Phase diagrams of mixtures of a polymer and a cholesteric liquid crystal under an external field[a]

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Abstract

We present a mean field theory to describe phase behaviors in mixtures of a polymer and a cholesteric liquid crystal in the presence of an external magnetic or electric field.We examine twist-untwist phase transitions and phase separations in the mixtures. It is found that a cholesteric-nematic phase transition (CNT) can be induced by not only the external field but also concentration and temperature. Depending on the strength of the external field, we predict cholesteric-paranematic (Ch+N), nematic-paranematic (N+pN), cholesteric-nematic (Ch+N) phase separations, etc, on the temperature-concentration plane.

1. Introduction

CHOLESTERIC-nematic phase transition was first studied by de Gennes[1] and Meyer.[2] Applying an external field perpendicular to a helical axis of a cholesteric phase, untwisting of the helix takes place with positive dielectric or diamagnetic anisotropy. We here assume that the thickness of a sample is sufficiently large and the boundary conditions can be neglected. On increasing the external field H, the pitch p of the cholesteric phase increases and diverge at a critical value H_c of the external field. When $H > H_c$, we have a nematic phase, oriented uniformly along the external field (Fig. 1). This is known as a field-induced twist-untwist transition (or CNT), which has been used in liquid crystal displays. It is well known that the critical field H_c is a linear function of the concentration of dopants in the dilute regime and the pitch of a helix is inverse proportional to the concentration. There are many studies of the CNT based on the Frank's elastic theory,[1] however, it can not describe the concentration dependences. To describe the concentration dependences, we need to consider binary mixtures of a liquid crystal and a polymer. Recently, developing the molecular theory of the cholesteric phase presented by Lin-Liu et.al.,[3] we have presented the molecular theory to describe phase behaviors of binary mixtures of a polymer and a cholesteric liquid crystal, by taking into account of the chiral coupling between the components.[4]

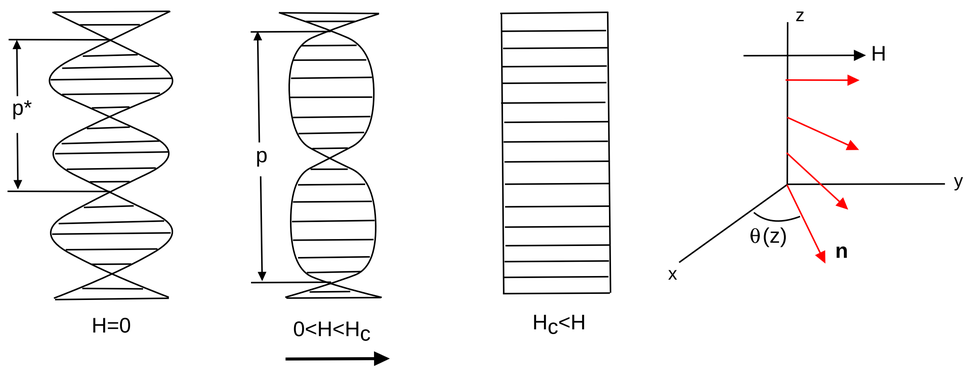

Figure 1: *Twist-untwist transition induced by an external field H. Cholesteric pitch is along z axis and the external field is taken along y axis.*

In this paper we develop our previous theory[4] to describe phase behaviors in mixtures of a cholesteric liquid crystal and a polymer chain in the presence of an external magnetic or electric field. We predict the field-induced CNT and novel phase separations on the temperature-concentration plane under an external field.

2. Free Energy

The free energy consists of the following three terms:

$$F = F_{mix} + F_{ani} + F_{ext}. \tag{1}$$

The first term in Eq. (1) is the free energy of isotropic mixing of a polymer (P) and a liquid crystal molecule (L) and is given by Flory-Huggins theory for polymer solutions:

$$\beta F_{mix}/V = \frac{\phi_L}{n_L}\ln\phi_L + \frac{\phi_P}{n_P}\ln\phi_P + \chi\phi_L\phi_P, \tag{2}$$

where ϕ_i is the volume fraction of the molecule $i(=L,P)$, χ is the Flory-Huggins interaction parameter between a liquid crystal and a polymer in an isotropic phase, and $\beta = 1/k_BT$.
The anisotropic part of the free energy F_{ani} in the second virial approximation can be given by

$$\begin{aligned} F_{ani} &= (1/\beta)\sum_{i=L,P}\rho_i\int f_i(\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega})\ln 4\pi f_i(\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega})d\mathbf{r}d\Omega \\ &+\frac{1}{2}\sum_{i,j=L,P}\rho_i\rho_j\int f_i(\mathbf{r}_1,\mathbf{\Omega}_1)f_j(\mathbf{r}_2,\mathbf{\Omega}_2)U_{ij}(\mathbf{r}_1,\mathbf{\Omega}_1;\mathbf{r}_2,\mathbf{\Omega}_2)d\mathbf{R}, \end{aligned} \tag{3}$$

where $d\mathbf{R} \equiv d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1\Omega_2$. The first term in Eq. (3) shows the entropy changes due to an orientational ordering and U_{ij} is the orientation-dependent intermolecular potential between two particles i and j $(i,j=L,P)$. We here take $U_{PP}=0$ because we consider non-nematic polymer chains in the constituent pure polymers. The lowest-order contributions to the interaction potential for the cholesteric phase are given by in a series of the Legendre polynomials:[3, 4]

$$\begin{aligned} U_{ij}(\mathbf{r}_1,\mathbf{\Omega}_1;\mathbf{r}_2,\mathbf{\Omega}_2) &= U_{ij,1}(\mathbf{r}_{12})(\mathbf{\Omega}_1\times\mathbf{\Omega}_2\cdot\hat{\mathbf{r}}_{12})P_1(\mathbf{\Omega}_1\cdot\mathbf{\Omega}_2) \\ &+U_{ij,2}(\mathbf{r}_{12})P_2(\mathbf{\Omega}_1\cdot\mathbf{\Omega}_2), \end{aligned} \tag{4}$$

where we truncated by $P_2(x)$. The potential $\beta U_{ij,1}(=c_{ij})$ shows the chiral interaction between two particle i and j. The term $\mathbf{\Omega}_1\times\mathbf{\Omega}_2\cdot\hat{\mathbf{r}}_{12}$ represents scalars coupling between orientational and spatial variables, where $\hat{\mathbf{r}}_{12} = (\mathbf{r}_2-\mathbf{r}_1)/|\mathbf{r}_{12}|$. The potential $\beta U_{ij,2}(=\nu_{ij})$ shows the intermolecular potential that accounts for the formation of a nematic phase in Maier-Saupe model.
The last term in Eq. (1) is the magnetic (or electric) free energy relevant to orientational order. When the external magnetic field $\mathbf{H}$ is applied to the molecule $i(=L,P)$ having a diamagnetic anisotropy $\Delta\chi_i$, the external free energy is given by[1]

$$F_{ext} = -\sum_{i=L.P}n_i\rho_i\int\Delta\chi_i H_\alpha Q^{(i)}_{\alpha\beta}(\mathbf{r})H_\beta d\mathbf{r} \tag{5}$$

where $Q^{(i)}_{\alpha\beta}(\mathbf{r})$ is the second rank orientational order parameter tensor of the molecule i.
Numerical parameters: nematic coupling $\epsilon_n = \nu_{LP}/\nu_{LL}$ and chiral coupling $\epsilon_x = c_{LP}/c_{LL}$ between unlike molecules.

3. Cholesteric pitch under an external field

In order to calculate the distortion free energy due to the spatial variation of the director in a cholesteric phase, we assume that the director is uniformly twisted along z axis with a pitch $p = 2\pi/q$:

$$\mathbf{n}(\mathbf{r}) = (\cos\theta, \sin\theta, 0), \tag{6}$$

The scalar order parameters do not depend on position $\mathbf{r}$ and θ is a function of z in our mean field approximations. We here set the magnetic field $\mathbf{H}$ is taken along y axis:

$$\mathbf{H} = (0, H, 0) \tag{7}$$

When $\Delta\chi_i > 0$, the molecules are oriented along the external field.
Minimizing the free energy we obtain the pitch p as a function of concentration ϕ_i and orientational order parameters S_i:

$$\frac{p}{p_0} = \frac{Q_0}{Q} = \frac{4}{\pi^2}K(c)E(c)\left(\frac{\phi_L S_L + 2\epsilon_n\phi_P S_P}{\phi_L S_L + 2\epsilon_x\phi_P S_P}\right), \tag{8}$$

where $K(c)$ and $E(c)$ is the complete elliptic integral of the first and second kind, respectively, and $p_0 = 2\pi d_0/Q_0$ is the pitch of a pure liquid crystal in the absence of the external field. When $\phi_P = 0$, Eq. (8) results in the pitch of the pure liquid crystal derived by de Gennes.[1]

4. Phase Diagrams

The phase diagrams on the temperature-concentration plane in the absence of an external field have been discussed in the previous paper[4] where we find the phase separation (Ch+I) between a cholesteric and an isotropic phase (see Fig.2(a)). Under an external field h_L, the CNT takes place, depending on temperature and concentration, and then the phase diagrams are drastically changed (see Fig.2(b) and Fig.3): Cholesteric (Ch), Isotropic (I), Nematic (N), paranematic (pN, or weak nematic) phase.

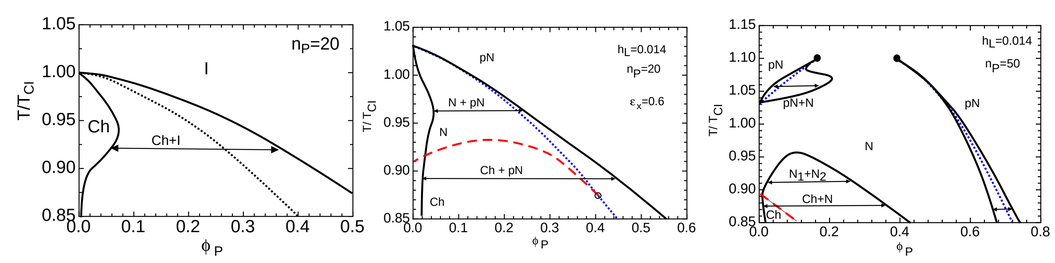

Figure 2: *Phase diagram in the absence of the external field $h_L = 0$ (a) and $h_L = 0.014$ (b). The solid curves are the binodal lines, the black (blue) dotted line shows the CIT (NpNT), and the dashed line is the CNT, which corresponds to the critical field. The NpNT temperature of the pure liquid crystal ($\phi_P = 0$) shifts to higher temperatures because of the external field. The CNT and NpNT lines meet at a critical end point (CEP), open circle. Below the CEP, the first order cholesteric-paranematic phase transition (ChpNT) appears. (c): Phase diagram for $\epsilon_x = 0.2$ and $n_P = 50$ with $h_L = 0.014$. The closed circles show a critical point (CP).*

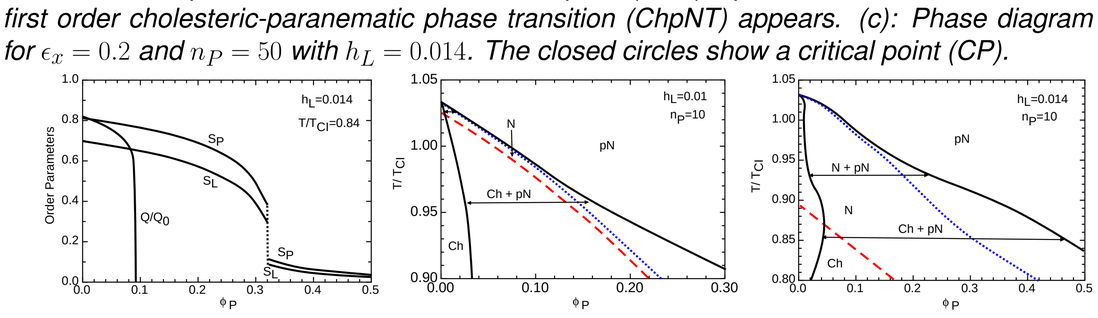

Figure 3: *(a) Orientational order parameters S_L, S_P, and the pitch wavenumber $Q/Q_0(\propto p^{-1})$ plotted against ϕ_P for $n_P = 10$. The second-order CNT takes place at $\phi_P \simeq 0.1$ and the first-order nematic-paranematic transition (NpNT) occurs at $\phi_P \simeq 0.32$. (b) (c): Phase diagram for $\epsilon_x = 0.2$ and $n_P = 50$ with $h_L = 0.01$ (b) and $h_L = 0.014$(c).*

5. Summary

(1) We have presented a mean field theory to describe phase behaviors in binary mixtures of a polymer and a cholesteric liquid crystal in the presence of an external magnetic or electric field.
(2) It is found that in the presence of the external field the CNT and NpNT take place in the mixtures, depending on temperature and concentration. On increasing the strength of the external field, the CNT temperature shifts to lower temperatures and the nematic phase appears between the pN and Ch phases.
(3) In the presence of the external field we find the various phase separations: Ch+pN, N+pN, N_1+N_2, Ch+N, and Ch+N+pN, although we only have the Ch+I coexistence in the absence of the external field. We demonstrate that a strong coupling between a polymer and a liquid crystal under the external field takes place various phase separations.

References

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