Elasticity Theory of 2D Chiral Phase Separation in Langmuir Monolayers

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Abstract

We build a theory of chiral phase separation in Langmuir films by taking into account the elasticity theory of liquid crystals and the mixing free energy of two enantiomers. The theory leads to a striped pattern with random width and sudden change of chirality from one domain to another, which agrees well with the experiment by Eckhardt et al. [Nature (London) 362, 614 (1993)].

Chiral phase separation (CPS) in Langmuir monolayers is an interesting phenomenon. Experimentally, several observations of pattern formation imply occurrence of CPS, in which the noticeable is the striped pattern obtained by Eckhardt et al. Selinger et al. built a Ginzburg-Landau theory to describe chiral symmetry breaking in 2D systems. However, substantial inconsistencies exists between the predicted textures and experiments on Langmuir monolayers. In our previous work, we built a theory of CPS with free energy

\[ F = \int \frac{1}{2} \cos \theta \left[ k_{11} (\nabla \cdot d)^2 + k_{22} (d \cdot \nabla \times d)^2 + k_{33} (d \times \nabla \times d)^2 - 2k_2 (d \cdot \nabla \times d) \right] dA \]

in which the first term is the elastic energy of cholesteric liquid crystals, and the second term is the mixing energy of two enantiomers in Bragg-Williams approximation (Fig. 1). The chiral modulus is assumed to be \( k_2 = k_{20} (2 \chi - 1) \), with \( \chi = N_L(r)/[N_L(r) + N_R(r)] \) the local chiral order parameter. \( A_0 \) is the average area of molecule. \( d = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \) is the 3D director, in which the tilt angle \( \theta \) is viewed as a constant. \( \alpha_0 = 4w/k_BT \) is the chiral discrimination (CD) coefficient, with \( w = (w_{LL} + w_{RR})/2 - w_{LR} \) denoting the difference of the nearest-neighbor interaction between identical and opposite enantiomers.

The Euler-Lagrange Equations are written as

\[ \Delta \phi = \phi_{xx} + \phi_{yy} - \frac{2k_{20}}{k} \cot \theta \left[ \chi_x \cos \phi + \chi_y \sin \phi \right] \]

\[ \lambda_L + \frac{k_BT}{A_0} \left[ \ln 1 - \chi + \alpha_0 (1 - 2 \chi) \right] - k_{20} \ln \theta \sin 2\theta (\phi_x \cos \phi + \phi_y \sin \phi) = 0, \]

where the one-elastic-constant approximation is used. Taking \( \chi_y \) and \( \phi_y \) as zero, we get the general 1D solution:

\[ \cos \phi = \frac{\sqrt{k_BT}}{k_{20} \cos \theta} \sqrt{\frac{G'(\chi)}{G'(\chi)}} \]

\[ x - x_0 = \frac{k \tan \theta}{8k_{20}} \int_{\chi_1}^{\chi_2} \left[ \frac{[G'(\chi')]^2 - 2G'(\chi')G''(\chi')}{G'(\chi')} \right]^{1/2} d\chi', \]

where \( G(\chi) = C + \chi \ln \chi + (1 - \chi) \ln (1 - \chi) + \alpha_0 \chi (1 - \chi) \), with \( C \) an integral constant. \( G'(\chi) \) and \( G''(\chi) \) are the first and second derivatives respectively.

As shown in Fig. 1, as \( \alpha_0 > 2 \), the mixing energy has two minima with chiral order parameter \( \chi_1 \) or \( \chi_2 = 1 - \chi_1 \). It is expectable that as \( \alpha_0 \gg 2 \), if all areas of the monolayer are with chiral order parameter
\( x = x_1 \) or \( x_2 \), the mixing energy would be greatly decreased. We emphasize that the characteristic of our model is the absence of the quadratic-gradient term of chiral order parameter, i.e. \((\nabla x)^2\) (which is important in the theory by Selinger et al.\(^3\)). This absence permits sudden change of \( x \) from one domain to another, and as \( C = x_1 \ln x_1 + x_2 \ln x_2 + a_0 x_1 x_2 \) leads to an extreme case of Eqs. (4) and (5) consisting of stripes with alternating chirality \( x_1 \) and \( x_2 \) and sudden-change edges (Fig. 2),

\[
\phi \equiv \pi/2, \quad x = \begin{cases} x_1, & x \in \cdots L_{-1}, L_1 \cdots, \\ x_2, & x \in \cdots L_{-2}, L_0, L_2 \cdots \end{cases},
\]

(6)

The widths of domains are not defined since in any domain \( x = \) constant. The inequality of the widths of stripes schematized in Fig. 2 is to show this point.

The sudden change of \( x \) among domains leads to a linear tension \( \lambda I = 2\rho (1-2x_1)^2w \) along the edges due to CD interaction, where \( \rho \) is the molecular linear density along the edge. This implies that patterns described by Eq. (6) with finite-width stripes is metastable, since the total energy would be lowered by a convergence of identically chiral bands and lowering of edge energy.

Noting that in case of CPS the CD coefficient \( a_0 \) must increase as molecular area decreases, we depict the picture of monolayer-compression-induced CPS qualitatively as following. When \( A_0 \) is large enough, \( a_0 \) is small and the monolayer is racemic. As \( a_0 > 2 \) holds due to compression, the two enantiomers begin to converge respectively. Small domains converge further to lower the edge energy, and at last the monolayer reaches a pattern of parallel stripes with width larger than certain length scale (some nanoscale free running distance of molecules in monolayer), then the whole system becomes metastable. We point out that as \( a_0 \) is quite large (about 14, as pointed in Ref. [5]), the energy barrier shown in Fig. 1 is quite high. It is just this energy barrier that blocks the permeation of molecules through the anti-chirality band and then stabilizes the metastable pattern.

The experimental images\(^2\) clearly shows nanoscale stripes, whose widths being different from each other. The equality \( \phi \equiv \pi/2 \) in Eq. (6) means that molecules tilt uniformly, which is also experimentally supported. The sudden change of chiral order parameter at the edge of domains is consistent with the sharp mutation of bond orientation\(^2\), and also homologous to the 3D CPS, in which two enantiomers separate into chiral crystals with sharp mutation of chirality at the interface.

![Graph](image_url)

**Fig. 1** Behavior of \( \zeta(x) = x \ln x + (1-x) \ln (1-x) + a_0 x (1-x) \).

**Fig. 2** Schematic of striped pattern.