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Molecular segregation in lyotropic complex fluids: A phenomenological approach

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A phenomenological approach describing the formation of segregated lyotropic mesophases from the isotropic solution is proposed. It provides the order-parameter symmetries of the transitions to the main periodically ordered mesophases. The order-parameter amplitudes are shown to be periodic functions of the probabilities for the surfactant molecules to be in the segregated regions. It allows us to work out the phase diagrams associated with the isotropic to segregated states. These phase diagrams exhibit regions of stability for partially and fully segregated states, and for direct and inverted mesophases. [S1063-651X(99)06801-4]

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I. INTRODUCTION

In surfactant solutions, the amphiphilic molecules self-assemble reversibly into a variety of spatially organized structures [1]. These include one-dimensional (sheetlike), two-dimensional (cylindrical type), and three dimensionally ordered (e.g., cubic, tetragonal, etc.) mesophases, as well as spatially disordered (micellar solutions), short-range ordered (sponge phases), and orientationally ordered (nematic, cholesteric) phases. Several approaches have been used for describing the aggregation and segregation processes leading to the formation of lyotropic structures, considered from a different point of view: as an assembly of fluid films (continuum elasticity approach [2]) as random surfaces (string field theory [3]), as monomers and dimers on a lattice (microscopic lattice modeling [4]), as macroscopic objects (Landau-Ginzburg approach [5]), etc. Because of their intrinsic self-consistent character, and of the mathematical difficulty to solve in a general way the problem of segregation (ordering) from an isotropic disordered state, the preceding models generally assume a specific transition mechanism [6], or equivalently a given symmetry for the transition order parameter [7]. The aim of the present work is to provide a general framework for a phenomenological description of the transitions to segregated lyotropic states, starting from the isotropic solution, and taking into account only the ordering nature of the segregation mechanism.

The paper is organized as follows. In Sec. II we clarify the group-theoretical properties underlying the symmetry and thermodynamic features of the transitions between the isotropic solutions and one, two, or three dimensionally ordered lyotropic mesophases. In Sec. III we show that the amplitudes of the order-parameter components associated with a segregation mechanism are periodic functions of the relevant variables describing the corresponding ordering mechanism. This allows us to work out the phase diagrams in which the isotropic, partially, and fully segregated phases are inserted. In Sec. IV the role of the surface energy is stressed, and taken as a secondary (nonsymmetry breaking) mechanism which is coupled to the primary segregation order parameter. Finally, we summarize our results and conclude (Sec. V).

II. LANDAU THEORY OF SEGREGATION

Let us consider the general symmetry of an isotropic state, i.e., the extended Euclidean Group $\tilde{E}_3 = O(3)\times\mathfrak{R}^3$, where $O(3)$ is the full orthogonal group and $\mathfrak{R}^3$ is the three-dimensional group of continuous translations. The irreducible representations (IR's) of $\tilde{E}_3$ are spanned by the basis functions [8]

$$\Phi^{\pm m}_{\vec{k}_j}(\vec{r},\theta,\varphi)=e^{i\vec{k}_j\cdot\vec{r}}Y^l_m(\theta,\varphi), \tag{1}$$

where the $\vec{k}_j$ are the infinite set of wave vectors ending on a sphere of given radius $|\vec{k}_j|$ and transforming one into another by the symmetry operations of $O(3)$. The $Y^l_m(m=-l,\ldots,+l)$ are the spherical harmonic of order l. The infinite-dimensional IR's of $\tilde{E}_3$ are denoted D^{m,k_j}. For given m, two conjugated functions $\Phi^{\pm m}_{\pm\vec{k}_j}$ are needed to construct a real (physically irreducible) representation.

Let $\rho_0(\vec{r})=cte$ be the probability density of a given type of molecule in the isotropic state, and $\rho_S(\vec{r})$ the corresponding probability density in a segregated state. The increment $\delta\rho=\rho_S(\vec{r})-\rho_0(\vec{r})$ can be expanded on the $\Phi^{\pm m}_{\vec{k}_j}$:

$$\delta\rho(\vec{r})=\sum_{k_j}\eta^{m,\vec{k}_j}\Phi^{\pm m}_{\vec{k}_j}(\vec{r},\theta,\varphi). \tag{2}$$

The coefficients $\eta^{m,\vec{k}_j}$ define the components of the infinite-dimensional order parameter (OP) associated with the transitions between the isotropic and segregated states. Since a transition corresponds to an ordering mechanism, *the* η^{m,k_j} *necessarily transforms as the IR denoted* D^{0,k_j}, *i.e., they correspond to the set* $(\eta^{0,\vec{k}_j})$ [which will be denoted hereafter as $(\eta_{\vec{k}_j})$]. This property results from the following arguments: any IR of $\tilde{E}_3$ is constructed from a small IR (τ_1) associated

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with the invariance group of *one branch* (say, $\vec{k}_1$) of the star $\vec{k}_1^*$, which is $G_{\vec{k}_1}=\mathrm{SO}(2)$ [9]. Since the ''unit cell'' of the parent isotropic state is reduced to a single subunit (molecule or micelle) which is invariant under all the symmetry operations of $\tilde{E}_3$, τ_1 will necessarily coincide, for an ordering mechanism [10], with the identity IR (totally symmetric) of SO(2) corresponding to $m=0$.

D^{0,k_j} is spanned by the basis functions $\Phi^0_{\vec{k}_j}=Y^0_0 e^{i\vec{k}_j\cdot\vec{r}}$, where the arbitrarily oriented wave vectors $\vec{k}_j$ belong to the same star. It follows immediately that the nth-power invariants of the OP components $I_n(\eta_{\vec{k}_j})$ correspond to products of the basis functions determined by the conditions $\Sigma_{i=1}^{n}\vec{k}_i=0$. Therefore, the variational free-energy density $F(\eta_{\vec{k}j})$, associated with the transition from the isotropic state, will contain invariants of all powers n except the linear invariant $I_1(\eta_{\vec{k}_j})$, which has been implicitly excluded from Eq. (2) by assuming a lowering of symmetry when going from the isotropic to the segregated state. In particular, (one or two) cubic invariants will be present. Therefore the transition to the segregated state is necessarily first order, except eventually at an isolated point of the phase diagram (Landau point) where the coefficient of the single cubic invariant vanishes identically.

Depending on the number of nonvanishing independent $\vec{k}_j$, and on the respective equilibrium values of the $\eta_{\vec{k}_j}$, different segregated phases can be stabilized below the isotropic solution, whose symmetries correspond to subgroups G of $\tilde{E}_3$. Thus the lamellar phase of symmetry $(G=D_{\infty_h})$ is described by one pair of wave vectors $|\vec{k}_\pm|=\pm\pi/d$, where d is the period along the normal to the lamellas. The corresponding nonvanishing components of the order parameter fulfill the equilibrium condition $\eta_{\vec{k}_+}=\eta_{\vec{k}_-}=\eta_{\vec{k}}$, which yields the effective free-energy density

$$F_1(\eta_{\vec{k}})=a_1\eta^2_{\vec{k}}+a_2\eta^3_{\vec{k}}+a_3\eta^4_{\vec{k}}+\cdots. \tag{3}$$

Two-dimensional cylindrical mesophases require two pairs of wave vectors: $\pm\vec{k}_1$ and $\pm\vec{k}_2$ (with $|\vec{k}_1|=|\vec{k}_2|$). One gets hexagonal $(G=C_{6v})$, square $(G=C_{4v})$, or C-centered rectangular $(G=C_{2v})$ mesophases for, respectively, an angle γ between $\vec{k}_1$ and $\vec{k}_2$ of 120°, 90°, or an arbitrary angle. In such cases, $\eta_{\vec{k}_1}=\eta_{\vec{k}_2}$ and the free-energy density has the form given by Eq. (3). If $\eta_{\vec{k}_1}\neq\eta_{\vec{k}_2}$, primitive rectangular $(G=C_{2v})$, monoclinic $(G=C_S)$, or triclinic $(G=C_1)$ cylindrical phases are obtained. The corresponding effective free-energy density is therefore

$$F_2(\eta_{\vec{k}_1},\eta_{\vec{k}_2})=a_1(\eta^2_{\vec{k}_1}+\eta^2_{\vec{k}_2})+a_2(\eta^3_{\vec{k}_2}-3\eta^2_{\vec{k}_1}\eta_{\vec{k}_2})+a_3(\eta^2_{\vec{k}_1}+\eta^2_{\vec{k}_2})^2+\cdots. \tag{4}$$

TABLE I. Column (a), equilibrium values of the order-parameter components for the phases denoted I to VI. Column (b), nature of the corresponding phases.

(a)	(b)
I $\eta_{\vec{k}_1}=\eta_{\vec{k}_2}=\eta_{\vec{k}_3}=0$	Isotropic
II $\eta_{\vec{k}_1}\neq 0,\eta_{\vec{k}_2}=\eta_{\vec{k}_3}=0$	Lamellar
III$^\pm$ $\pm\eta_{\vec{k}_1}=\eta_{\vec{k}_2}=\eta_{\vec{k}_3}$	Cubic
IV$^\pm$ $\pm\eta_{\vec{k}_1},\eta_{\vec{k}_2}=\eta_{\vec{k}_3}$ $(\eta_{\vec{k}_1}>\eta_{\vec{k}_2})$	Tetragonal or rhombohedral
V $\eta_{\vec{k}_1},\eta_{\vec{k}_2}=\eta_{\vec{k}_3}$ $(\eta_{\vec{k}_2}>\eta_{\vec{k}_1})$	*C* orthorhombic
VI $\eta_{\vec{k}_1},\eta_{\vec{k}_2},\eta_{\vec{k}_3}$	*P* orthorhombic, monoclinic, or triclinic

Three-dimensional mesophases involve three pairs of independent k vectors $(\pm\vec{k}_1,\pm\vec{k}_2,\pm\vec{k}_3)$ for mesophases displaying a primitive lattice. Four pairs of wave vectors are needed for a face-centered lattice, whereas six pairs of independent wave vectors are required for describing a body-centered lattice. The equilibrium values of the corresponding six-, eight-, or twelve-component order parameters determine the actual symmetry of the segregated mesophases. When all the components are equal, one gets cubic phases, and the effective free-energy density has again the form given by Eq. (3). For unequal components of the order parameter, lower symmetry phases are stabilized. As an illustration, let us consider the variational free-energy density which is associated with three pairs of wave vectors:

$$F_3(\eta_{\vec{k}_1},\eta_{\vec{k}_2},\eta_{\vec{k}_3})=a_1(\eta^2_{\vec{k}_1}+\eta^2_{\vec{k}_1}+\eta^2_{\vec{k}_1})+a_2\eta_{\vec{k}_1}\eta_{\vec{k}_2}\eta_{\vec{k}_3}+a_3(\eta^4_{\vec{k}_1}+\eta^4_{\vec{k}_2}+\eta^4_{\vec{k}_3})+\cdots. \tag{5}$$

It may describe seven different segregated mesophases depending on the equilibrium values of the $\eta_{\vec{k}_i}$. Their symmetries are summarized in Table I, as well as the corresponding values of the order-parameter components $\eta_{\vec{k}_i}$. Figures 1(a) and 1(b) show the location of the phases in the space of the invariants $I_1=\eta^2_{\vec{k}_1}+\eta^2_{\vec{k}_2}+\eta^2_{\vec{k}_3}$, $I_2=\eta_{\vec{k}_1}\eta_{\vec{k}_2}\eta_{\vec{k}_3}$, and $I_3=\eta^4_{\vec{k}_1}+\eta^4_{\vec{k}_2}+\eta^4_{\vec{k}_3}$.

III. PARTIALLY AND FULLY SEGREGATED STATES DIRECT AND INVERTED MESOPHASES

The considerations developed in the preceding section provide a general framework for determining the order-parameter symmetries for the phase transitions from an isotropic solution to segregated mesophases. However, they are insufficient for describing a number of specific features of lyotropic mixtures, such as (i) the difference which has to be made between fully and partially segregated states corresponding, respectively, to a maximal and nonmaximal probability of the surfactant molecules to be in the segregated regions, i.e., in partially segregated mesophases such as bicontinuous mesophases the segregated and solvent regions are not fully separated; (ii) the existence of inverted (reverse) micellar phases, which display exchanged configurations with respect to the corresponding direct mesophases [1]. In this section we show that such properties can be included in our approach by taking into account the dependence on the relevant variational parameters of the amplitudes of the OP components $\eta_{\vec{k}_i}$.

Let us denote $\xi_{\vec{k}_i}$ the normalized probabilities for the surfactant molecules to be in the segregated regions, in the di-

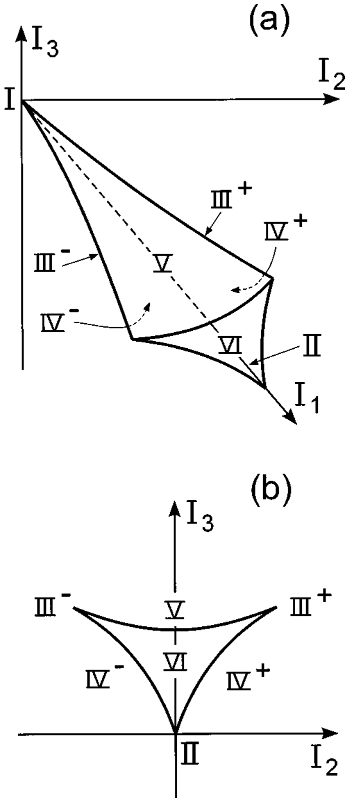

FIG. 1. Location of the phases corresponding to the order-parameter expansion defined by Eq. (5): (a) in the (I_1,I_2,I_3) space of the invariants; (b) in a cross section $I_1=cte$. The notation of the phases is given in Table I.

rections defined by the $\vec{k}_i$ vectors, and assume the OP components $\eta_{\vec{k}_i}$ to be functions of the $\xi_{\vec{k}_i}$ variables. The explicit forms of the $\eta_{\vec{k}_i}(\xi_{\vec{k}_i})$ functions for a given segregated phase can be obtained by minimizing, with respect to $\eta_{\vec{k}_i}$, the thermodynamic potential:

$$\int\left\{F[\eta_{\vec{k}_i}(\xi_{\vec{k}_i})]+\sum_{i=1}^{n} g_i(\nabla\eta_{\vec{k}_i})^2\right\}d^n\xi_{\vec{k}_i}, \tag{6}$$

where the integral is over a volume in the $\xi_{\vec{k}_i}$ space. F is the free-energy density and the Ginzburg g_i invariants account for the fluctuations of the $\eta_{\vec{k}_i}$ with respect to the $\xi_{\vec{k}_i}$. Let us first consider a transition to a lamellar phase. Using the effective OP expansion $F_1(\eta_{\vec{k}})$ given by Eq. (3) yields the equation of state

$$g\frac{d^2\eta_{\vec{k}}}{d\xi_{\vec{k}}^2}=a_1\eta_{\vec{k}}+\frac{3}{2}a_2\eta_{\vec{k}}^2+2a_3\eta_{\vec{k}}^3+\cdots. \tag{7}$$

When the right-hand expansion is restricted to the third power, Eq. (7) coincides with the general elliptic equation [11] which can be solved exactly [12]. More generally, the bifurcation from the solution $\eta_{\vec{k}}(0)=0$, which corresponds to the nonsegregated isotropic solution, to the solution $\eta_{\vec{k}}=\eta_{\vec{k}}(\xi_{\vec{k}})\neq 0$, corresponding to a partially or fully segregated state, can be obtained by linearizing Eq. (7) around the value $\eta_{\vec{k}}(0)=0$ [13]. One gets the second-order linear differential equation

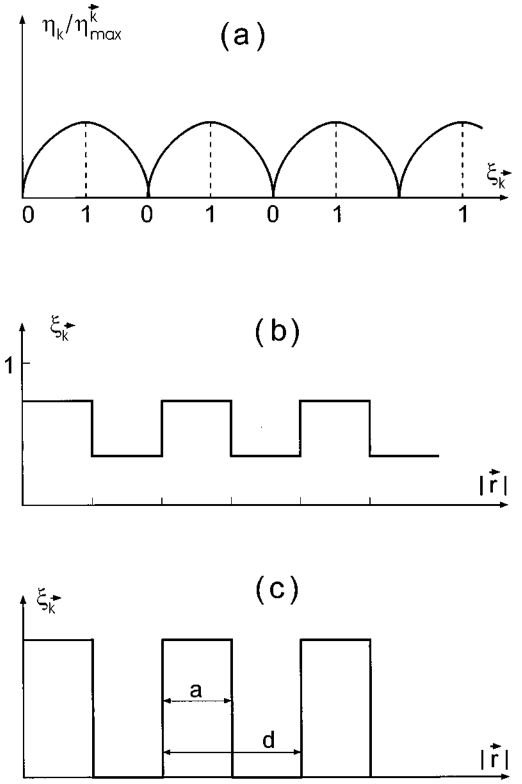

FIG. 2. (a) Periodic dependence of the order parameter $\eta_{\vec{k}}$ as a function of the $\xi_{\vec{k}}$ variable, as given by Eq. (9). (b) and (c) Normalized probability of surfactant molecules as a function of the space variable $|\vec{r}|$ in a partially segregated (b) or fully segregated (c) state. In (c), a and d are, respectively, the thickness of the lamellas and the period in the direction perpendicular to the lamellas.

$$g\frac{d^2\eta_{\vec{k}}^*}{d\xi_{\vec{k}}^2}=a_1^*\eta_{\vec{k}}^*, \tag{8}$$

where $\eta_{\vec{k}}^*$ is the eigenfunction corresponding to the eigenvalue a_1^* at which the solution $\eta_{\vec{k}}(\xi_{\vec{k}})\neq 0$ branches off the solution $\eta_{\vec{k}}(0)=0$. Taking into account the boundary conditions defining the initial isotropic state $[\eta_{\vec{k}}^*(0)=0]$ and fully segregated state $[\eta_{\vec{k}}^*(1)=1]$,one finds the asymptotically exact solution [13] in the vicinity of the point $a_1=a_1^*$, which is expressed as

$$\eta_{\vec{k}}(\xi_{\vec{k}})=\eta^{\vec{k}}_{\max}\left|\sin\frac{\pi}{2}\xi_{\vec{k}}\right|, \tag{9}$$

where the amplitude $\eta^{\vec{k}}_{\max}$ is to be determined by the nonlinear terms in Eq. (7), and depends on the coefficients g, $a_1-a_1^*,a_2,a_3,\ldots$. Figure 2(a) shows the periodic dependence of $\eta_{\vec{k}}/\eta^{\vec{k}}_{\max}$ on $\xi_{\vec{k}}$ in the direction $\vec{r}$ perpendicular to the lamellas, determined by $\vec{k}$ in reciprocal space. Thus, $\xi_{\vec{k}}$ is defined in successive intervals [0,1] and [1,0] in which $\eta_{\vec{k}}$ takes periodically values corresponding to partially $(0<\eta_{\vec{k}}<1)$ or fully $(\eta_{\vec{k}}=1)$ segregated states. Figures 2(b) and 2(c) represent the normalized probability of surfactant molecules as a function of the space variable $\vec{r}$ in a partially segregated [Fig. 2(b)] and fully segregated [Fig. 2(c)] state.

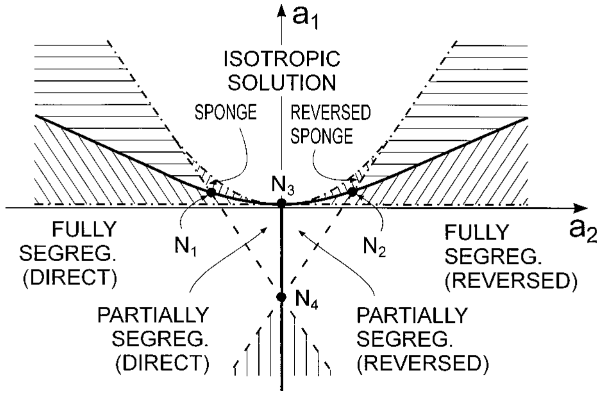

FIG. 3. Phase diagram associated with the equation of state (11). Full, dashed, and dashed-dotted lines are, respectively, first-order, second-order, and limit of stability lines. Hatched surfaces are regions of coexistence of the isotropic solution with the partially or fully segregated phases. N_1, N_2, and N_3 are three-phase points. N_4 is a four-phase point.

For the one-dimensional periodic lamellar phase, $\xi_{\vec{k}}$ can be written in the form of a Fourier series:

$$\xi_{\vec{k}}(\vec{r})=A_{\vec{k}}\sum_{j=1}^{\infty}\frac{\sin|j\pi\xi_0|}{j}\cos(j\vec{k}\cdot\vec{r}+\varphi_j), \tag{10}$$

which expresses the spatial distribution of molecules in the direction $\vec{r}$ defined by $\vec{k}$. ξ_0 is the average concentration of surfactant in the isotropic solution. The normalizing coefficient $A_{\vec{k}}$ is comprised between 0 and $2/\pi$.

Introducing the function $\eta_{\vec{k}}(\xi_{\vec{k}})$ given by Eq. (9) in the effective free-energy density $F_1(\eta_{\vec{k}})$, restricted to the fourth power in $\eta_{\vec{k}}$, one gets, by minimizing $F_1(\eta_{\vec{k}}(\xi_{\vec{k}}))$ with respect to the $\xi_{\vec{k}}$ variable, the equation of state

$$\eta_{\vec{k}}\frac{\partial\eta_{\vec{k}}}{\partial\xi_{\vec{k}}}\{2a_1+3a_2\eta_{\vec{k}}+4a_3\eta_{\vec{k}}^2\}=0. \tag{11}$$

In addition to the isotropic solution ($\eta_{\vec{k}}=0$ for $\xi_{\vec{k}}=0$), one obtains the fully segregated states for $|\cos(\pi/2)\,\xi|=0$, i.e., for $\xi_k^e=1$, and the partially segregated states for the equilibrium values of η_k:

$$\eta_k^e=\sin\frac{\pi}{2}\xi_k^e=-\frac{3a_2\pm\sqrt{9a_2^2-32a_1a_3}}{8a_3}. \tag{12}$$

Accordingly, in constrast to the fully segregated states which correspond to fixed limit values of ξ_k^e $(=1)$, the ξ_k^e values associated with partially segregated states vary with the phenomenological coefficients in $F_1(\eta_k)$, i.e., with temperature.

Figure 3 shows the phase diagram associated with the equation of state (11) assuming a_3 is a positive constant, and with the corresponding stability condition: $d^2F_1/d\xi_{\vec{k}}^2\geqslant 0$. Thus, the partially and fully segregated lamellar phases, which display identical symmetries $D_{\infty h}$, correspond to distinct regions of the phase diagram. These regions are separated by lines of *second-order topological transitions*, which are determined by the property that the probability $\xi_{\vec{k}}$ reaches its maximum value $\xi_{\vec{k}}=1$. The two, partially and fully segregated, lamellar phases can be reached from the isotropic solution across lines of first-order transitions which merge at two symmetric three-phase points N_1 and N_2. More generally, the phase diagram of Fig. 3 is symmetric with respect to the a_1 axis ($a_2=0$), or equivalently, with respect to the change in sign of $\eta_{\vec{k}}$: Each partially or fully segregated phase possesses a symmetric analog corresponding to an opposite sign for $\eta_{\vec{k}}$. Defining negative values of ξ_k as the normalized probability for solvent molecules to be in the segregated regions leads to the interpretation that two symmetric phases, with respect to the a_1 axis, in the phase diagram of Fig. 3 correspond, respectively, to a *direct* micellar phase ($\eta_{\vec{k}}>0$) and its *reversed* analog ($\eta_{\vec{k}}<0$).Figure 3 shows that the directed-reversed phase transition is first order, the corresponding first-order transition line being limited by a three-phase point N_3 and by a four-phase point N_4, at which partially and fully segregated, direct and reversed, mesophases merge. Note that when taking into account higher degree terms in F_1, the phase diagram of Fig. 3 becomes asymmetric with respect to the a_1 axis, but its essential features remain unchanged, i.e., the direct and reversed mesophases still correspond to left- and right-hand side regions of the phase diagram, although their locations become nonsymmetric with respect to the a_1 axis.

In the phase diagram of Fig. 3, there exists a region within the isotropic phase which is bounded by a line of first-order transitions and a metastability line. This region (denoted ''sponge'' in the figure) can be depicted as being formed by a system of locally ordered but randomly distributed domains, without long-range spatial correlation. This is reminiscent of the description proposed for sponge phases [14], which are locally anisotropic phases with no long-range order, and are bounded by the isotropic micellar solution and by ordered (e.g., lamellar) phases. Such an interpretation is consistent with the sensitivity of sponge phases to external perturbations, and with their flow birefringent property, which results from the local anisotropy. The current model of sponge phases [14] in terms of local bicontinuous (lamellar) domains actually corresponds to the metastability region located between the isotropic phase and the partially segregated lamellar phase. Figure 3 shows as well the existence of reverse sponge phases, which have been reported experimentally [15]. Note that the direct and reverse sponge phases meet only at the three-phase point N_3.

The preceding results also hold for two- and three-dimensional segregated mesophases for which the effective free-energy density reduces to $F_1(\eta_{\vec{k}})$, in the case where the probability $\xi_{\vec{k}}$ is the same for the different relevant directions $\vec{k}_i$, i.e., for hexagonal, square, or cubic lyotropic mesophases. By contrast, when the effective OP components $\eta_{\vec{k}_i}$ display different equilibrium values, or when the $\xi_{\vec{k}_i}$ variables are independent, Eqs. (7)–(10) have to be generalized. For example, let us consider the case of a primitive rectangular, cylindrical mesophase associated with two effective components $\eta_{\vec{k}_1}\neq\eta_{\vec{k}_2}$, which are functions of the two independent variables $\xi_{\vec{k}_1}$ and $\xi_{\vec{k}_2}$. Using the form F_2 of the free-energy density given by Eq. (4), the minimization of the thermodynamic potential (6) yields two equations of state:

$$g_i\,\Delta\eta_{\vec{k}_i}=\frac{\partial F_2}{\partial\eta_{\vec{k}_i}}\quad (i=1,2), \tag{13}$$

where the Laplacian takes the form

$$\Delta\eta_{\vec{k}_i}=\frac{\partial^2\eta_{\vec{k}_i}}{\partial\xi^2_{\vec{k}_1}}+\frac{\partial^2\eta_{\vec{k}_i}}{\partial\xi^2_{\vec{k}_2}}\quad (i=1,2). \tag{14}$$

The linearization of Eq. (13) around the equilibrium values of the $\eta_{\vec{k}_i}$ in the isotropic solution $[\eta_{\vec{k}_1}(0,0)=\eta_{\vec{k}_2}(0,0)]$ leads to Schrödinger-type equations:

$$\Delta\eta^*_{\vec{k}_i}=\frac{a_1^*}{g_i}\,\eta^*_{\vec{k}_i}\quad (i=1,2), \tag{15}$$

which, in the segregated state, possess asymptotically exact solutions of the form

$$\eta_{\vec{k}_i}=\eta_{\max}^{\vec{k}_i} fi(\xi_{\vec{k}_1},\xi_{\vec{k}_2})\quad (i=1,2), \tag{16}$$

where the $fi(\xi_{\vec{k}_1},\xi_{\vec{k}_2})$ are periodic functions which can be determined explicitly, taking into account the boundary conditions and the actual periodicities of the rectangular phase. As in the one-dimensional case, one obtains fully segregated states under the conditions

$$\frac{\partial\eta_{\vec{k}_i}}{\partial\xi_{\vec{k}_1}}=\frac{\partial\eta_{\vec{k}_i}}{\partial\xi_{\vec{k}_2}}=0\quad (i=1,2). \tag{17}$$

Partially segregated states correspond to the equilibrium values of the $\eta_{\vec{k}_i}$ given by the equations of state

$$\frac{\partial F}{\partial\eta_{\vec{k}_i}}=0\quad (i=1,2) \tag{18}$$

but may also be realized if one of the conditions (17) is not fulfilled. Figure 4 shows the general topology of the phase diagram associated with the free-energy density $F_2(\eta_{\vec{k}_1},\eta_{\vec{k}_2})$, restricted to the fourth powers in $\eta_{\vec{k}_1}$ and $\eta_{\vec{k}_2}$, and satisfying the equations of states (17), (18), and the corresponding stability conditions. It contains three partially segregated phases denoted I$(0<\eta_{\vec{k}_1}<1,\eta_{\vec{k}_2}=0)$, II$(\eta_{\vec{k}_1}=1,0<\eta_{\vec{k}_2}<1)$ and III$(0<\eta_{\vec{k}_1}\neq\eta_{\vec{k}_2}<1)$, their fully segregated limit phases $\mathrm{I}_{\mathrm{lim}}(\eta_{\vec{k}_1}=1,\eta_{\vec{k}_2}=0)$ and $\mathrm{II}_{\mathrm{lim}}(\eta_{\vec{k}_1}=\eta_{\vec{k}_2}=1)$ and the corresponding reverse analogs I_R, II_R, III_R, $\mathrm{I}^R_{\mathrm{lim}}$, $\mathrm{II}^R_{\mathrm{lim}}$. It also contains the sponge (S) and reverse sponge (SR) phases as well as three-phase points (N_1,N_2,N_5,N_6), four-phase points (N_3,N_4), a five-phase point (L_1) and a six-phase point (L_2). The direct-to-reverse phase transitions III-III_R and $\mathrm{II}_{\mathrm{lim}}$-$\mathrm{II}^R_{\mathrm{lim}}$ are first order, whereas phases I and I_R, II and II_R, or S and SR can only meet at one point in the phase diagram. Note again that the exact symmetry of the phase diagram with respect to the a_1 axis is lost when taking into account high degree terms in $F_2(\eta_{\vec{k}_1},\eta_{\vec{k}_2})$.

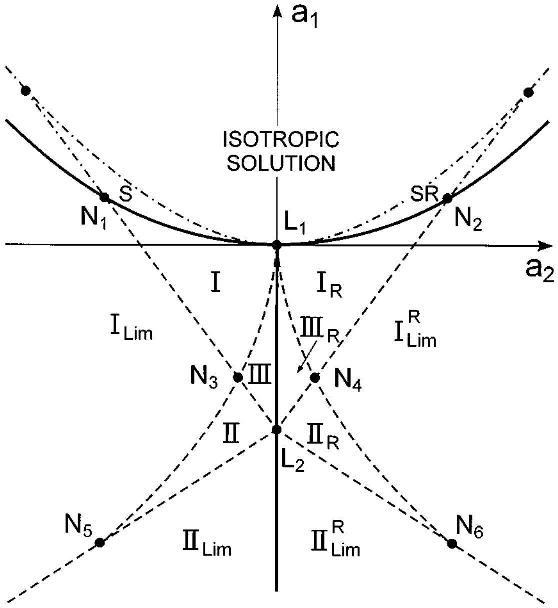

FIG. 4. Phase diagram associated with the free-energy density given by Eq. (4), and the equations of state (17) and (18). The lines have the same meaning as in Fig. 3. The notation of the phases and N-phase points is given in the text.

IV. THE SURFACE ENERGY IN THE SEGREGATION MECHANISM

For a full description of the mechanism leading to the formation of segregated lyotropic mesophases, one has to take into account the elastic surface energy, which determines the actual shape of the interfaces between the molecular aggregates and the solvent. Starting from a molecular solution one obtains the various types of micellar shapes and topologies using the Helfrich current approach [2,16]. In this approach the primary mechanism for the formation of micelles within an isotropic solution is described by a two-component order-parameter (C_1,C_2), where C_1 and C_2 are the principal curvatures [2,16]. For transitions to periodically ordered lyotropic states, (C_1,C_2) can be used as a *secondary* order parameter, which couples to the primary ordering order parameter $(\eta_{\vec{k}_i})$. Two main different types of couplings can be found.

(i) For a transition to a one dimensionally ordered segregated state (lamellar), one finds a biquadratic coupling which yields the total free-energy density:

$$F[\eta_{\vec{k}}(\xi_{\vec{k}}),J]=F_1(\eta_{\vec{k}}(\xi_{\vec{k}}))+\frac{K}{2}J^2+\frac{\delta}{2}\eta^2_{\vec{k}}J^2, \tag{19}$$

where $F_1[\eta_k(\xi_k)]$ is given by Eq. (3) and Eq. (9). $J=C_1+C_2$ is the total curvature of a symmetric bilayer (which has to be replaced by $J-J_0$ in the case of a spontaneously curved bilayer [16], J_0 being the spontaneous curvature). Minimization of F with respect to J gives a zero spontaneous equilibrium value for J in the segregated state, i.e., it corresponds to the flat surfaces of the lamellas $(C_1=C_2=0)$.

(ii) For two and three dimensionally ordered mesophases, assuming a single effective order-parameter component $\eta_{\vec{k}}$, one has a total free-energy density of the form

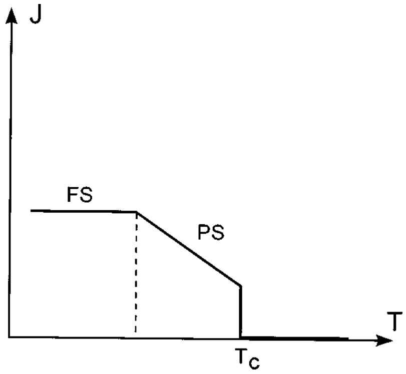

FIG. 5. Temperature dependence of the total curvature J induced by a segregation mechanism, as deduced from Eq. (21), when going across partially segregated (PS) and fully segregated (FS) phases.

$$F[\eta_k(\xi_k),J]=F_1[\eta_k(\xi_k)]+\frac{K}{2}J^2+\frac{\delta}{2}\eta_k^2J \qquad (20)$$

which contains a linear-quadratic coupling invariant. The *induced* equilibrium value of J in the segregated phase is

$$J=-\frac{\delta}{K}\eta_k^2(\xi_k). \qquad (21)$$

Since J varies as the square of the effective order parameter, the temperature dependence of J will display two different regimes, which are represented in Fig. 5. After increasing almost linearly within the partially segregated state, J reaches a constant saturated value in the fully segregated states. A more complex variety of behaviors can be found when more than one effective order-parameter component has to be taken into account in the segregation mechanism, or when higher degree invariants in J are considered in Eqs. (19) and (20).

V. SUMMARY AND CONCLUSIVE REMARKS

In summary, the present paper provides a framework for a phenomenological approach to the phase transitions which take place between the isotropic solutions and the various types of lyotropic mesophases. The following results have been obtained.

(i) The OP symmetries associated with the onset of one, two, and three-dimensional ordered mesophases have been worked out. They involve a finite number of OP components $\eta_{\vec{k}i}$, transforming as the IR $D^{0,ki}$ of the extended Euclidean group, from which one can deduce the form of the free-energy density associated with the transition.

(ii) Taking as variational parameters for the segregation-ordering mechanism the probabilities $\xi_{\vec{k}_i}$ for the surfactant molecules to be in the segregated regions, in the directions defined by $\vec{k}_i$, it has been shown that $\eta_{\vec{k}_i}$ can always be written as periodic functions of $\xi_{\vec{k}_i}$. Consequently, one obtains fully segregated phases as limit states (for $\xi_{\vec{k}_i}=1$) to the partially segregated phases ($0\leqslant\xi_{\vec{k}_i}<1$), and reverse phases as anti-isostructural states ($\eta_{\vec{k}_i}<0$) with respect to their direct analogs ($\eta_{\vec{k}_i}>0$). These results are reminiscent of the similar properties shown for displacive reconstructive transformations in crystals [17]. It suggests that despite its weakly first-order character, the transition from the isotropic solution to a segregated periodic phase is of the reconstructive type.

(iii) In the segregation mechanism, the surface energy plays the role of a secondary order parameter. The resulting induced curvatures may vary with temperature in the partially segregated states, reaching a limit constant value in the fully segregated states.

A number of general results concerning the topology of the phase diagrams of lyotropic systems can also be inferred from the preceding approach. Thus for a given order-parameter symmetry, only definite ordered mesophases may appear below the isotropic solution. For example, in the phase diagram of Fig. 1 only cubic ($\mathrm{III}^{\pm}$) and lamellar (II) phases can be reached directly from the isotropic solution (I) across a line of transitions. On the other hand, the phase diagram of Fig. 3 reveals that the region in which the sponge phase should be found is located between the isotropic phase and the adjacent partially segregated phase.

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