

## Pattern formation and chiral phase separation by compression: Racemic monolayer viewed as Bragg-Williams binary cholesterics

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The monolayer of racemic amphiphiles is studied as a film of cholesteric liquid crystal (ChLC), mixed by the left- and right-handed chiral enantiomers. The chiral phase separation (CPS) and molecular orientation pattern are analyzed by Bragg-Williams theory for binary mixtures and the curvature-elastic model of ChLC. It is shown that below a certain critical temperature a compression can induce transition from racemic phase to CPS phase with a stripe-pattern formation. This gives a clear explanation of CPS in a racemic monolayer recognized by Lundquist [Ark. Kemi. **17**, 183 (1960)], and observed recently by Eckhardt *et al.* [Nature (London) **362**, 614 (1993)]. [S1063-651X(99)11301-1]

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In nature, it is so abundant that the two molecular enantiomers of left- and right-handed chirality usually combine to form a racemic dimer. The means of separation of the dimers into distinct phases of optical activity, the chiral phase separation (CPS), are of critical importance in physics, chemistry, biology, and geology [1], and have been realized through experiments going back to Pasteur in 1848 in isolation of enantiomers of sodium tartrate by crystallization [2], and to Jungfleish in 1882 in the localization of crystallization of individual enantiomers on suitably disposed seeds [3]. However, the major challenge in the study is, on the theoretical side, to understand the mechanism of chiral symmetry breaking (CSB) in CPS. The study of CPS in the three-dimensional (3D) state is especially difficult because both left- and right-handed chiral molecules have been classically regarded as exact mirror images and, therefore, are energetically equivalent in bulk due to the molecular rotation. It is natural to think that this difficulty may be reduced in a monolayer of racemic amphiphiles at the air/water interface, because the molecular rotation of the amphiphiles is limited due to the hydrophobic interaction between the amphiphiles and the water. In fact, a remarkable progress of the study in a 2D system was performed by Lundquist in the 1960s [4]. Recognizing the importance of steric factors in the living system, such as in the architecture of the lipoprotein membranes of cells, Lundquist found that at a temperature below 20 °C the racemic monolayer of the methyl ester of 2-methylhexacosanoic acid shows a pressure plateau in each pressure-area isotherm. This was interpreted as a 2D phase transition region, from the expanded phase to the condensed 2D crystalline phase. At that time, however, there were no methods available for the direct crystallographic study for the crystalline phase. In 1993, a significant advance was made by Eckhardt *et al.* [5]. By transferring such a monolayer of surface pressure from a water surface onto mica, and using atomic-force microscopy, they detected that the phase transition at the region of small molecular areas is a CPS transition, specifically a transition from rectangular lattices of a molecular packing structure (racemic phase) into a chiral phase in which the enantiomers form two antipodal oblique lattices distinguished by some stripes (see Figs. 1–4 in [5]).

In physics, the CSB and stripe formation have been extensively studied in hexatic liquid-crystal (LC) films [6], monolayers [7,8], smectic films [8], and thin ferroelectric LC's [9]. These papers show that the phase separation of enantiomers is not the only mechanism leading to CSB and stripe-pattern formation, e.g., breaking up-down symmetry also leads to the same qualitative behavior [9]. In the theoretical approach presented in [8] by Selinger *et al.*, the CSB and stripe-pattern formation and the formation of other patterns are described with the help of the Landau free-energy expansion in terms of the chiral order parameter, hence it serves to describe the temperature effect in CSB. So far, however, there has been no approach to the investigation connecting the CPS and 2D phase transition in racemic monolayers by compression. Identifying the CSB or CPS associated with stripe-pattern formation induced by surface pressure [4,5] therefore becomes an urgent task in theory.

In this paper, we propose a continuum theory for a description of the surface-pressure-induced CPS in the racemic monolayers. Our approach follows a previous work dealing with tilted chiral lipid membranes [10] by viewing a monolayer as a film of cholesteric liquid crystal (ChLC). However, to describe the racemic property the ChLC is considered a mixture of the left- and right-handed chiral enantiomers with the same molecular number. Instead of using a linear chiral curvature elastic energy term, as done in [10], here we introduce the complete 3D-director elastic free energy density of a ChLC [11],

$$g_{LC} = \frac{1}{2} \left[ k_{11} (\nabla \cdot \mathbf{d})^2 + k_{22} \left( \mathbf{d} \cdot \nabla \times \mathbf{d} - \frac{k_2}{k_{22}} \right)^2 + k_{33} (\mathbf{d} \times \nabla \times \mathbf{d})^2 \right], \quad (1)$$

to describe the free energy of the molecular orientation in monolayers. Here,  $\mathbf{d} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$  is the 3D-director field and  $k_{11}$ ,  $k_{22}$ , and  $k_{33}$  are the splay, twist, and bend elastic constants; however, the chiral modulus  $k_2$  now is naturally defined as

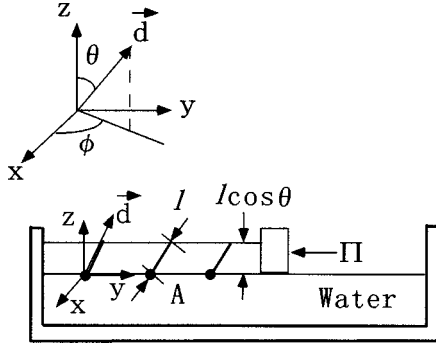


FIG. 1. Geometry of the monolayer of racemic amphiphiles at the air/water interface. The thickness of the monolayer is  $l \cos \theta$ , where  $l$  is the average length of the molecules along their long axis, and  $\theta$  is the average value of the angle between the molecular long axis and the normal of the air/water interface. The total bulk volume of the monolayer is  $V = l \cos \theta A = l \cos \theta N A_0$ , where  $N$  is the molecular number,  $A$  is the total area, and  $A_0$  is the molecular area. Therefore, one has the relation  $\cos \theta = V_0 / l A_0$ , where  $V_0 = V / N$ .

$$k_2 = k_{20} [2\chi(\mathbf{r}) - 1], \quad \chi = N_L(\mathbf{r}) / [N_L(\mathbf{r}) + N_R(\mathbf{r})], \quad (2)$$

where  $k_{20} > 0$  is the chiral elastic constant for the pure left-handed chiral phase,  $N_L(\mathbf{r})$  and  $N_R(\mathbf{r})$  are the local densities of the left- and right-handed chiral enantiomers, respectively, and  $\chi(\mathbf{r})$  is obviously the chiral order parameter that characterizes the CPS: (i) left-handed chiral phase for  $1 \geq \chi > 1/2$ ; (ii) racemic phase for  $\chi = 1/2$ ; and (iii) right-handed chiral phase for  $1/2 > \chi \geq 0$ . With the improvement in description, we are now able to deal with the CSB dependence not only on temperature  $T$  and the chirality ( $k_{20}$ ), but also on the surface-pressure  $\Pi$  and molecular area  $A_0$ . Because in the discussed phase transition region the monolayers have been known as LC or crystalline [4,5], the incompressibility in volume causes the angle  $\theta$ , the angle between the director  $\mathbf{d}$  and the normal of the monolayers, to be uniform as (see Fig. 1)

$$\cos \theta = V_0 / l A_0, \quad (3)$$

where  $l$  is the average molecular length and  $V_0$  is the average molecular volume of the amphiphiles; both are constant. In other words, the chiral order parameter  $\chi$ , the orientation pattern  $\phi(\mathbf{r})$ , and the molecular area  $A_0$  (which is relating to surface pressure  $\Pi$ ) have been incorporated together into the elastic free-energy density  $g_{LC}$ . Another important step in the present theory is that we also consider the additional free energy of the mixing effect by the Bragg-Williams approach in the study of binary alloy [12]:

$$F_{MIX} = \frac{1}{A_0} \int \left\{ -\frac{z}{2} w_{RR} - \frac{z}{2} (w_{LL} - w_{RR}) \chi + z w \chi (1 - \chi) + k_B T [\chi \ln \chi + (1 - \chi) \ln (1 - \chi)] \right\} dA, \quad (4)$$

where  $dA/A_0$  gives the local density of molecules,  $k_B$  is the Boltzmann constant,  $w = (1/2)(w_{LL} + w_{RR}) - w_{LR}$ , with  $-w_{\alpha\beta}$  ( $\alpha, \beta = L, R$ ), denoting the nearest-neighbor interaction energy between the  $\alpha$ -handed enantiomer and the  $\beta$ -handed one, and  $z$  is the number of nearest-neighbor inter-

actions of one molecule. Obviously, the last term in the integrand associated with  $k_B T$  is the entropy increase on mixing, and the other terms relating to  $w_{\alpha\beta}$  are the enthalpy of mixing calculated by the so-called Bragg-Williams approximation. For the present case of experiment discussed in [5], we have  $z = 4$  for 2D rectangular and oblique lattices and  $w_{LL} = w_{RR}$ ; hence, by neglecting the first constant term we can reduce Eq. (4) to

$$F_{MIX} = \frac{k_B T}{A_0} \int [\chi \ln \chi + (1 - \chi) \ln (1 - \chi) + \alpha_0 \chi (1 - \chi)] dA, \quad (5)$$

where  $\alpha_0 = 4w/k_B T$ . As a definition of  $w$ , the positive  $\alpha_0$  favors CPS and consists of short range repulsive interaction, which would be increasing with compression. For example, let's say  $w \rightarrow \infty$ ,  $F_{MIX}$  takes its minimum at  $\chi = 0, 1$ , the complete CPS state. On the other hand, the entropy favors the racemic phase, e.g.,  $T \rightarrow \infty$ , then  $\chi = 1/2$  minimizes  $F_{MIX}$ . Before getting into actual calculations, therefore, we can see the CPS transition as just the result of competition between the entropy (temperature  $T$ ) and enthalpy (compression or molecular area  $A_0$ ). To understand it quantitatively, we must combine the curvature elastic energy and the Bragg-Williams mixing energy as the free energy for the binary ChLC film as

$$F = l \cos \theta \int g_{LC} dA + F_{MIX} + \lambda \int \left( \chi - \frac{1}{2} \right) dA, \quad (6)$$

where  $\lambda$  is the Lagrange multiplier associated with the condition of  $\int (\chi - 1/2) dA = 0$ , a condition according to the fact that the initial phase before compression is a racemic phase, i.e.,  $\int N_L dA = \int N_R dA$ . The equilibrium equations for both  $\phi(\mathbf{r})$  and  $\chi(\mathbf{r})$  are obtained by minimizing the free energy. These equations and their solutions show that the CSB or CPS is associated with the complex localization of individual enantiomers in the monolayers, the CPS pattern formation dependent on  $T$  and  $A_0$ . It is shown that below a certain critical temperature a compression can induce a phase transition from the racemic phase to the CPS phase with a stripe-pattern formation. This gives a clear and direct explanation of CPS in the monolayers of racemic amphiphiles observed by Lundquist [4] and Eckhardt *et al.* [5].

In the actual calculation, we take a Cartesian coordinate  $xyz$  as illustrated in Fig. 1, where the plane of  $z = 0$  is the air/water interface. For convenience, the one-constant approximation as  $k_{11} = k_{22} = k_{33} = k$  is used. The curvature energy density [Eq. (1)] in terms of  $\phi$  is

$$g_{LC} = \frac{1}{2} [k \sin^2 \theta (\phi_x^2 + \phi_y^2) - k_2 \sin 2\theta (\cos \phi \phi_x + \sin \phi \phi_y) + k_2^2 / k], \quad (7)$$

where  $\phi_x = \partial \phi / \partial x$  and  $\phi_y = \partial \phi / \partial y$ . Since the free energy  $F$  is a function of  $\phi(x, y)$  and  $\chi(x, y)$ , we can derive two Euler-Lagrange (EL) equations from the variation of  $F$  with respect to  $\phi$  and  $\chi$  [13]. The first EL equation mainly relates to  $\phi$  as

$$\Delta \phi = \phi_{xx} + \phi_{yy} = \frac{1}{k} \cot \theta [k_{2,x} \cos \phi + k_{2,y} \sin \phi], \quad (8)$$

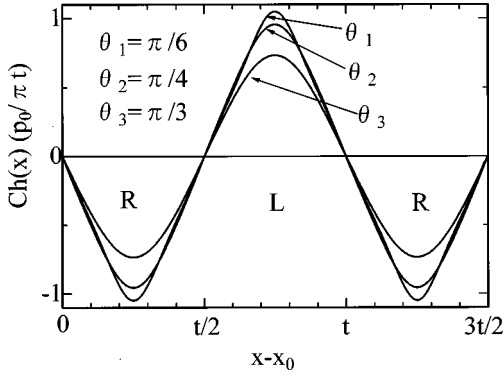


FIG. 2.  $\theta$  dependence of the effective chiral order parameter  $ch(x) = \chi - \frac{1}{2}$ , which characterizes the chirality (positive for left-handed chiral phase and negative for right-handed phase) and the strength of the chiral phase separation. The unit of  $\chi - \frac{1}{2}$  used in the calculation is  $p_0/t$ , where  $p_0$  is the pitch of the equilibrium helical structure for the pure chiral phase in bulk and  $t$  is the period of the stripe. The calculation is based on Eq. (16), with the strong chirality case of  $\eta \rightarrow 1$ .

obtained by  $\delta F / \delta \phi = 0$ , where  $\Delta$  is 2D Laplace operator,  $k_{2,x} = \partial k_2 / \partial x$ , and  $k_{2,y} = \partial k_2 / \partial y$ . Note that in the pure racemic phase ( $k_2 = 0$ ) and the pure chiral phases ( $k_2 = k_{20}$  or  $k_2 = -k_{20}$ ), Eq. (8) is identical to the 2D pattern equation in usual LC's,  $\Delta \phi = 0$  [11].

The second EL equation derived from  $\delta F / \delta \chi = 0$  is given by

$$\lambda + \frac{k_B T}{A_0} \left[ \ln \frac{\chi}{1-\chi} + \alpha_0 (1-2\chi) \right] + k_{20} l \cos \theta \left[ \frac{2k_2}{k} - \sin 2\theta (\phi_x \cos \phi + \phi_y \sin \phi) \right] = 0. \quad (9)$$

Interestingly, at the high temperature limit, i.e., let  $T \rightarrow \infty$ , the equation predicts an obvious solution of  $\chi = 1/2$ , which is nothing but a pure racemic phase, i.e., an isotropic phase. This is a reasonable result in LC physics [11], and consistent with the observation by Lundquist [4] that the CPS transition for a racemic mixture must occur below some critical temperature (see Fig. 2, and the text on p. 399 of [4b]).

In principle, Eqs. (8) and (9), associated with  $\int (\chi - 1/2) dA = 0$ , give complete conditions for determining  $\lambda$ ,  $\phi$ , and  $\chi$  at any  $T$  and  $A_0$ . However, it is quite a task to find general solutions for Eqs. (8) and (9) analytically, owing to their high-order nonlinearity. Fortunately, our interest is in the phase transition region, the proximity of  $\chi = 1/2$ . Therefore, we have  $\ln[\chi/(1-\chi)] \approx 4(\chi - 1/2)$ , and Eq. (9) becomes

$$k_2^* = \eta k_{20} (2\chi - 1) = \frac{k}{2} \left[ \sin 2\theta (\phi_x \cos \phi + \phi_y \sin \phi) - \frac{\lambda}{l k_{20} \cos \theta} \right], \quad (10)$$

where  $\eta = 1 + k(2 - \alpha_0)k_B T / 2V_0 k_{20}^2$ . Taking partial derivations with respect to  $x$  and  $y$ , respectively, gives

$$\chi_x = \frac{k \sin 2\theta}{4 \eta k_{20}} [\phi_x \cos \phi + \phi_y \sin \phi]_x, \\ \chi_y = \frac{k \sin 2\theta}{4 \eta k_{20}} [\phi_x \cos \phi + \phi_y \sin \phi]_y, \quad (11)$$

where  $\chi_x = \partial \chi / \partial x$ ,  $[\ ]_x = \partial [\ ] / \partial x$ , and so on. Substituting Eq. (11) into Eq. (8), we have the following equation for  $\phi$ :

$$\Delta \phi = \eta^{-1} \cos^2 \theta [\psi_x \cos \phi + \psi_y \sin \phi], \quad (12)$$

where  $\psi = \phi_x \cos \phi + \phi_y \sin \phi$ ,  $\psi_x = \partial \psi / \partial x$ , and  $\psi_y = \partial \psi / \partial y$ . It can be seen that for strong chirality, i.e.,  $k/k_{20} = p_0/2\pi \rightarrow 0$ , where  $p_0$  is the pitch of the equilibrium 3D helical structure of the corresponding ChLC [12], we have  $\eta \rightarrow 1$ . In what follows we assume that  $\eta > 0$  is always held to emphasize the effect of strong chirality.

In general, Eqs. (10) and (12), in conjunction with Eq. (3), predict that the compression of monolayers can induce the CPS and the corresponding formation of a complex orientation pattern with either 1D or 2D structures. Some implicit and analytic 2D solutions of Eq. (12) have been found [13]. For simplicity and for comparing with the experiment (Fig. 4 in [5]), here we only report the result of the 1D case. Let  $\phi_y = 0$  and  $\psi_y = 0$ , and we can change Eq. (12) to an ordinary differential equation as

$$\frac{d^2 \phi}{dx^2} = \cos^2 \theta^* \left[ \cos \phi \frac{d}{dx} \cos \phi \frac{d}{dx} \phi \right], \quad (13)$$

where  $\cos^2 \theta^* = \eta^{-1} \cos^2 \theta$ . The solutions of Eq. (13) represent the possible 1D patterns that result from minimizing the free energy  $F$  given in Eq. (6). First, we have the solution of  $\phi = \phi_0$ , where  $\phi_0$  is a constant. This solution corresponds to the racemic phase, i.e., the strip of infinite period with  $F = (N_L + N_R) (\ln \frac{1}{2} + \frac{1}{4} \alpha_0) k_B T$ , regarded as the initial phase. Second, we have the implicit and general solutions that show a striped pattern parallel to the  $y$  axis with finite period, i.e., the CPS phase [13]:

$$x - x_0 = \left( \frac{t}{4} \right) E \left[ \phi(x) - \frac{\pi}{2}, \cos \theta^* \right] / E \left[ \frac{\pi}{2}, \cos \theta^* \right], \quad (14)$$

where  $x_0$  and  $t$  are two integral constants; the latter is also the period of the stripe;

$$E(\phi, \cos \theta^*) = \int_0^\phi \sqrt{1 - \cos^2 \theta^* \sin^2 \phi'} d\phi' \quad (15)$$

is a second ellipse integral. With Eq. (14) and  $\int (\chi - 1/2) dA = 0$ , we obtain from Eq. (10)  $\lambda = 0$ , and the effective chiral order parameter of the CPS pattern, or localization of enantiomers, corresponding to the stripe

$$ch(x) \equiv \chi(x) - \frac{1}{2} = \frac{p_0 \sin 2\theta \cos \phi(x) E(\pi/2, \cos \theta^*)}{2 \pi \eta t \sqrt{1 - \cos^2 \theta^* \cos^2 \phi(x)}}, \quad (16)$$

as shown schematically in Fig. 2. Chiral separation becomes stronger as  $\theta$  decreases, indicating that the separation is just

a result of monolayer compression. Substituting the stripe solution Eq. (14) into Eq. (1), we can show the elastic energy [the first integral in Eq. (6)] in an area of  $x \times y = t \times L$  to be [13]

$$F_C = 8kLl \cos \theta \sin^2 \theta [(\eta^{-1} - 1)K^*E^* + (2 - \eta^{-1})E^{*2}]/t, \quad (17)$$

and dividing by the molecular number of the area,  $N = l \cos \theta L / V_0$  (see Fig. 1), yields the elastic energy per molecule

$$f_C = F_C / N = 8kV_0 \sin^2 \theta [(\eta^{-1} - 1)K^*E^* + (2 - \eta^{-1})E^{*2}]/t^2. \quad (18)$$

Here,  $E^* = E(\pi/2, \cos \theta^*)$  is the complete second ellipse integral, and  $K^*$  is the complete first ellipse integral as

$$K^* = \int_0^{\pi/2} d\phi / \sqrt{1 - \cos^2 \theta^* \sin^2 \phi}. \quad (19)$$

In the proximity of the racemic to CPS transition we can expand the integrand of Eq. (5) in power of  $(\chi - 1/2)$ ,

$$F_{MIX} = \frac{k_B T}{A_0} \int \left[ \ln \frac{1}{2} + \frac{1}{4} \alpha_0 + (2 - \alpha_0) \left( \chi - \frac{1}{2} \right)^2 + \frac{4}{3} \left( \chi - \frac{1}{2} \right)^4 \right] dA. \quad (20)$$

Substituting Eqs. (14) and (16) into Eq. (20), and dividing by the molecular number  $N$ , with a lengthy calculation [13], we obtained the Bragg-Williams mixing energy per molecule

$$f_{MIX} = k_B T \left[ \ln \frac{1}{2} + \frac{1}{4} \alpha_0 + (2 - \alpha_0) \eta^{-1} (E^* K^* - E^{*2}) \times \left( \frac{p_0 \sin \theta}{\pi t} \right)^2 + \frac{4}{3} \eta^{-2} (\sin^{-2} \theta^* E^{*4} - 2K^* E^{*3} + E^{*4}) \left( \frac{p_0 \sin \theta}{\pi t} \right)^4 \right]. \quad (21)$$

Hence, the free energy per molecule can be expressed as a quadratic function of  $q^2 = (p_0 \sin \theta / \pi t)^2$  as

$$f = f_C + f_{MIX} = a_0 - a_2 q^2 + a_4 q^4, \quad (22)$$

with

$$a_0 = (1/4) k_B T (\alpha_0 - 4 \ln 2),$$

$$a_2 = (\alpha_0 - 2) (E^* K^* - E^{*2}) \eta^{-1} k_B T - 8kV_0 (\pi/p_0)^2 [(2 - \eta^{-1})E^{*2} + (\eta^{-1} - 1)K^*E^*],$$

and

$$a_4 = (4/3) (E^{*4} / \sin^2 \theta^* - 2K^* E^{*3} + E^{*4}) \eta^{-2} k_B T.$$

It is clear that the racemic to CPS transition occurs under the necessary condition  $a_2 > 0$ . This requires at least  $\alpha_0 > 2$ . From the definition of  $\alpha_0 = 4w/k_B T$ , we have the critical temperature

$$T_c = 2w/k_B = [(w_{LL} + w_{RR}) - 2w_{LR}] / k_B, \quad (23)$$

below which the racemic to CPS phase transition can happen. This is what was observed by Lundquist [4]. The critical period of the CPS structure ( $t_c$ , at which the free energy of the CPS phase is equal to that of the racemic one, i.e.,  $t \rightarrow \infty$ ) can be obtained as  $t_c = (p_0 \sin \theta / \pi) \sqrt{a_4 / a_2}$ . Performing minimization of  $f$  with  $t$  gives the equilibrium period of  $t_m = \sqrt{2} t_c$ . Obviously, existence of definite  $t_m$  again needs  $a_2 > 0$ , in the case of strong chirality [i.e.,  $\eta \rightarrow 1$  and  $\theta^* \rightarrow \theta$ , hence,  $E^*$  and  $K^* \rightarrow E(\cos \theta)$  and  $K(\cos \theta)$ , respectively], we need  $K(\cos \theta) / E(\cos \theta) - 1 > 8kV_0 (\pi/p_0)^2 / [4w - 2k_B T]$ . From the property of both complete ellipse integrals of  $K$  and  $E$ , the inequality reveals that  $\theta$  must be less than a critical angle of  $\theta_c$ , given by

$$K(\cos \theta_c) / E(\cos \theta_c) = 1 + 8kV_0 \left( \frac{\pi}{p_0} \right)^2 / (4w - 2k_B T). \quad (24)$$

Accordingly, from Eq. (3), CPS occurs at the following condition:

$$A_0 < A_c = V_0 / l \cos \theta_c. \quad (25)$$

We then find that compression plays a critically important role for CPS with stripe-pattern formation.

In a quantitative sense, the present theory can be understood by comparing it with the experiment and calculation by Eckhardt *et al.* [5]. The authors found the energies of the oblique (CPS phase with  $\chi = 0.1$ ) and rectangular (racemic phase with  $\chi = 1/2$ ) differ by  $\sim 7.7$  kJ Mole $^{-1}$ , with the former being more stable. From our theory, the Bragg-Williams formula (5), we then have  $f(\chi = 1/2) - f(\chi = 0.1) = k_B T [\ln(1/2) + \alpha_0/4] = 7.7 \times 10^3 \times 10^7$  erg /  $6 \times 10^{23} = 1.3 \times 10^{-13}$  erg, the difference of free energies per molecule between the racemic and complete CPS phases. Taking  $k_B T = 4 \times 10^{-14}$  erg at  $T = 20^\circ\text{C}$  we obtained  $\alpha_0 = 14.2$ , which satisfies  $\alpha_0 > 2$ , the request of the critical temperature condition (23). From the value of  $\alpha_0$  we can estimate the difference of the nearest-neighbor interaction energies  $w = (1/2)(w_{LL} + w_{RR}) - w_{LR} = (1/4)\alpha_0 k_B T = 1.42 \times 10^{-13}$  erg, which is well comparable to the membrane (bilayer of amphiphiles) curvature modulus  $2lk \sim 10^{-13}$  erg obtained by Helfrich by viewing the membranes as LC films [14]. It is also worth noting that the present assumption of strong chirality is invalid for the usual thermotropic ChLC's with a pitch of order 1  $\mu\text{m}$  [11] because, inserting the order of pitch, the above estimate of  $\alpha_0 = 14.2$ , and the typical values  $k = 10^{-6}$  erg/cm,  $V_0 = 10^{-21}$  cm $^3$ , and  $T = 300$  K into the formula of  $\eta$  [defined after Eq. (10)], gives the parameter of  $\eta - 1$  to be of order  $10^3$ . This is in strong contradiction with the assumption  $\eta - 1 \ll 1$  (or, at least,  $\eta < 1$ ) used above. In other words, the present theory is valid only if the chirality is two orders of magnitude larger compared with usual thermotropic ChLC's, i.e., with a pitch of order 0.01  $\mu\text{m}$ . This is quite possible in the case of chiral amphiphiles observed by Eckhardt and co-workers in [5]. In [10], it is shown that the pitch in the bilayer of tilted chiral amphiphiles viewed as ChLC's can be determined by the formula (see  $p_{ch}$  in Eq. (91) of [10b]):  $p_0 = p_{ch} = 2\pi\rho_0 \sin^2 \theta / (1 + \sin^2 \theta)$ . Here,  $\rho_0$  is

the radius of the helical tubes formed by the tilted chiral bilayer [15], and  $\theta$  is the tilt angle of the hydrocarbon chains of the amphiphiles from the normal of the surface of the bilayer. The order of diameter of the tubes is  $0.5 \mu\text{m}$  [15], and tubes of diameter  $0.05 \mu\text{m}$  are also found [16]. Therefore, if  $\sin\theta$  is of order 0.1 then  $p_0$  of order  $0.01 \mu\text{m}$ , as the chiral amphiphiles, is confirmed by the tube formation [15]. This shows the validity of our model for the observation reported in [5], because the pitch of the chiral amphiphiles in the monolayer should be same as in their bilayer. These confirm the reasonability of the present theory: The CPS of the monolayer of amphiphiles and its associated pattern formation can be well discussed as a film of Bragg-Williams binary cholesterics of the left- and right-handed chiral enantiomers.

It is important to point out that the irrelevance between dipole moment and chirality excludes the possible influence of electrostatic interaction on the CPS phase transition. Here we would like to predict [13,17] that the additional surface pressure, due to the CPS phase transition, can be calculated by the formula  $\delta\Pi = -\partial f/\partial A_0$ , which appears as a function form of  $-b_3 A_0^{-3} + b_5 A_0^{-5} + \dots$ , with  $b_3, b_5 > 0$ , and adds to the typical pressure-area isotherms of the 2D van der Waals equation of state [18]. This is the mechanism of the pressure plateau in the area-pressure isotherms associated with the CPS transition [4,5].

Finally, we would like to discuss the connection between the present theory and those given in [8]. In [8], the elastic energy is expressed by the function of gradients of the 2D director  $\mathbf{c} = (\cos\phi, \sin\phi, 0)$ , which is parallel to the project

direction of molecular director  $\mathbf{d}$  in the  $xy$  plane [see Eq. (1) in [8]]. With a lengthy calculation [13], we have shown that the elastic energy given in Eq. (1) can be also expressed with the function of the gradients of  $\mathbf{c}$  as

$$g_{LC} = \frac{1}{2} k_{11} \sin^2 \theta (\nabla' \cdot \mathbf{c})^2 + \left[ \frac{1}{2} k_{22} \sin^2 \theta \cos^2 \theta + \frac{1}{2} k_{33} (\sin^4 \theta - 4 \sin^2 \theta) \right] \times (\mathbf{z} \cdot \nabla' \times \mathbf{c})^2 + 2k_{33} \sin^2 \theta (\nabla' \times \mathbf{c})^2 - k_2 \sin \theta \cos \theta (\mathbf{z} \cdot \nabla' \times \mathbf{c}) - 2k_2 \sin^2 \theta (\mathbf{c} \cdot \nabla' \times \mathbf{c}) + 2(k_{22} - k_{33}) \sin^3 \theta \cos \theta (\mathbf{c} \cdot \nabla' \times \mathbf{c}) (\mathbf{z} \cdot \nabla' \times \mathbf{c}) + 2(k_{22} - k_{33}) \sin^4 \theta (\mathbf{c} \cdot \nabla' \times \mathbf{c})^2 + \frac{1}{2} k_2^2 / k_{22}, \quad (26)$$

where  $\nabla' = (\partial_x, \partial_y, 0)$  and  $\mathbf{z} = (0, 0, 1)$  is the normal vector of the monolayer. Obviously, this formula, which involves all possible combinations of linear and quadratic gradients of  $\mathbf{c}$ , is more complete than those used in [8] and [9] [see, Eq. (1) in [8] and Eq. (2) in [9a]]. Moreover, in the present theory we focus on the separation of chiral enantiomers so that we introduce the chiral order parameter  $\xi$  defined in Eq. (2), which is also different from those used in [8,9]. However, the terms of the gradients of the chiral order parameters are taken into account in the theoretical treatment in the same way as shown in Eq. (11) and in [8,9].

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