

Theory of the lamellar-hexagonal transformation: Tilted mesophases in lyotropic systems

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A phenomenological model of the lamellar-hexagonal transformation in lyotropic systems is described. A classification is given of the mesophase symmetries that may arise in the transformation process. The approach is shown to apply in an analogous but different way to the transformation between tilted mesophases. [S1063-651X(97)13211-1]

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Two-dimensional (2D) hexagonal mesophases are often found in the phase diagrams of complex fluid systems. In lyotropic mixtures [1], one of the most common mesophase configurations is that of the “middle soap” phase (labeled E in Ekwall’s notation [2]), which consists of parallel amphiphilic rods in hexagonal array, composed of radially disposed molecules of amphiphiles, with the hydrocarbon parts directed inwards and the hydrated polar groups facing outwards. In the phase diagrams of many ternary systems [2] the E phase is found with the hexagonal F phase, which is composed by aggregates of the inverted type having outwards hydrocarbon chains and inwards polar groups: The E and F phases occupy generally a region of the phase diagram located around a concentration $c = 1/2$ of surfactant in water, at low and high concentrations of cosurfactant, respectively [2]. Other mesophases displaying hexagonal lattices have been identified in lyotropics, such as the “complex” hexagonal phase (H_c)³, or the rhombohedral ($R3m$) phase, in which the planar hexagonal networks of short rods are stacked regularly in a three-dimensional lattice [4].

The most general sequence of phases in which the 2D hexagonal structures appear usually involves the lamellar mesophase from which the E and F phases are separated either by a two-region phase, i.e., by a first-order reconstructive transition, or by intermediate mesophases (e.g., rectangular, monoclinic, cubic, etc.). The first aim of this article is to give a phenomenological description of the lamellar-hexagonal transformation, and of the possible types of related intermediate mesophases. The model, which has been recently introduced in the case of the lamellar tetragonal transformation [5], makes use of a single symmetry breaking mechanism, consisting in the undulation of the interfaces between the molecular aggregates and the solvent. Another motivation of the present work is to show that when assuming oriented interfaces, the model provides a basis for the description of the various types of tilted mesophases that have been found in lyotropic systems [6], namely, the “ripple” ($P_{\beta'}$) and lamellar hexatic ($L_{\beta'}$) phases found, for example, in lecithin [7].

Figure 1(a) shows a two-dimensional view of one of the sequences of mesophases assumed in our approach. It de-

composes the successive steps of the transformation between the lamellar (L) and hexagonal (H) phases in the plane perpendicular to the lamellae. One can see that the reorganization of the mesophases results from a periodic undulation of the interfaces separating the molecular aggregates and the solvent. Such a type of periodic distortion has been currently reported for lamellar phases when varying the concentration of surfactant and the temperature [8]. Thus, the L - H transformation takes place across two types [undulated lamellar (\tilde{L}) and rectangular (R)] of intermediate phases, which are separated by a topological transition.

Restricting ourselves to a 2D description [5] of the sequence of Fig. 1(a), the minimal space group that contains the symmetry operations associated with the mesophases is $G_0 = C_{6v} \times \mathbb{R}^2$, where C_{6v} is the hexagonal point group and \mathbb{R}^2 denotes the continuous translations in the (x, y) plane. G_0 will be taken as the parent symmetry in our model, and is not *a priori* associated with a concrete structure. In order to formalize the transformation process represented in Fig. 1(a), one can take each equilibrium state as formed by an assembly of two types of regions, denoted M and W , separated by the interfaces, and corresponding respectively to the molecular aggregates and to the solvent. The equation of the interfaces can be written as $\psi(x, y) = 0$, where the ψ function is assumed to be positive in the M region and negative in the W region. Since all the phases are periodic, with at least one of the hexagonal translations $Z_x = (a, 0)$ and $Z_y = (0, a)$ [Fig. 1(b)], $\psi(x, y)$ can be developed in Fourier series:

$$\psi(x, y) = \sum_{(n,p)=-\infty}^{+\infty} \psi_{np} e^{(2i\pi/a)(nx+py)}, \quad (1)$$

where n and p are integers. The coefficients of the first harmonics of this series are ψ_{01} , Ψ_{10} , ψ_{1-1} . Together with their complex conjugate ($\psi_{01}^* = \psi_{-01}$, $\Psi_{10}^* = \Psi_{-10}$, $\psi_{1-1}^* = \psi_{-11}$) they form the basis of a six-dimensional irreducible representation (IR) of G_0 , denoted Γ^+ hereafter. Γ^+ is associated with the wave vector $\mathbf{k}_1 = (2\pi/a, 0)$, whose star \mathbf{k}_1^* has six branches [9] ($\pm \mathbf{k}_1, \pm \mathbf{k}_2, \pm \mathbf{k}_3$) shown in Fig. 1(b). The corresponding little group [9] $G_{k1} = C_s = \{C_1, \sigma_y\}$ possesses two one-dimensional IR’s τ^+ and τ^- . Γ^+ is constructed from the identity IR τ^+ .

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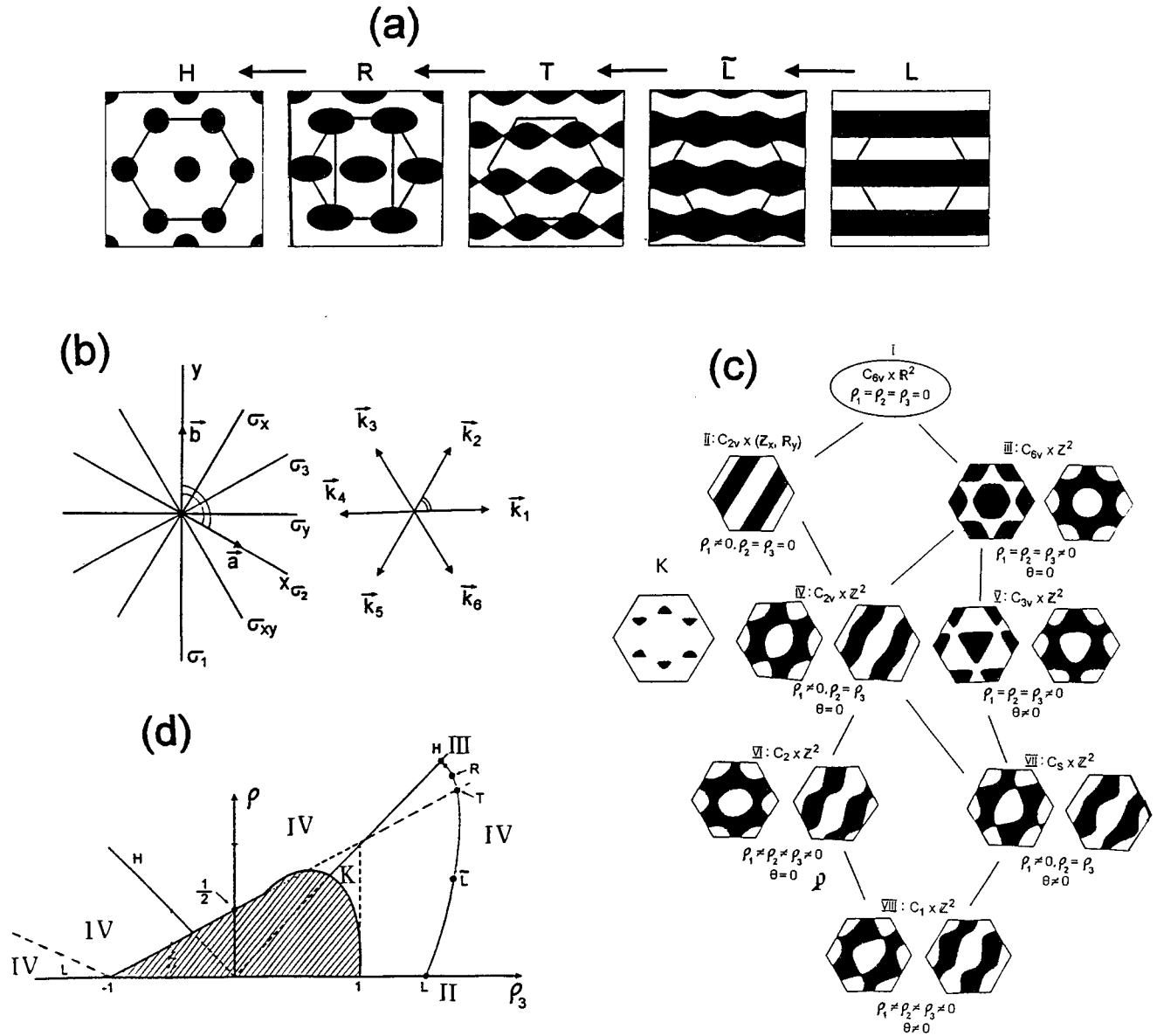


FIG. 1. (a) Sequence of phases involving the lamellar (L), undulated lamellar (\tilde{L}), rectangular (R), and hexagonal (H) mesophases. T represents a topological transition. (b) Orientation of the hexagonal axes and planes with respect to the wave vectors \vec{k}_i forming the branches of the star \vec{k}_1^* . (c) Classification of the mesophases corresponding to the minima of $F(\rho_i, \theta)$. The figures represent one or two among the possible configurations of the phases. Above and below each figure the corresponding symmetry groups and equilibrium values of the order-parameter components are given. (d) Configuration of the order-parameter space ϵ assuming the conditions $\rho_1 = \rho_2 = \rho$ and $\theta = 0$. The hatched area represents a region of nonphysical states. The dashed line corresponds to topological transition states.

One can write $\psi_{10} = \rho_1 e^{i\theta_1}$, $\psi_{01} = \rho_2 e^{i\theta_2}$, and $\psi_{-1} = \rho_3 e^{i\theta_3}$. Since G_0 is a group depending on two continuous parameters (R_x, R_y), two among the phases θ_i , say θ_1 and θ_2 , are Goldstone variables, i.e., their shift does not modify the geometry of the phases but only displaces them globally in space. Hence one has four effective order-parameter components ρ_1, ρ_2, ρ_3 and $\theta = \theta_1 - \theta_2 + \theta_3$. With this notation our model can be described in two successive steps.

(1) A Landau-type approach that makes use of the transformation properties of the order-parameter components by G_0 . One can construct four independent invariants [9]: $I_1 = \rho_1^2 + \rho_2^2 + \rho_3^2$, $I_2 = \rho_1^4 + \rho_2^4 + \rho_3^4$, $I_3 = \rho_1^2 \rho_2^2 \rho_3^2$, and

$I_4 = \rho_1 \rho_2 \rho_3 \cos \theta$. The corresponding order-parameter expansion has the general form

$$F(\rho_i, \theta) = a_1 I_1 + a_2 I_1^2 + \dots + b_1 I_2 + b_2 I_2^2 + \dots + c_1 I_3 + \dots + d_1 I_4 + d_2 I_4^2 + \dots + e_{12} I_1 I_2 + e_{13} I_1 I_3 + e_{14} I_1 I_4 + \dots \quad (2)$$

Minimization of F with respect to the ρ_i and θ yields at the utmost seven possible stable states. The symmetries and configurations of the corresponding mesophases are summarized in Fig. 1(c). Therefore, in addition to the L, H, \tilde{L} , and R

phases one gets four other stable mesophases (rhombohedral and monoclinic) corresponding to subgroups of the L and H symmetries. Note that two different configurations (cylindrical or lamellar) can be proposed for some of the phases, and that the R and \tilde{L} phases correspond to the same symmetry and equilibrium conditions. Note also that an additional micellar configuration having a Kagomé lattice [denoted K in Fig. 1(c)] can be proposed for phase IV.

(2) The possibility of describing topological transitions between lamellar and cylindrical states cannot be derived from a minimization of expansion (2), but is made possible when taking into account the equation expressing the periodic undulation of the interfaces. Keeping only the first harmonics in Eq. (1), and assuming $\theta_1 = \theta_2 = 0$, $\theta = \theta_3$, the equation of the interfaces is

$$\psi(x,y) = \psi_{00} \left\{ \eta_1 \cos\left(\frac{2\pi x}{a}\right) + \eta_2 \cos\left(\frac{2\pi y}{a}\right) + \eta_3 \cos\left[\frac{2\pi}{a}(x-y) + \theta\right] + 1 \right\} = 0, \quad (3)$$

where $\eta_i = \rho_i / \psi_{00}$ ($i = 1-3$). Introducing in Eq. (3) the equilibrium values of the ρ_i and θ for each phase, and using the condition that $\psi > 0$ for the M region and $\psi < 0$ for the W region, one finds the distribution of phases shown in Fig. 1(d) in the order-parameter space $\varepsilon = (\rho_1, \rho_2, \rho_3, \theta)$, in which it has been assumed $\rho_1 = \rho_2 = \rho$ and $\theta = 0$. One can see that the L and H phases occupy respectively the ρ_3 axis and the diagonals ($\rho = \rho_3$) of the ε space, whereas the \tilde{L} and R phases are separated by a topological transition line of equation $\rho = 1/2(\rho_3 + 1)$ for $\rho_3 \geq 1$. The thermodynamic path indicated by the arrow in Fig. 1(d) corresponds to the sequence of phases of Fig. 1(a). Note that the hatched region surrounding the origin ($|\rho_3| < 1$) is excluded from the ε space, i.e., it does not correspond to physical states. This specificity of the order-parameter space results from the reconstructive character of the transition [10].

Accordingly, combining the formalism of the Landau theory [9] and the effective symmetry breaking mechanism, allows one to describe the transformation between the lamellar and hexagonal phases. The first harmonics in Eq. (1) determine the expression of $\psi(x,y)$ and the order-parameter symmetry, which provides the form of the thermodynamic potential F . Minimization of F yields in turn the equilibrium values of the order-parameter components, which give, using $\psi(x,y)$, the form of the M and W regions, i.e., the mesophase configurations.

Equation (3) expresses that a change in the sign of ψ_{00} , for identical values of the ρ_i and θ , changes the sign of ψ , i.e., it corresponds to the replacement of the M regions by the W regions and vice versa, for the same equilibrium configurations. This can be interpreted [5] as the transformation from a direct to a reversed mesophase, since these mesophases have approximately exchanged configurations with the same basic geometry. Hence, the direct and inverted mesophases are obtained for the same values of the ρ_i and θ but in different subspaces (strata) of the ε space, denoted ε_+ and ε_- , corresponding to opposite values of ψ_{00} . Accordingly, if the distribution of mesophases shown in Fig. 1(c) takes

place in the ε_+ stratum, an identical distribution holds for ε_- in which all the mesophases are reversed [5]. The two strata intersect for infinite values of the ρ_i .

In the model developed up to now, the amphiphilic molecules have been implicitly assumed to be, on average, orthogonal to the interfaces. This corresponds to the most common configuration found in ordered lyotropic mesophases. There exist, however, some examples, such as the $L_{\beta'}$ and $P_{\beta'}$ mesophases found in interacting lipid membranes [6,7] or the L_2 phases of Langmuir films [11], where the sticklike molecules are tilted with respect to the interfaces, in a smectic- C type configuration [Fig. 2(a)]. We will now show that the description of such systems with oriented interfaces can be related to the other IR of G_0 , denoted Γ^- , corresponding to the same wave vector \mathbf{k}_1 , and constructed from the nonsymmetric IR τ^- of G_{k1} .

Figure 2(b) shows the undulation mechanism corresponding to a lamellar-hexagonal transformation when assuming oriented interfaces. One can note that in the lamellar phases the M regions form bilayers: two consecutive layers have opposed orientations and two successive bilayers are in phase opposition in the undulation process. After the topological transition, the bilayers become vesicles forming an hexagonal array.

The orientation of the interfaces can be expressed by a vector field:

$$\Psi(\mathbf{r}) = \psi_a(x,y)\mathbf{a} + \psi_b(x,y)\mathbf{b} \quad (4)$$

with $\mathbf{r} = x\mathbf{a} + y\mathbf{b}$ in hexagonal coordinates. Ψ is either a polar vector or an axial vector, depending on whether the molecules have, respectively, a polar symmetry or a nonpolar symmetry compatible with an axial vector (e.g., C_{nh}). In the first case the value of $|\Psi|$ corresponds to the projection of the molecular vector on the surfaces, while in the second case it coincides with the projection of the molecular axial vector on the normal to the surfaces. For nonaxial or polar symmetries containing the point group D_2 , the mechanism shown in Fig. 2(b) cannot take place.

ψ_a and ψ_b can be expressed in Fourier series:

$$\psi_{a,b}(x,y) = \sum_{(n,p)=-\infty}^{+\infty} \psi_{n,p}^{a,b} e^{(2i\pi/a)(nx+py)}. \quad (5)$$

Considerations similar to those developed for untilted systems lead to a simplified form for ψ_a and ψ_b : one restricts to the coefficients of the first harmonics in Eq. (5), which are $\psi_{01}^a, \psi_{10}^b, \psi_{-11}^a + \psi_{-11}^b$, and their complex conjugates, which form the six components, spanning Γ^- , of the tilted lamellar-hexagonal transition order parameter. Writing $\psi_{01}^a = \rho_1 e^{i\theta_1}$, $\psi_{10}^b = \rho_2 e^{i\theta_2}$, and $\psi_{-11}^a + \psi_{-11}^b = \rho_3 e^{i\theta_3}$, and assuming $\theta_1 = \theta_2 = 0$, one gets (1) in the case of a polar molecular symmetry:

$$\begin{aligned} i\Psi(\mathbf{r}) = & \{ \rho_2 \sin(2\pi y/a) + \rho_3 \sin[2\pi/a(y-x) - \theta] \} \mathbf{a} \\ & + \{ -\rho_1 \sin(2\pi x/a) + \rho_3 \sin[2\pi/a(y-x) - \theta] \} \mathbf{b}, \end{aligned} \quad (6)$$

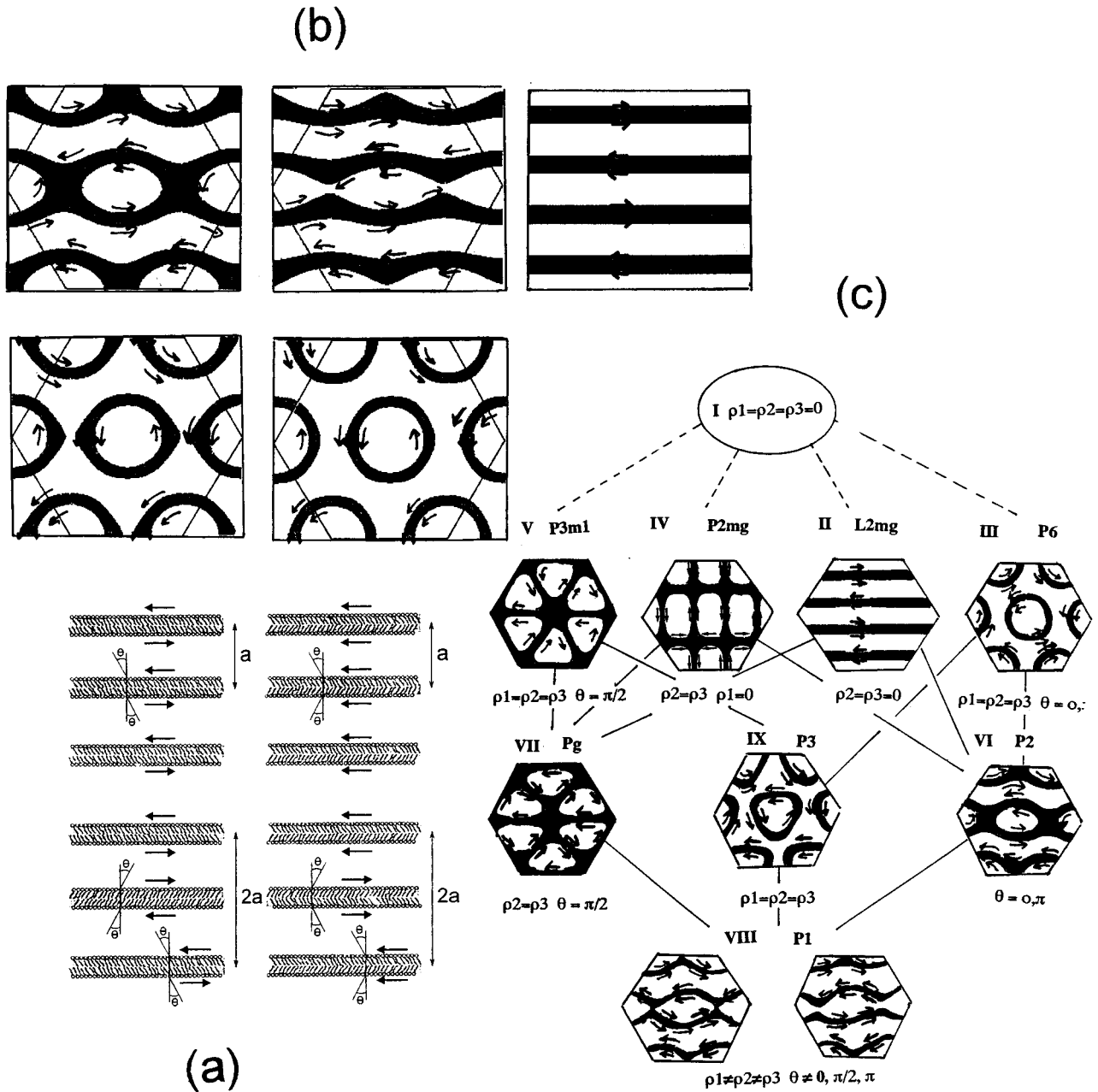


FIG. 2. (a) Schematic representation of the various types of tilted bilayer lamellar phase. The arrows give the orientation of the interfaces corresponding to the projection on the surfaces of the molecular vector. (b) Sequence of mesophases giving rise to a direct hexagonal phase in the case of a polar molecular symmetry. (c) Classification of the mesophases corresponding to the minima of the potential $F(I_1, I_2, I_3, I_4)$. The figure represents one of the possible configurations of the mesophases. The unconventional notation $L2mg$ expresses the existence of a continuous translation along one direction, compatible with the space symmetry $P2mg$.

which is a transverse wave of polar vectors, i.e., the field lines are parallel to the interfaces between the M and W regions. (2) when Ψ is an axial vector, one has

$$i\Psi(r) = \{\rho_1 \sin(2\pi x/a) - \rho_3 \sin[2\pi/a(y-x) - \theta]\} \mathbf{a} + \{\rho_2 \sin(2\pi y/a) + \rho_3 \sin[2\pi/a(y-x) - \theta]\} \mathbf{b}, \tag{7}$$

which is a wave of axial vectors perpendicular to the interfaces. In both cases, the equation of the interfaces is

$$\{\rho_1 \cos(2\pi x/a) + \rho_2 \cos(2\pi y/a) + \rho_3 \sin[2\pi/a(y-x) - \theta]\}^2 = K, \tag{8}$$

where K is a constant representing an additional degree of freedom of the system: the form of the interfaces is a secondary non-symmetry-breaking order parameter.

The transformation properties of the ρ_i and θ by Γ^- yield four independent invariants: I_1, I_2, I_3 , and $I_4' = \rho_1^2 \rho_2^2 \rho_3^2 \cos(2\theta)$. Minimization of the corresponding order-parameter expansion $F(\rho_i, \theta)$ leads to eight possible states,

which differ by the form and orientation of the interfaces. Figure 2(c) illustrates the symmetries and configurations of the corresponding mesophases. Four types of tilted mesophases can be distinguished:

(1) The phases denoted II and VI in Fig. 2(c), which correspond to tilted lamellar (L) and undulated tilted lamellar (\tilde{L}) configurations. The L phase has the smectic- C type bilayer ordering, currently observed in lyotropic systems. The \tilde{L} phase is analogous to the $P_{\beta'}$ “ripple” phase, first identified in lecithin [6] and more recently disclosed in the analogous dimyristoyl (DMPC) [7] and dipalmitoyl (DPPC) [12] systems. It has a long wavelength in-plane modulation of the lamellae with an orthorhombic symmetry [12].

(2) The orthorhombic cylindrical phase denoted IV.

(3) The cylindrical phases, denoted III, V, and IX, which possess hexagonal 2D lattices with hexagonal or rhombohedral point groups. No tilted phases of this sort are presently known in complex fluid systems.

(4) The phases denoted VII and VIII in Fig. 2(c), which may display either a cylindrical or a lamellar configuration with a monoclinic symmetry. The three $L_{\beta'}$ structures found by Smith *et al.* [7] in DBMC may materialize two among these phases. Thus the $L_{\beta I}$ and $L_{\beta F}$ mesophases represent two different monoclinic configurations of phase VII, with the molecules tilted either between or towards nearest neighbors in an hexagonal array. In the intermediate $L_{\beta L}$ phase the tilting direction varies continuously between the $L_{\beta F}$ and $L_{\beta I}$ configurations and can be identified to phase VIII. Another tilted phase ($L_{c'}$) of phospholipid water system was found by Chen *et al.* [13]. Its in-plane arrangement may correspond to the monoclinic symmetry of phase VI. The variety of

tilted lamellar-hexatic phases that have been disclosed in Langmuir films of fatty acids [13] (L_2, L_2', L_2'') can be interpreted into a similar framework, although one has to take into account the additional effect of the surface field. Note that when considering shapes of interfaces described by more than one degree of freedom, qualitatively different configurations than those represented in Fig. 2(c) can be obtained.

In summary two main results have been derived from the phenomenological approach to lyotropic systems proposed in this article: (i) a classification of the mesophase symmetries that may arise at the lamellar-hexagonal reconstructive transition, and their description within a unified model. (ii) A description of the tilted mesophases that may be stabilized with lamellar and hexagonal configurations. Finally, let us emphasize that our approach differs from the Landau-type models, which have attempted to describe the formation of hexagonal phases in complex fluids [14], or the “ripple” and hexatic mesophases [15,16], since in contrast to these models, it relies on a single symmetry breaking mechanism. By contrast, we would like to mention the work of Laradji *et al.* [17], which was brought to our attention by the Referee. Although these authors start from different premises they obtain in diblock copolymer systems, sequences of phases very similar to the ones found in the present article for untilted mesophases.

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