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Modelling interactions in microemulsion phases

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Résumé. — Nous présentons dans cet article une description unifiée des interactions dans les phases liquide isotrope et cristal liquide de microémulsions. Un modèle microscopique est utilisé pour tenir compte des termes d'énergie entropique, de courbure et d'interaction et on discute la stabilité relative des phases isotrope (microémulsion), lamellaire et hexagonale.

Abstract. — In this paper we present a unified description of the interactions in liquid isotropic and liquid crystal phases of microemulsions. A microscopic model taking into account the entropic, bending and interaction free energies is used to deduce theoretical phase diagrams and the relative stability of the isotropic (microemulsion), lamellar and hexagonal phases is discussed.

The ability of surfactant in solution to aggregate is at the origin of the lyotropic liquid crystal phases [1]. The main structures formed in solution by surfactant are evidenced by the typical phase diagram given in figure 1. The phase termed L is a liquid isotropic phase of small, usually spherical, aggregates (micelles). The D phase is lamellar and consists of infinite double layers of surfactant separating layers of water. The E phase is hexagonal and consists of infinite cylinders of surfactant organized into a two-dimensional hexagonal lattice.

The complete understanding of the phase diagram of a pure surfactant in solution is a complicated problem. The structure of these phases is driven by the microscopic interactions and involves the so called hydrophobic effect [2]. The order of magnitude of the interaction energy per surfactant \( E = \gamma \Sigma \) (where \( \gamma \) is the oil-water interfacial tension and \( \Sigma \) the polar head area of the surfactant) is about \( 8 k_B T \) at room temperature, taking typical values \( \gamma \approx 50 \text{ dyne/cm} \) and \( \Sigma \approx 60 \text{ Å} \) (a reasonable value for a usual surfactant in the micellar phase). The fact that the energy \( E \) is larger than \( k_B T \) explains why a large part of the phase diagram is occupied by organized phases (lyotropic liquid crystal phases). Moreover, geometrical constraints such as the packing of the chains [3] are strong and their effect on the structure predominate [4].

In some interesting cases, using a special surfactant or a mixture of surfactants, these constraints may vanish [5]. The microemulsion phases correspond to

![Experimental phase diagram of sodium palmitate and water.](http://dx.doi.org/10.1051/jphys:019860047070125700)
this category. For these systems, two main properties allow some drastic modifications:

i) The interface between hydrophobic and hydrophilic microscopic regions is now saturated [5, 6] and the area per polar head $\Sigma$ can be considered as constant (this is not true for phases of pure surfactant in solution).

ii) The characteristic length scale related to the curvature of the interface (typically $100\ \text{Å}$ or more) is large compared with the molecular length.

These two properties imply that the surface tension between oil and water vanishes. Consequently, the relevant terms of the free energy are now of the order of $k_b T$. In addition, the curvature of the film can be described using an elastic energy.

The phase diagrams of these mixtures present isotropic and liquid crystalline phases [7]. The isotropic phase can be described in large regions of the phase diagram as phases of droplets of water (oil) in oil (water) surrounded by an uncompressible film of surfactant. These phases can be modelled using a simple fluid free energy. However the micellar shape and size must be considered as variable. Consequently, in addition to the entropic and interaction terms classically introduced for simple fluids, a curvature energy should be considered. Following this description, the lamellar and hexagonal phases correspond to a system of infinite disk-like or rod-like micelles and are modelled within the same theoretical framework.

In the following we present a simple description of a system of surfactant in solution in order to describe the competition between the micellar, lamellar and hexagonal phases. The effect of the interactions including short range attractive forces which are known to exist in microemulsion systems [7-9] will be discussed.

The presentation of interactions between aggregates of surfactant in solution is given in the first part. A unified description of the interactions in the micellar, lamellar and hexagonal phases is introduced in the second part. The microscopic model used to generate the theoretical phase diagrams is presented in the third part. A discussion of these phase diagrams is given in the last section.

1. General remarks on interactions in microemulsion phases.

Considering microemulsion systems, two situations lead to a description in terms of interacting particles in a continuous medium: they are obtained when a small amount of oil (water) is added to a surfactant in water (oil) solution.

When aggregates of ionic surfactant are in solution in water rich medium, the most important interactions are the long range electrostatic and short range Van der Waals (VDW) forces. These interactions are modelled by the well known DLVO theory [10] which satisfactorily describes micellar systems [11, 12]. The repulsive electrostatic forces are dominant but screened when salt is added. Then the resulting force can be attractive and may lead to a liquid-gas like phase transition [13]. A similar situation can be obtained with a nonionic surfactant [14].

The structure of oil rich microemulsions can be described as a system of droplets of water surrounded by a film of surfactant into an oil rich continuous phase. Interactions between these droplets are either attractive or repulsive [15]. When attractive and strong enough, these interactions lead to a liquid-liquid phase separation and to a critical point [16-18]. This attraction is the consequence of the overlapping between the surfactant films of the droplets and is short range [8, 9, 18, 19].

In summary, a system of both direct or inverted micelles is often described by taking into account short range attractive interactions.

Interactions in lyotropic liquid crystal phases have been less studied. VDW forces are generally required to explain their stability [5, 20]. Helfrich [21] has shown that undulations can lead to steric repulsions between membranes which are proportional to the inverse of the elastic modulus of curvature $K$. For classical lyotropic systems the interface is composed of surfactant, a typical value of $K$ is $10^{-12}\ \text{erg}$, and the resulting strengths of the steric and VDW forces are approximately the same. In microemulsions the interface is generally composed of surfactant and alcohol which leads to a smaller value of $K$ [5, 22, 23]. In this case the membrane undulation may generate the dominant energy. Moreover this mechanism brings into contact the interfaces of two neighbouring layers. By analogy with micellar and microemulsion systems one should assume that these contacts may generate attractive interactions. We will utilize this remark in the following sections to give a unified description of the interactions in the different phases considered.

2. Unified description of interactions and entropy in lyotropic phases of microemulsions.

We will describe in the following the interactions between aggregates in the three considered phases (i.e. isotropic liquid micellar, lamellar and hexagonal phases).

2.1 ISOTROPIC PHASE. — The entropic part of the free energy of interacting micelles is usually described as a system of hard spheres. The most realistic expression of the corresponding free energy $F_s$ as a function of the volumic fraction $\phi$ of the particles reads [24]:

$$
\frac{F_s}{V} = \frac{k_b T}{v} \left( \phi \ln \phi - \phi + \frac{\phi^2 (4 - 3 \phi)}{(1 - \phi)^2} \right)
$$

(1)

where $V$ and $v$ are the total volume of the system and the volume of a particle, respectively. $k_b$ is the
Boltzmann constant and $T$ is the absolute temperature.

The perturbative two-body interaction between particles can be introduced through an extra term $F_i$ which reads \cite{17}:

$$F_i = -\frac{k_b T}{v} A \phi^2$$  \hspace{1cm} (2)

where $A$ is the second virial coefficient written as a dimensionless constant which is directly related to the pair interaction potential. Following this definition, attractive interactions are described with a positive value of $A$.

Since we like to describe non-spherical objects, the free energies given above should be generalized. The second virial coefficient $A$ can account for interactions between anisotropic micelles and the generalization of $F_i$ is straightforward and will be given in part 3. The simplest way to modify $F_i$ is to introduce an effective volume for each rotating particle. For example a disk-like micelle with a radius $R$ and a thickness $t$ occupies an effective volume $v_{\text{eff}} = 4/3 \pi R^3$ rather than $v = \pi R t$. For a rod-like micelle with a radius $R$ and a length $L$ the effective volume will be $2 \pi L^2 R$. Taking this effect into account, the excess mixing entropy is modified and $F_i$ now reads:

$$F_i = \frac{k_b T}{v} \left( \phi \ln \phi - \phi + \phi \frac{\phi_{\text{eff}} (4 - 3 \phi_{\text{eff}})}{(1 - \phi_{\text{eff}})^2} \right)$$  \hspace{1cm} (3)

with $\phi_{\text{eff}} = \phi \cdot v_{\text{eff}} / v$.

Many more satisfactory methods exist to describe the packing entropy for concentrated anisotropic hard particles \cite{25, 26}. However, the crude approximation presented above is the simplest one and gives the right dependence of the second virial coefficient as a function of dissymmetry \cite{27}.

### 2.2 LAMELLAR PHASE.

The interaction between two undulating membranes was first established by Helfrich \cite{21} and generalized by Sornette and Ostrowsky \cite{28} to account for finite size effects. The expression for $\Delta f_i$, the loss of entropy per unit surface, for two membranes separated by an average distance $d$ is given by \cite{21}:

$$\Delta f_i = k_b T \cdot \frac{3 \pi^2}{128} \cdot (\frac{k_b T}{K}) \cdot \frac{1}{d^3}$$

where $K$ is the curvature elastic modulus.

Using this expression, the free energy per unit volume of a system of $N$ interacting lamellae reads:

$$\frac{F_i}{V} = k_b T \cdot \frac{3 \pi^2}{128} \cdot (\frac{k_b T}{K}) \cdot \frac{1}{d^3}$$

where $V = N \cdot d \cdot S$ is the total volume ($S$ is the surface area of a lamellar sheet).

Introducing the volume fraction of lamellae of thickness $d_0$: $\phi = d_0 / d$, $F_i$ reads:

$$\frac{F_i}{V} = k_b T \cdot \frac{3 \pi^2}{128} \cdot (\frac{k_b T}{K}) \cdot \frac{\phi^3}{d_0^3}.$$  \hspace{1cm} (4)

This free energy describes the loss of entropy due to contacts between neighbouring membranes. $k_b T$ is lost for each contact. This point of view can be extended in a crude way to describe the effect of a short range potential, resulting for example from the overlap between the aliphatic tails of the surfactant molecules.

To account for this interaction we introduce an energy $F_i$ describing a gain of $\beta k_b T$ per contact, thus:

$$F_i = -j F_s.$$  \hspace{1cm} (5)

### 2.3 HEXAGONAL PHASE.

The arguments developed above can also be used to describe the interactions between infinite cylinders in a hexagonal (or rectangular) phase (note that a phase of finite cylinders may also be described as a polymer-like structure \cite{29}; however we do not consider this possibility in the following). Considering a hexagonal structure, the expression of the steric repulsion between two cylinders is not available, and will be determined below \cite{30}.

Following Helfrich \cite{31}, the mean square of the displacement $u$ with respect to the equilibrium position of a cylinder of radius $R$ and of length $L$ is:

$$\langle u^2 \rangle = \frac{k_b T \cdot L^3}{48 \pi K R}$$

where $K$ has the same significance as above.

To compute the average number of contacts between two cylinders placed on a hexagonal lattice of unit cell $d$, we follow a technique similar to that introduced by Helfrich \cite{21} to describe interacting membranes. Consider first a cylinder of radius $R$ placed inside a nonpenetrable cylindrical cavity of radius $d$. The bending fluctuations of the rod are limited by $d$. Introducing $\langle u^2 \rangle = d^2$ in the preceding formula, $L$ should be identified with $l$, the mean distance between two contacts between the cylinder and the cavity, thus:

$$l = \left( 48 \pi R d^2 k_b T \right)^{1/3}.$$  \hspace{1cm} (6)

The mean number of contacts per unit length is simply equal to $1/l$. The corresponding loss of entropy per unit length (assuming a loss of $k_b T$ per contact) is:

$$\Delta f = k_b T \left( \frac{k_b T}{48 \pi K R d^2} \right)^{1/3}.$$  \hspace{1cm} (7)

If the cylinder is placed on a two dimensional hexagonal lattice, the occurrence of contacts with its six neighbours can be obtained from the above formula taking into account a geometrical multiplicative factor $G$, which is approximately equal to $6 R / \pi d$. 

1259

MODELLING INTERACTIONS IN LYOTROPIC PHASES
The free energy $G.\Delta f$ is equivalent to the energy density introduced in the preceding section for the lamellar phase and allows the determination of the entropic term in the hexagonal phase:

$$F_s = \frac{k_b T}{V} \cdot \frac{12}{\sqrt{3} \pi} \left( \frac{R^2 k_b T}{48 \pi K} \right)^{1/3} \cdot \frac{1}{d^{11/3}}$$

where $V = \sqrt{3/2} \cdot N \cdot L \cdot a^2$ is the total volume of the system ($L$ is the length of a cylinder). The volume fraction of cylinder $\phi$ is the ratio between the cross sectional area ($\pi R^2$ of the cylinder and the surface area ($\sqrt{3} \cdot a^2/2$ of the unit cell). Thus $\phi$ is simply related to $d$ through:

$$\phi = \frac{2 \pi R^2 \sqrt{3} \cdot d^2}{\sqrt{3} \pi a^2}.$$

Consequently:

$$F_s = \frac{k_b T}{V} \cdot \frac{12}{\sqrt{3} \pi} \left( \frac{R^2 k_b T}{48 \pi K} \right)^{1/3} \cdot \frac{\phi^{11/6}}{R^{11/3}}.$$

(6)

Following the same procedure as for the lamellar case, a short range interaction can be described with an extra term:

$$F_i = -jF_s.$$  

(7)


3.1 PHENOMENOLOGICAL EXPRESSION FOR THE BENDING ENERGY. — The writing of the total free energy of a system of $N$ monodisperse interacting micelles requires, in addition to the entropic and interaction terms described above, the introduction of the bending energy $F_b$. To give an explicit form to $F_b$, a microscopic model of particles should be introduced. Quite generally $F_b$ is given by:

$$F_b = N \int dS \cdot K(C - C_0)^2.$$

Here $C$ is the local curvature equal to $(1/R_1 + 1/R_2)$ ($R_1$, $R_2$ are the two principal radius of curvature), and $C_0$ is the optimum natural curvature of the interface. The sum is extended over the surface of each object. The resulting expression of $F_b$ for different realistic shapes has been computed by Turkевич et al. [32]. The saddle bending energy has not been introduced in our description since it requires the introduction of an extra parameter to essentially modify the relative stability of the hexagonal and lamellar phases [29].

In order to keep the effect of deformation without introducing complicated algebra, we model the deformed particles by parallelepipeds as shown in figure 2. The description of the objects with two different lengths is preserved by the introduction of $b \neq a$. Within this model we will assume that the curvature of a face $a.b$ is constant and given by:

$$C = (2/a + 2/b).$$

Thus, for a particle the bending energy $f_b$ reads:

$$f_b = \frac{K}{2} \cdot \left[ \left( \frac{2}{a} + \frac{2}{b} - \frac{4}{a_0} \right)^2 4ab + \left( \frac{4}{b} - \frac{4}{a_0} \right)^2 2b^2 \right].$$

(8)

where $a_0/2$ is the natural radius of curvature. As expected, the minimum of $f_b$ is realized when $a = b = a_0$. Moreover for an isotropic object ($a = b \neq a_0$), $f_b$ is proportional to the surface area ($\pi a^2$) of the object and to the square of the difference between the actual and optimum curvatures ($4/b - 4/a_0^2$).

For a system of $N$ particles, using the relation $N = 4/V$, the bending energy reads:

$$F_b = \frac{N \cdot K}{v} \cdot \left( \frac{2}{a} + \frac{2}{b} - \frac{4}{a_0} \right)^2 4ab + \left( \frac{4}{b} - \frac{4}{a_0} \right)^2 2b^2.$$

(9)

where $v = ab^2$ is the volume of a particle.

Since the above expression is valid whatever the value of $e = b/a$, the limits of (9) for $e = 0$ and $e = +\infty$ give the bending energy of an infinite cylinder and of an infinite lamella respectively.

3.2 GEOMETRICAL CONSTRAINT. — Experimentally, assuming that the area per surfactant $S$ is constant, the volume of surfactant $V_s$ fixes the total amount of interface $S$. This condition introduces a geometrical constraint which is easily expressed as a relation between $a$ and $b$.

$$S = \Sigma V_s/v_s = N(4ab + 2b^2).$$

where $v_s$ and $V_s$ are the molecular and total volume of surfactant respectively.

Introducing $x$ as the ratio between the volume fraction of objects and the volume fraction of surfactant:

$$x = \frac{Na b^2}{V_s} \quad \text{one obtains:} \quad \frac{2}{b} + \frac{1}{a} = \frac{1}{a_*}$$

Fig. 2. — Model for particles of different shapes rod-like ($b < a$); spherical ($b = a$); disk-like ($b > a$).
where $a^* = 2 \chi v_0 / \Sigma$ is a characteristic length typically of order 100 Å. Using the above relation $a$ and $b$ can be simply related to $e = b/a$ and $a^*$:

$$b = (2 + e) a^* \quad \text{and} \quad a = (2 + e) a^*/e. \quad (10)$$

### 3.3 Writing the Free Energies of the Different Phases.

The total free energy $F$ of the different phases is $F = F_1 + F_2 + F_3$. Considering the isotropic phase first, $F$ is obtained using relations (2), (3), (8) and (10) with $v = ab^2$, it reads:

$$F^i a^*^3 \over V k_b T V = \frac{e}{(e + 2)^3} A_1(\phi, e) + 16 \phi k A_2(\phi) \quad (11)$$

with $k = K/k_b T$ and:

$$A_1 = \phi \ln \phi - \phi + \frac{\phi \phi_{eff}(4 - 3 \phi_{eff})}{(1 - \phi_{eff})^2} - A \phi^2$$

$$A_2 = \frac{e^2 + 4 \phi + 1}{2(e + 2)^2} +$$

$$+ \frac{a^* x e^2 + 4(\alpha - 1) e + 2(2 \alpha - 1)}{(e + 2)^2}$$

with $\alpha = a^* / a_0$.

Using the model described above $v_{eff} \approx b^3$ for $b > a$ and $v_{eff} \approx a^* b$ for $b < a$. Thus $\phi_{eff} = \phi e$ for $b > a$ and $\phi/e$ for $b < a$. To link these two formulae continuously for $e = 1$ we choose the following:

$$\phi_{eff} = \phi(\alpha - 1 + 1/e).$$

In the case of spherical inverted micelles of microemulsions the interaction increases with the radius of the micelle [18]. A simple description is obtained by taking $A$ proportional to the surface of contact between two objects. Transposed to the model, $A$ becomes proportional to $a^*$:

$$A = j_0 a^2.$$

The free energy of the lamellar phase results from the addition of formulae (4), (5) and (9), taking their limit for $b = \infty$ and $v = ab^2$. Moreover, the free energy expression (11) must be minimized with respect to the additional variable $e = b/a$.

### 3.4 Conclusion.

The expressions given above for the three phases (isotropic lamellar and hexagonal) can be used to compute the phase diagrams. Although the simplifications made above may change the actual position of the phase transition lines, the competition between the entropy, interaction and bending energy is preserved. Consequently we think that our model is able to predict a realistic topology for the phase diagrams. Further sophistication of the model may include other structures induced by attractive interactions.

The calculation of phase diagrams for different values of the parameters will be given in the following section.

### 4. Determination of Phase Diagrams.

Expressions (11), (12) and (13) allow the comparison of the stability of the different phases for a given set of the parameters $(k, j_0, j, f, f', a)$. Moreover the free energy expression (11) must be minimized with respect to the additional variable $e = b/a$.

Analytical study of $F'(e)$ shows that this function presents either one or two minima which are solutions of the equation:

$$\phi = \phi(e - 1 + 1/e).$$

A numerical method (Newton technique) was used to determine the solutions of (14). When two minima $e_1$ and $e_2$ are found, the comparison of the corresponding values of $F'(e)$ gives the optimum shape $e_{opt}$.

For a set of parameters the optimum free energy $F(\phi)$ is determined for a given $\phi$ as the smallest value among $F'(\phi, e_{opt}), F'(\phi)$ and $F'(\phi)$. The resulting associated shape $e_{opt}$ is either $e_{opt} \to \infty$ or $0$.

If $F'(\phi)$ is monotonically, the resulting phase for a given value of $\phi$ is directly given by the value of $e_{opt}$.
Fig. 3. — Shape of the free energy $F(\phi)$ when a phase separation occurs. $\phi_1$ and $\phi_2$ are the limits of the two phase equilibrium domain.

When $F(\phi)$ is not monotonical, a phase separation occurs. Figure 3 illustrates this situation and shows the region where two phases are in equilibrium with the two volumic fractions $\phi_1$ and $\phi_2$.

The complete phase diagram can be explored with several two-dimensional cuts keeping constant four parameters. In the following we shall represent the phase diagram in $\alpha$, $\phi$ planes. Moreover we will assume that $\alpha$ takes the same value in two phases in equilibrium. Further sophistication of the model would be obtained considering a possible phase separation due to $\alpha$.

Since we like to discuss the role of interactions, we will present, after examples of phase diagrams without interactions, typical effects of either repulsive or attractive forces.

**Phase diagrams without interactions.**

In this special case only one parameter $k$ (in addition to $\alpha$) is required. $j_0$, $j'$, and $j''$ are equal to zero. Values of $\alpha$ ranging between 0 and 2 will be considered. For classical lyotropic systems $k$ is typically 2. Since we study microemulsion systems where $k$ is expected to be smaller, we will explore values of $k$ ranging between 0.1 and 10.

Figure 4 gives three phase diagrams for $k$ equal to 0.1, 0.2 and 1. The three expected phases are found: $L$ is the liquid phase and $D$ and $E$ are the lamellar and hexagonal ones respectively. In these cases the phase $L$ always corresponds to spherical objects ($e_{opt} = 1$). All the phase transitions are first order with phase separations. For large value of $k$ (greater than 0.4) the succession $L$, $E$, $D$ is observed as $\alpha$ decreases (see Fig. 4a) in agreement with the previous work of Safran [29]. For $\phi$ smaller than 0.5 (where the model is the most realistic), when $k$ decreases (Figs. 4b, 4c) the isotropic phase is stabilized to the prejudice of the liquid crystal phases. This behaviour is in agreement with the argument of De Gennes [5], who explains the microemulsion stability as resulting of a low value of $k$.

**Effect of interactions.**

The interactions can be introduced through the two parameters $j_0$ and $j$ related to the liquid and liquid crystal phases respectively. The determination of the relation between these two parameters requires a microscopic description of the forces. However, in the following we will consider these two parameters as independent except insofar as maintaining the same signs, i.e. to preserve their repulsive ($j_0 > 0$ and $j > 0$) or attractive ($j_0 < 0$ and $j < 0$) character. Moreover since the isotropic interaction is introduced as $j_0 \alpha^2$, the relative magnitude of isotropic and anisotropic interactions is given by the ratio $j_0 \alpha^2/j$. No extra terms are needed to describe repulsive interactions. On the contrary, positive values of $j'$ and $j''$ are required for attractive forces.

The main effect of repulsive forces on phase diagram is straightforward. Depending on the ratio $j_0/j$ either the liquid or liquid crystal phases are destabilised. In the latter case the competition between the bending energy (which for small values of $\alpha$ favors extreme deformations) and the interaction energy (which favors the liquid phase) leads to the appearance of a liquid phase of anisotropic objects $L_D$. Figure 5 gives an example of such a behaviour. Note that the phase $L_D$ is separated from the liquid phase of spherical objects $L$ by a first order phase separation. The obtained deformation is in this case disc-like with values of $e$ between 1.5 (for $\alpha \approx 0.19$) and 12 (for $\alpha \approx 0.14$).

The effect of attractive interactions can be discussed comparing figures 4 and 6. Considering first figure 6a (to be compared with 4b for which $k$ is also equal to 0.2), it is clear that the main effect of introducing a negative $j_0$ is the appearance of a liquid-liquid phase transition limited by a critical point $P_c$. For spherical objects ($e = 1$) the coordinates of $P_c$ are: $\phi_{cr} \approx 0.14$, $\alpha_c \approx \sqrt{10.4}/j$. Note that these values are independent of the curvature energy. Moreover the introduction of attractive interactions in the liquid crystal phases favours the occurrence of the $D$ phase for higher $\alpha$. The role of increasing the isotropic interactions is shown in figures 6b and 6c. As $j_0$ increases, $\alpha_c$ decreases (Fig. 6b) until the L-L domain meets the L-D one.
Fig. 5. — Theoretical phase diagram for : k = 1.0, j₀ = 1.0, j = 100.0, j' = j" = 0.0. Details are given in insert.

Fig. 6. — Theoretical phase diagrams for : (a) k = 0.2, j₀ = -100.0, j = -15.0, j' = j" = 50.0; (b) same as above but j₀ = -200.0; (c) same as above but j₀ = -300.0.

Fig. 7. — Theoretical phase diagrams for : (a) k = 1.0, j₀ = -150.0, j = -15.0, j' = j" = 50.0; (b) same as above but j₀ = -200.0.

Fig. 8. — Theoretical phase diagrams for : (a) k = 0.2, j₀ = -200.0, j = -20.0, j' = j" = 50.0; (b) k = 1.0, j₀ = -200.0, j = -27.0, j' = j" = 50.0.

(53). In this case the liquid domain L is separated into two parts L₁ and L₂. Moreover a three-phase equilibrium takes place instead of the critical point. The same sequence is found for higher values of k.

The same sequence is found for higher values of k. As an example, figure 7 shows the effect of j₀ when k = 1. In this case the L-L domain meets the L-E one. Another way to separate the L domain into L₁ and L₂ is to increase the attractive interactions in the liquid crystal phases without changing j₀. This effect is illustrated by figures 8a and 8b which should be compared to figures 6b and 7a respectively.

5. Concluding remarks.

The phase diagrams given in the preceding section show that our model is able to describe the competition between the liquid, lamellar and hexagonal phases. Due to the form of the bending energy, the liquid phase is generally composed of spherical objects. The disk or rod-like deformations remain marginal, in agreement with the previous work of Safran [33]. However non-spherical particles may exist when repulsive interactions in the liquid crystal phases are dominant. Such a situation might be found when unscreened electrostatic interactions remain.

The effect of the attractive interactions is mainly to induce a phase separation between two isotropic phases of micelles. This phase transition can lead to a separation of the isotropic phase region L into two domains L₁ and L₂. Moreover, attractive interactions in the lamellar phase stabilizes this phase for large values of \( \alpha \) (which is related to the spontaneous radius of curvature).

In summary we have proposed a unified description of the interactions in liquid and crystal liquid phases of microemulsions. This description was utilized to introduce a microscopic mean field model based on the competition between the bending and interaction...
energies. This model accounts for the topology of experimental phase diagrams of surfactant in solution. Other improvements are still possible. For example a better description of the liquid crystal phases would be realized including positional (smectic or columnar) or orientational (nematic) order parameters.

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[30] The calculation of the interactions between cylinders was made in collaboration with D. Sornette.