

Further we should, in principle, minimize the free energy with respect to $\varphi(\mathbf{r})$ in order to determine the actual structure of the mixture. Thus the construction of the phase diagram may be completed. However, this way appears to be too complicated even in momentum space. Instead, we apply the so-called direct variational method widely used in the physics of liquid crystals (see for example, [5]). By choosing the proper trial function we can compare the corresponding free energies for different phases. We must note, that the structure of expressions (12)–(15) for the excess free energy of the system differs both from the corresponding expressions for the case of the usual binary or ternary mixtures without surfactants and that of thermotropic liquid crystals. The main difference, induced by the chosen form of the interaction from equation (4), is hidden in the specific k dependence of the inverse susceptibility $\chi(k)^{-1}$ and the effective coupling constant $\tilde{\gamma}$. This difference leads to new physical effects, in particular, the formation of the isotropic microinhomogeneous phase is predicted. Besides, as in thermotropic liquid crystals [5], the usual succession of crystalline phases may be altered.

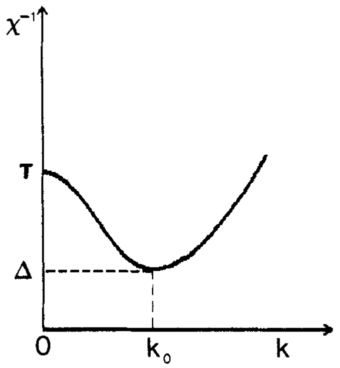

Figure 1. Inverse susceptibility of an oil/water/surfactant system.

Now, we turn to the k dependence of the inverse susceptibility (see figure 1). At small values of $c_0 (c_0 < c_0^*$, where $c_0^* = (Ab_1/\lambda^2)(r_0/\xi)^2)$ the presence of the surfactant does not lead to any change of phase structure. This case corresponds to the usual isotropic molecular solution. Incidentally, two variants are possible: $\tau > 0$ (one phase region) and $\tau < 0$ (two phase (water/oil) region). In the latter case all formulae given here remain unchanged with τ replaced by $\tilde{\tau} = \tau + \tilde{\varphi}^2 > 0$, where $\tilde{\varphi}$ is proportional to the equilibrium value of density difference between oil and water phases. When $c_0 > c_0^*$ a minimum in the k dependence of the inverse susceptibility at finite values of k appears: for such values of k, $b(k)$ becomes negative. It means that the formation of a locally inhomogeneous structure in the surfactant solution is preceded by passing through the so-called Lifshitz point where $b(k=0)=0$ [6]. Note, that $b(k) < 0$ for $0 < k < k^* = \varepsilon^{1/2}\kappa$, where $\varepsilon \equiv (c - c_0^*)/c_0^*$. Therefore the Lifshitz line is defined by the condition $\varepsilon = 0$.

First, let us consider the symmetric case when $v = 0$. In reality it corresponds to equal solubility of a surfactant in both oil and water as well as to an oil/water ratio close to unity. In this case the phase transition is second order and occurs when

$$\Delta = \chi(k_0)^{-1} = 0,$$

where k_0 corresponds to the minimum of the function $\chi(k)^{-1}$ (see figure 1):

$$k_0 \approx [(1+\varepsilon)^{1/2} - 1]^{1/2}\kappa. \tag{16}$$

We find

$$\Delta \simeq \tau - b_1 r_0^2 \kappa^2 [(1+\varepsilon)^{1/2} - 1]^2 = 0, \tag{17}$$

which defines the second order phase transition line $\tau_{tr}(\varepsilon)$ (see figure 2). This line separates the homogeneous isotropic one phase mixture from the locally inhomogeneous one ($k_0 > 0$). This phase can be either isotropic (bicontinuous symmetric microemulsion) or an anisotropic liquid crystal (lamellar, hexagonal, etc.). The Lifshitz line ($k_0 = 0$, $\varepsilon = 0$) separates the states, both one phase and two phase, with their different k dependence of the susceptibility. When $\varepsilon > 0$ the system tends to form a structure with selected values of k_0. For such values of k_0 $b(k)$ is always negative. We define the critical Lifshitz point as a point where $b(k=0) = 0$ and $\Delta = 0$. In this point the process of the formation of the supramolecular structure with $k_0 \rightarrow 0$ is accompanied by critical consolution (see review in [7]).

The line $\tau = 0$ describes the usual critical consolute points while $\varepsilon < 0$. When ε becomes positive the line of the critical consolute points no longer exists. At negative

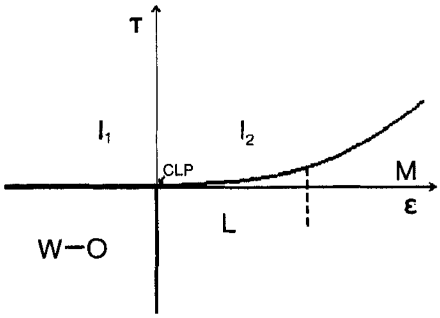

Figure 2. The phase diagram of an oil/water/surfactant system in the vicinity of the critical Lifshitz point. I_1 is the one phase molecular solution, I_2 is the molecular solution with a maximum at a non-zero wavevector in the structure factor (no stable inhomogeneities), W–O is the two phase region, M is the isotropic bicontinuous microemulsion, and L is the lamellar phase.

values of τ the Lifshitz line ($\varepsilon = 0, k_0 = 0$) coincides with the condition of the stability limit of the modulated phase

$$(\partial^2 \Delta\Phi / \partial k^2)_{k=k_0} = 0.$$

Thus it is a line of second order transitions between the two phase molecular solution and modulated (lamellar or bicontinuous) phase. The order parameter for this transition is k_0. If the modulated phase is lamelar, k_0^{-1} is the length of the spatial density wave.

The detailed structure of the new phase may be found with the help of the direct variational method. We have considered four possible trial functions $\varphi(\mathbf{r})$, corresponding to cubic (BCC), hexagonal, lamellar (or smectic A) and isotropic microemulsion structures

$$\varphi_{\mathrm{BCC}} = [\psi/12^{1/2}] \sum_{k_j} \exp(i\mathbf{k}_j\mathbf{r}), \quad j = 1, \ldots, 12, \tag{18}$$

$$\varphi_{\mathrm{HEX}} = [\psi/6^{1/2}] \sum_{k_j} \exp(i\mathbf{k}_j\mathbf{r}), \quad j = 1, \ldots, 6, \tag{19}$$

$$\varphi_{\mathrm{L}} = [\psi/2^{1/2}] \sum_{k_j} \exp(i\mathbf{k}_j\mathbf{r}), \quad j = 1, 2, \tag{20}$$

$$\varphi_{\mathrm{M}} = [\psi/N^{1/2}] \sum_{k_j} \exp[i\mathbf{k}_j\mathbf{r} + \vartheta(\mathbf{k}_j)], \quad j = 1, \ldots, N \tag{21}$$

where $\mathbf{k}_j$ are the basic wavevectors. Let us consider the definition of the trial function $\varphi_{\mathrm{M}}(\mathbf{r})$ for isotropic microemulsion (bicontinuous) phase introduced in equation (21). The phase variables $\vartheta(\mathbf{k}_j) = -\vartheta(-\mathbf{k}_j)$ have been chosen as random values within the interval from $-\pi$ to π. The distribution function is equal to $1/2\pi$. Next we assume that a set of the basic wavevectors $\mathbf{k}_j(|\mathbf{k}_j| = k_0, j = 1, \ldots, N \gg 1)$ has the following properties:

(i) vectors $\mathbf{k}_j$ are distributed uniformly in all momentum space directions,

(ii) there are no vectors $\mathbf{k}_{j_1}$, $\mathbf{k}_{j_2}$, $\mathbf{k}_{j_3}$, $\mathbf{k}_{j_4}$, which satisfy the condition $\mathbf{k}_{j_1} + \mathbf{k}_{j_2} + \mathbf{k}_{j_3} + \mathbf{k}_{j_4} = 0$ but simultaneously do not lie on the same plane.

The structure of the phase appears to be insensitive to the second assumption, however the latter leads to a considerable simplification of calculations.

It is easy to show that the mean value of the function $\varphi_M(\mathbf{r})$ is equal to zero, and the function $G(|\mathbf{R}|)$ defined by the relation

$$G(|\mathbf{R}|)=\langle\varphi_M(\mathbf{r})\varphi_M(\mathbf{r}+\mathbf{R})\rangle_V=(1/V)\int d\mathbf{r}\ \varphi_M(\mathbf{r})\varphi_M(\mathbf{r}+\mathbf{R})$$

can be calculated in the case when $N\to\infty$. We find

$$G(|\mathbf{R}|)=\psi^2\sin(k_0R)/(k_0R),$$

where

$$\psi=G(0)^{1/2}=(\langle\varphi_M^2\rangle_V)^{1/2}.$$

Since k_0^{-1} appears to be the only characteristic length in the isotropic system we expect that the function $\varphi_M(\mathbf{r})$ represents the isotropic microemulsion (bicontinuous) phase.

Substituting the functions (18)–(21) into the expression for the free energy (12) we obtain the following expressions for the effective coupling constants:

$$\gamma_L^*=(1/16)\gamma-(3/64)D\varepsilon^2,$$

$$\gamma_{HEX}^*=(5/48)\gamma-(3/64)D\varepsilon^2,$$

$$\gamma_{BCC}^*=(5/32)\gamma-(19/384)D\varepsilon^2,$$

$$\gamma_M^*=(1/8)\gamma-(1/12)D\varepsilon^2,$$

where

$$D=(\lambda^2b_1/\beta)\kappa^2r_0^2.$$

In order to compare the values of the free energy at the minima it is sufficient to compare the values of the effective coupling constants. We can see that among the four structures considered only two can be formed when $\varepsilon\ll 1$: lamellar and bicontinuous. Incidentally, the lamellar phase precedes the microemulsion if $0<\tau<(3/7)(\beta\gamma/\lambda^2)$; however the latter result is strongly connected with the choice of the trial function and cannot be regarded as general. The total phase diagram can be completed only by taking account of asymmetric terms in the free energy. In such a way, the dilute microemulsions and the actual succession of liquid-crystalline phases can be obtained; this will be the subject of a later publication. Here we note only one but non-trivial result. Accounting for the cubic term $v\varphi^3$ in the free energy (see equation (2)) we have found that at values of

$$\tau>\tau^*=(15/51)(\gamma\beta/\lambda^2)+(51/270)(v^2/\gamma),$$

$$\varepsilon>\varepsilon^*=(60\gamma/51Ab_1)^{1/2}(\beta/\lambda)(\xi/r_0)$$

a hexagonal crystalline phase precedes the BCC lattice. This result shows that the specific interaction between amphiphiles with density gradients may alter the conventional succession of crystalline phases in surfactant solutions.

Now we make a few comments concerning the relation between our model and that proposed by Chen *et al.* [3]. The phase, called a microemulsion in [3], is the homogeneous molecular solution with a maximum at the non-zero wave-vector in its structure factor. This phase corresponds to the region I_2 in our phase diagram (see figure 2) and differs from the usual molecular solution only in the fluctuations (there are no stable microemulsion droplets).

Taking into account the q dependence of the fourth coupling constant γ we have obtained the thermodynamically stable isotropic phase (M), which we call a bicontinuous microemulsion phase. There is no corresponding region in the phase diagram of [3]. Our phase diagram is analogous to that in thermotropic liquid crystals in the vicinity of a smectic C– smectic A– multicritical point [8]. In the vicinity of this point the nematic (less ordered) region is divided by the Lifshitz line into the two parts: region with A-type smectic fluctuations and a C-type one. In the region of the C-type smectic fluctuations the equilibrium value of smectic C order parameter is still zero just as in the region I_2 of our phase diagram the equilibrium value of $\varphi(k_0 \neq 0) = 0$.

In conclusion we would like to emphasize the main result of this work: the presence of a surfactant in a liquid mixture leads to a radical change of the phase diagram. The new isotropic but microinhomogeneous phase may become more preferable than any lyotropic liquid-crystalline phases.

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