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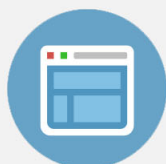
Theory of polymer-dispersed cholesteric liquid crystals

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A mean field theory is presented to describe cholesteric phases in mixtures of a polymer and a cholesteric liquid crystal. Taking into account an anisotropic coupling between a polymer and a liquid crystal, we examine the helical pitch, twist elastic constant, and phase separations. Analytical expressions of the helical pitch of a cholesteric phase and the twist elastic constant are derived as a function of the orientational order parameters of a polymer and a liquid crystal and two intermolecular interaction parameters. We also find isotropic-cholesteric, cholesteric-cholesteric phase separations, and polymer-induced cholesteric phase on the temperature-concentration plane. We demonstrate that an anisotropic coupling between a polymer and a liquid crystal can stabilize a cholesteric phase in the mixtures. Our theory can also apply to mixtures of a nematic liquid crystal and a chiral dopant. We discuss the helical twisting power, which depends on temperature, concentration, and orientational order parameters. It is shown that our theory can qualitatively explain experimental observations. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4828940]

I. INTRODUCTION

In a common nematic phase, the nematic director **n** is homogeneous through a system, although, a cholesteric liquid crystal phase is a chiral nematic: the director **n** is uniformly twisted along a perpendicular axis called helical axis. The distance along the helical axis for the director to twist 2π is called pitch $p = 2\pi/q$, which depends on temperature and concentration in a system. Since p is comparable to an optical wavelength, the periodicity results in Bragg scattering of light beams. This mesoscopic helical structure becomes the basis of optoelectronic applications such as a twisted nematic liquid crystal display.[1,2]

Cholesteric liquid crystals consist of either chiral molecules which are optically active molecules or nematic molecules with chiral dopants.[3–5] At small concentration of a chiral dopant, the pitch is inversely proportional to the concentration of the chiral dopant.[3] Such cholesteric phase can be stabilized or modified by polymer networks.[1,6] It is known as the polymer-stabilized cholesteric liquid crystals for electro-optical displays.[7–10] The pitch and the physical properties of cholesterics can be controlled by mixing cholesteric liquid crystals and polymer chains, or photo reactive molecules.[2,11–13]

It has been shown both experimentally[14–17] and theoretically[18–25] that in mixtures of a polymer and a liquid crystal (so-called polymer dispersed liquid crystals: PDLCs), phase separations between an isotropic and a nematic or a smectic phase appears below the nematic-isotropic phase transition (NIT) temperature of the pure liquid crystal.[2] For strong anisotropic (attractive) interactions between polymers and liquid crystals, it has been recognized that a smectic phase can be induced in a nematic liquid crystal mixture.[26–28] Such

induced nematic phases have also been predicted in polymer-liquid crystal mixtures.[29] However, theoretical attempts for cholesteric phases in the mixtures are not numerous.[30–33]

To describe cholesteric phases, the chiral dispersion intermolecular interactions have been treated by many authors.[30–48] The configuration of the constituent ith molecule is characterized by its position vector $\mathbf{r}_i$ and its orientation vector $\mathbf{\Omega}_i$. It has been shown that the intermolecular chiral interaction is given by the term $(\mathbf{\Omega}_1 \times \mathbf{\Omega}_2 \cdot \hat{\mathbf{r}}_{12})P_1(\mathbf{\Omega}_1 \cdot \mathbf{\Omega}_2)$ in the lowest order, where $\hat{\mathbf{r}}_{12} = (\mathbf{r}_1 - \mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|$. The chiral interaction must be odd in $\mathbf{\Omega}_1 \cdot \mathbf{\Omega}_2$, while the nematic interaction be even. The appearance of this term distinguishes cholesterics from nematics and determines the cholesteric pitch in an equilibrium state. Lin-Liu *et al.* have taken into account the chiral potential in a series of the Legendre polynomials, truncated by $P_3(\mathbf{\Omega}_1 \cdot \mathbf{\Omega}_2)$.[40] They found that the pitch depends on temperature through a ratio of orientational order parameters in the form $[P_4(x)/P_2(x)]^2$. We here treat the chiral free energy in the lowest order.

The aim of this paper is to develop a mean field theory to describe cholesteric phases in mixtures of a liquid crystal and a polymer chain. Developing the molecular theory of the cholesteric phase presented by Lin-Liu *et al.*,[40–42] we derive the free energy of mixtures of a chiral liquid crystal and a polymer chain. Our main original contribution is to taking into account the chiral coupling between a polymer and a liquid crystal in the lowest order. As the results, we obtain analytical expressions of the pitch of the cholesteric phase and the twist elastic constant as a function of orientational order parameters of a polymer and a liquid crystal. We demonstrate that the anisotropic coupling between a polymer and a liquid crystal can stabilize the cholesteric phase in the mixtures. We also find phase separations between isotropic-cholesteric and cholesteric-cholesteric phases. Our theory can also apply to mixtures of a non-chiral nematic liquid crystal and a chiral molecule. It is well known that a small amount of a chiral

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dopant in a non-chiral nematic liquid crystal phase induces a cholesteric phase with a helical pitch, which is inversely proportional to the concentration of the chiral dopant molecules.[3] We find that the chiral coupling between a liquid crystal and a chiral dopant creates a helical twisting power, which is given as a function of the concentration of chiral dopants and orientational order parameters.

In Sec. II, we extend a mean field theory to describe binary mixtures of a cholesteric liquid crystal and a polymer chain. In Sec. III, we show some numerical results of pitch, twist elastic constant, and phase diagrams for the mixtures. In Sec. IV, pitch and helical twisting power in mixtures of a non-chiral nematic liquid crystal and a chiral molecule are discussed.

II. FREE ENERGY OF MIXTURES OF A POLYMER AND A CHOLESTERIC LIQUID CRYSTAL

A. Chiral free energy

Consider a binary mixture of a liquid crystal molecule and a polymer chain for which a nematic ordering is forbidden in the constituent pure polymer chains. To describe cholesteric phases of the mixtures, we develop a mean field model proposed by Lin-Liu *et al.*[40–42] We here take into account an anisotropic coupling between polymers and liquid crystals.

Let N_P is the number of a polymer chain with n_P segments and N_L be the number of a low-molecular weight liquid crystal molecule of length L and diameter D. The volume of a liquid crystal and that of a polymer chain are given by $v_L = (\pi/4)D^2 L$ and $v_P = a^3 n_P$, respectively. Let $\phi_L = v_L N_L/V$ and $\phi_P = v_P N_P/V$ be the volume fraction of the liquid crystal and the polymer, respectively, where V is the volume of the system: $\phi_L + \phi_P = 1$. Using the axial ratio $n_L = L/D$ of the liquid crystal, the volume per liquid crystal molecule is given by $v_L = a^3 n_L$, where we define $a^3 = (\pi/4)D^3$.

The free energy consists of the following two terms:

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

The first term in Eq. (1) is the free energy of mixing of a polymer and a liquid crystal molecule and is given by Flory-Huggins theory for polymer solutions:[49]

$$a^3 \beta F_{mix}/V = \frac{\phi_L}{n_L}\ln\phi_L + \frac{\phi_P}{n_P}\ln\phi_P + \chi\phi_L\phi_P, \tag{2}$$

where χ is the Flory-Huggins interaction parameter between a liquid crystal and a polymer in an isotropic phase and $\beta \equiv 1/k_B T$; T is the absolute temperature, k_B is the Boltzmann constant.

The second term in Eq. (1) shows the free energy for cholesteric phases. The configuration of a constituent molecule is characterized by its position vector $\mathbf{r}$ and its orientation unit vector $\mathbf{\Omega}$, defined by a polar angle θ and an azimuthal angle φ, or solid angle $d\Omega(=\sin\theta d\theta d\varphi)$, in a fixed coordinate frame. Let $f_i(\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega})$ be the orientational distribution function of a constituent molecule $i(=L, P)$, where $\mathbf{n}(\mathbf{r})$ is the local director. It should be noted that the distribution function depends only on the relative angle between

the local director $\mathbf{n}(\mathbf{r})$ and the molecular orientation vector $\mathbf{\Omega}$. The anisotropic part of the free energy in the second virial approximation can be given by

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

where $d\mathbf{R}\equiv d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1\Omega_2$ and $\rho_i = N_i/V$ is the number density. The first term in Eq. (3) shows the entropy changes due to 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:[40]

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

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and we have truncated by $P_2(x)$. Lin-Liu *et al.* have taken into account the intermolecular potential in a series of the Legendre polynomials by $P_4(\mathbf{\Omega}_1\cdot\mathbf{\Omega}_2)$,[40] however there are some unknown numerical parameters related to the interaction. Equation (4) is useful to reduce the number of the unknown numerical parameters. The potential $U_{ij,1}$ shows the chiral interaction between two particles 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. The potential $U_{ij,2}$ shows the intermolecular potential that accounts for the formation of a nematic phase, which has been used in Maier-Saupe[50] and Onsager models.[51] Following the symmetry consideration for cholesteric phases, we require that the first term in Eq. (4) is odd in $\mathbf{\Omega}_1\cdot\mathbf{\Omega}_2$ and the second term be even.

Substituting Eq. (4) into (3), the anisotropic free energy can be expressed as

$$\beta F_{ani}/V = \sum_{i=L,P}\rho_i\int f_i(\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega})\ln 4\pi f_i(\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega})d\mathbf{r}d\Omega$$
$$+\beta(F_1 + F_2)/V, \tag{5}$$

where we have the chiral component of the free energy

$$\beta F_1/V = \frac{1}{2}\sum_{i,j=L,P}\rho_i\rho_j\int f_i(\mathbf{n}(\mathbf{r}_1)\cdot\mathbf{\Omega}_1)f_j(\mathbf{n}(\mathbf{r}_2)\cdot\mathbf{\Omega}_2)$$
$$\times\beta U_{ij,1}(\mathbf{r}_{12})(\mathbf{\Omega}_1\times\mathbf{\Omega}_2\cdot\hat{\mathbf{r}}_{12})P_1(\mathbf{\Omega}_1\cdot\mathbf{\Omega}_2)d\mathbf{R}, \tag{6}$$

and the usual nematic free energy

$$\beta F_2/V = \frac{1}{2}\sum_{i,j=L,P}\rho_i\rho_j\int f_i(\mathbf{n}(\mathbf{r}_1)\cdot\mathbf{\Omega}_1)f_j(\mathbf{n}(\mathbf{r}_2)\cdot\mathbf{\Omega}_2)$$
$$\times\beta U_{ij,2}(\mathbf{r}_{12})P_2(\mathbf{\Omega}_1\cdot\mathbf{\Omega}_2)d\mathbf{R}. \tag{7}$$

The degree of local orientational order for a given $f_i(\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega})$ can be specified by the second rank order parameter tensor $Q_{\alpha\beta}^{(i)}(\mathbf{r})$ of the molecule i and in general is a function

of position:

$$Q_{\alpha\beta}^{(i)}(\mathbf{r}) \equiv \int d\Omega f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) \left(\frac{3}{2} \Omega_\alpha \Omega_\beta - \frac{1}{2} \delta_{\alpha\beta} \right)$$

$$\equiv \left\langle \frac{3}{2} \Omega_\alpha \Omega_\beta - \frac{1}{2} \delta_{\alpha\beta} \right\rangle, \qquad (8)$$

where Ω_α is the Cartesian component of the molecular orientation vector $\mathbf{\Omega} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ at a position $\mathbf{r}$.

Using Eq. (8), the averages over Ω_1 and Ω_2 in Eqs. (6) and (7) yield

$$\int f_i(\mathbf{n}(\mathbf{r}_1) \cdot \mathbf{\Omega}_1) f_j(\mathbf{n}(\mathbf{r}_2) \cdot \mathbf{\Omega}_2) \qquad (9)$$

$$\times (\mathbf{\Omega}_1 \times \mathbf{\Omega}_2 \cdot \hat{\mathbf{r}}_{12}) P_1(\mathbf{\Omega}_1 \cdot \mathbf{\Omega}_2) d\Omega_1 d\Omega_2$$

$$= \frac{4}{9} \epsilon_{\alpha\beta\gamma} (r_\alpha/r) Q_{\mu\beta}^{(i)}(\mathbf{r}_1) Q_{\mu\gamma}^{(j)}(\mathbf{r}_2), \qquad (10)$$

and

$$\int f_i(\mathbf{n}(\mathbf{r}_1) \cdot \mathbf{\Omega}_1) f_j(\mathbf{n}(\mathbf{r}_2) \cdot \mathbf{\Omega}_2) P_2(\mathbf{\Omega}_1 \cdot \mathbf{\Omega}_2) d\Omega_1 d\Omega_2$$

$$= \frac{2}{3} Q_{\alpha\beta}^{(i)}(\mathbf{r}_1) Q_{\alpha\beta}^{(j)}(\mathbf{r}_2), \qquad (11)$$

respectively, where $\epsilon_{\alpha\beta\gamma}$ is Levi-Civita antisymmetric tensor of the third rank and $r \equiv |\mathbf{r}_{12}|$.

We here assume that the $Q_{\alpha\beta}^{(j)}(\mathbf{r}_2)$ does not change appreciably over the range of the potential and can be expanded in the Taylor series about $\mathbf{r}_{12}$:

$$Q_{\alpha\beta}(\mathbf{r}_2) = Q_{\alpha\beta}(\mathbf{r}_1) + r_\kappa \frac{\partial Q_{\alpha\beta}(\mathbf{r}_1)}{\partial r_\kappa}$$

$$+ \frac{1}{2} r_\kappa r_\lambda \frac{\partial^2 Q_{\alpha\beta}(\mathbf{r}_1)}{\partial r_\kappa \partial r_\lambda}. \qquad (12)$$

Substituting Eq. (12) into Eqs. (10) and (11), the free energy (Eq. (6)) is given by

$$\beta F_1/V = \frac{1}{2} \rho_L^2 C_{LL} \int \frac{4}{9} \epsilon_{\alpha\beta\gamma} Q_{\mu\beta}^{(L)}(\mathbf{r}_1) \partial_\alpha Q_{\mu\gamma}^{(L)}(\mathbf{r}_1) d\mathbf{r}_1$$

$$+ \rho_L \rho_P C_{LP} \int \frac{4}{9} \epsilon_{\alpha\beta\gamma} Q_{\mu\beta}^{(L)}(\mathbf{r}_1) \partial_\alpha Q_{\mu\gamma}^{(P)}(\mathbf{r}_1) d\mathbf{r}_1, \qquad (13)$$

and the free energy (Eq. (7)) is given by

$$\beta F_2/V = \frac{1}{2} \rho_L^2 A_{LL} \int \frac{2}{3} Q_{\alpha\beta}^{(L)}(\mathbf{r}_1) Q_{\alpha\beta}^{(L)}(\mathbf{r}_1) d\mathbf{r}_1$$

$$+ \rho_L \rho_P A_{LP} \int \frac{2}{3} Q_{\alpha\beta}^{(L)}(\mathbf{r}_1) Q_{\alpha\beta}^{(P)}(\mathbf{r}_1) d\mathbf{r}_1$$

$$+ \frac{1}{2} \rho_L^2 B_{LL} \int \frac{1}{3} Q_{\alpha\beta}^{(L)}(\mathbf{r}_1) \partial_\mu \partial_\mu Q_{\alpha\beta}^{(L)}(\mathbf{r}_1) d\mathbf{r}_1$$

$$+ \rho_L \rho_P B_{LP} \int \frac{1}{3} Q_{\alpha\beta}^{(L)}(\mathbf{r}_1) \partial_\mu \partial_\mu Q_{\alpha\beta}^{(P)}(\mathbf{r}_1) d\mathbf{r}_1, \qquad (14)$$

where we define

$$A_{ij} = \int \beta U_{ij,2}(\mathbf{r}_{12}) d\mathbf{r}_{12}, \qquad (15)$$

$$B_{ij} = \int \beta U_{ij,2}(\mathbf{r}_{12}) z^2 d\mathbf{r}_{12}, \qquad (16)$$

$$C_{ij} = \int \beta U_{ij,1}(\mathbf{r}_{12}) \frac{z^2}{r} d\mathbf{r}_{12}, \qquad (17)$$

and we have assumed that the distance between the centers of two particles is small z along the z axis. This expression is now in the form of the integral of a potential energy. We here employ a simple square well interaction potential with a short range d_0, which is the order of the particle size.[40] With this approximation we can take

$$A_{ij} = -v_{ij} v_{ij}, \qquad (18)$$

$$B_{ij} = -\frac{1}{3} v_{ij} v_{ij} d_0^2, \qquad (19)$$

$$C_{ij} = -v_{ij} c_{ij} d_0, \qquad (20)$$

where v_{ij} is the average volume between the particles i and j in random orientations: $v_{LL} = (\pi/4) L^2 D$ and $v_{LP} = (\pi/4) L D^2 n_P$. The interaction parameter $v_{LL}(\equiv -U_{LL,2}/k_B T > 0)$ corresponds to the orientational-dependent (Maier-Saupe) interaction parameter between liquid crystal molecules for a nematic phase and $v_{LP}(\equiv -U_{LP,2}/k_B T)$ is the nematic interaction parameter between a liquid crystal and a polymer. When $v_{LP} > 0$, it means the attractive interaction between a liquid crystal and a polymer chain. The chiral interaction parameter $c_{LL}(\equiv -U_{LL,1}/k_B T > 0)$ corresponds to the strength of the chirality between cholesteric liquid crystal molecules and $c_{LP}(\equiv -U_{LP,1}/k_B T)$ is that between a liquid crystal and a polymer. The physico-chemical origin of the nematic interaction v_{LP} comes from a straightening of polymer chains due to the anisotropic coupling with liquid crystals. When a polymer chain is flexible, the strength of the orientational-dependent interaction is weak and we can take $v_{LP} = 0$. On the other hand, for a semiflexible polymer chain, the value of v_{LP} can have a finite value. The larger v_{LP} value implies that the nematic phase tends to be more stable in the mixed state than in their pure phase.

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 pitch $p = 2\pi/q$:

$$\mathbf{n}(\mathbf{r}) = (\cos qz, \sin qz, 0), \qquad (21)$$

and the tensor order parameter can be expressed as[52]

$$Q_{\alpha\beta}^{(i)}(\mathbf{r}_1) = S_i \left(\frac{3}{2} n_\alpha(\mathbf{r}_1) n_\beta(\mathbf{r}_1) - \frac{1}{2} \delta_{\alpha\beta} \right), \qquad (22)$$

where S_i is the scalar orientational order parameter of the particle $i(= L, P)$:

$$S_i = \int P_2(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) d\Omega. \qquad (23)$$

The scalar order parameters do not depend on $\mathbf{r}$ in our mean field approximations.

Substituting Eqs. (21) and (22) into Eqs. (13) and (14), we obtain the anisotropic free energy:

$$F_{ani} = F_{nem} + F_{dis}, \tag{24}$$

where we have separated the anisotropic free energy into two parts. One is the nematic free energy of Maier-Saupe type:[50]

$$a^3 \beta F_{nem}/V = \sum_{i=L,P} \frac{\phi_i}{n_i} \int f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) \ln 4\pi f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) d\mathbf{r} d\Omega$$
$$- \frac{1}{2}\phi_L^2 S_L^2 v_{LL} - \phi_L \phi_P S_L S_P v_{LP}, \tag{25}$$

and the other is the distortion free energy due to the spatial variation of the director:

$$a^3 \beta F_{dis}/V = -\frac{1}{2}\phi_L^2 S_L^2 g_{LL}(Q) - \phi_L \phi_P S_L S_P g_{LP}(Q), \tag{26}$$

where we define $Q \equiv q d_0$,

$$g_{LL}(Q) \equiv -\frac{1}{2}v_{LL}Q^2 + c_{LL}Q, \tag{27}$$

and

$$g_{LP}(Q) \equiv -\frac{1}{2}v_{LP}Q^2 + c_{LP}Q. \tag{28}$$

B. Distribution functions in an equilibrium state

The orientational distribution function $f_L(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega})$ of the liquid crystals and $f_P(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega})$ of the polymer chains are determined by the anisotropic free energy (Eq. (24)) with respect to these functions: $(\delta F_{ani}/\delta f_i) = 0$, under the normalization condition:

$$\int f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) d\Omega = 1. \tag{29}$$

We then obtain

$$f_L(x) = \frac{1}{Z_L} \exp[n_L(\phi_L S_L G_{LL}(Q) + \phi_P S_P G_{LP}(Q)) P_2(x)] \tag{30}$$

and

$$f_P(x) = \frac{1}{Z_P} \exp[n_P \phi_P S_P G_{LP}(Q) P_2(x)], \tag{31}$$

where we define

$$G_{LL}(Q) \equiv v_{LL} + g_{LL}(Q) \tag{32}$$

and

$$G_{LP}(Q) \equiv v_{LP} + g_{LP}(Q). \tag{33}$$

The constants Z_L and Z_P are determined by the normalization condition as $Z_L = 4\pi I_0[Q]$ and $Z_P = 4\pi J_0[Q]$, respectively. The functions I_m and J_m are defined as

$$I_m[Q] \equiv \int_0^1 [P_2(x)]^m \exp[n_L(\phi_L S_L G_{LL}(Q)$$
$$+ \phi_P S_P G_{LP}(Q)) P_2(x)] dx \tag{34}$$

and

$$J_m[Q] \equiv \int_0^1 [P_2(x)]^m \exp[n_P \phi_P S_P G_{LP}(Q) P_2(x)] dx, \tag{35}$$

respectively, where $m = 0, 1, 2. \ldots$

Substituting Eqs. (30) and (31) into (23), the scalar orientational order parameters S_L and S_P can be determined by the two coupled- self-consistency equations:

$$S_L = I_1[Q]/I_0[Q], \tag{36}$$

$$S_P = J_1[Q]/J_0[Q]. \tag{37}$$

Using the distribution functions, Eqs. (30) and (31), the anisotropic free energy (Eq. (5) or Eq. (24)) for the cholesteric phase is given by

$$a^3 \beta F_{ani}/V = \frac{1}{2}\phi_L^2 S_L^2 G_{LL}(Q) + \phi_L \phi_P S_L S_P G_{LP}(Q)$$
$$- \frac{\phi_P}{n_P} \ln J_0[Q] - \frac{\phi_L}{n_L} \ln I_0[Q]. \tag{38}$$

When $Q = 0$, Eq. (38) results in the nematic free energy.[22,25]

The chemical potential of a liquid crystal molecule is given by

$$\beta \mu_L = \beta(\partial F/\partial N_L)_{N_P}$$
$$= n_L \left[\frac{1}{n_L} \ln \phi_L + \left(\frac{1}{n_L} - \frac{1}{n_P} \right) \phi_P + \chi \phi_P^2 \right.$$
$$+ \frac{1}{2} S_L^2 \phi_L^2 G_{LL}(Q) + S_L S_P \phi_L \phi_P G_{LP}(Q)$$
$$\left. - \frac{1}{n_L} \ln I_0[Q] \right], \tag{39}$$

and that of a polymer:

$$\beta \mu_P = \beta(\partial F/\partial N_P)_{N_L}$$
$$= n_P \left[\frac{1}{n_P} \ln \phi_P + \left(\frac{1}{n_P} - \frac{1}{n_L} \right) \phi_L + \chi \phi_L^2 \right.$$
$$+ \frac{1}{2} S_L^2 \phi_L^2 G_{LL}(Q) + S_L S_P \phi_L \phi_P G_{LP}(Q)$$
$$\left. - \frac{1}{n_P} \ln J_0[Q] \right]. \tag{40}$$

C. Cholesteric pitch and twist elastic constant

The cholesteric pitch $p^*(= 2\pi d_0/Q^*)$ in an equilibrium state can be derived by minimizing the anisotropic free energy F_{ani} (Eq. (38)) with respect to Q:

$$Q^* = Q_0 \left[\frac{1 - [1 - 2\epsilon_x(\frac{S_P}{S_L})]\phi_P}{1 - [1 - 2\epsilon_n(\frac{S_P}{S_L})]\phi_P} \right], \tag{41}$$

where we define $Q_0 \equiv c_{LL}/v_{LL}$, $\epsilon_n \equiv v_{LP}/v_{LL}$, and $\epsilon_x \equiv c_{LP}/c_{LL}$. We have $Q^* = 0$ for $S_L = 0$. The equilibrium value Q^* of the pitch depends on two orientational order parameters in the form S_P/S_L, hence it is temperature and concentration dependent. The cholesteric pitch p^* can be given by

$p^*/p_0 = Q_0/Q^*$, where p_0 is the pitch of the pure liquid crystal. When $\phi_P = 0$, the pitch of the pure liquid crystal is given by $p_0 = 2\pi d_0/Q_0$ and a constant, or temperature independent. By solving the coupled equations (36) and (37), using Q^*, we can obtain the values of two orientational order parameters S_L and S_P as a function of temperature and concentration.

When $\phi_P \ll 1$, we obtain

$$Q^* \simeq Q_0\left[1 + 2(\epsilon_x - \epsilon_n)\frac{S_P}{S_L}\phi_P \cdots\right]. \tag{42}$$

When $\epsilon_x > \epsilon_n$ ($\epsilon_x < \epsilon_n$), the pitch $p(\propto 1/Q)$ decreases (increases) with increasing ϕ_P. The value of $(\epsilon_x - \epsilon_n)S_P/S_L$ corresponds to the "microscopic twisting power" of the solute, depending on the nature of both solute and solvent molecules.[3] The value of the cholesteric pitch also strongly depends on the chiral twisting power ϵ_x between a polymer and a liquid crystal. Using Eq. (41), the distortion free energy (Eq. (26)) yields

$$a^3\beta F_{dis}/V = \frac{1}{2}v_{LL}\phi_L S_L\left(\frac{1}{2}\phi_L S_L + \epsilon_n\phi_P S_P\right)$$
$$\times[(Q - Q^*)^2 - Q^{*2}]. \tag{43}$$

When $Q = Q^*$ the total free energy has a minimum and the cholesteric phase with $Q = Q^*$ is always more stable than the nematic phase with $Q = 0$. There is no nematic-cholesteric phase transitions in our model.

The term in the distortion free energy (Eq. (26)) proportional to Q^2 can be identified as a bare twist elastic constant (K_{22}) and then we obtain

$$(a/k_B T)K_{22} = \frac{v_{LL}}{2}S_L^2\left[\phi_L^2 + \epsilon_n\left(\frac{S_P}{S_L}\right)\phi_L\phi_P\right]. \tag{44}$$

When $\phi_P = 0$, the twist elastic constant of the pure liquid crystal molecule is given by[52]

$$(a/k_B T)K_{22}^\circ = \frac{1}{2}v_{LL}S_L^2. \tag{45}$$

In Section III, we show some numerical results of the physical properties of the cholesteric phase.

III. MIXTURES OF A CHOLESTERIC LIQUID CRYSTAL AND A POLYMER

In our numerical calculations we have three interaction parameters related to cholesteric ordering: the chiral interaction parameter ϵ_x, the nematic interaction ϵ_n between a polymer and a liquid crystal, and the pitch $Q_0(\equiv c_{LL}/v_{LL} = 2\pi d_0/p_0)$ of the pure liquid crystal. We can estimate as $Q_0 \simeq 0.01$ for the typical pitch $p_0 = 3000$ Å and the length $d_0 = 30$ Å of a liquid crystal molecule. We here define the reduced temperature

$$\tau \equiv T/T_{CI} = 4.55/(n_L v_{LL}), \tag{46}$$

where T_{CI} shows the cholesteric-isotropic phase transition (CIT) temperature of a pure liquid crystal. The numerical parameters are given as a function of the temperature τ: $c_{LL} = Q_0 v_{LL}$, $c_{LP} = \epsilon_x c_{LL}$, and $v_{LP} = \epsilon_n v_{LL}$.
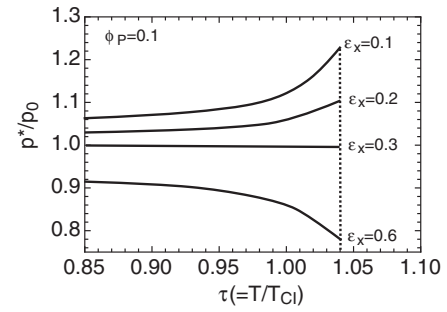

FIG. 1. Cholesteric pitch $p^*/p_0(= Q_0/Q^*)$ plotted against temperature for various values of ϵ_x for $\epsilon_n = 0.3$ and $\phi_P = 0.1$. The pitch strongly depends on the chiral interaction parameter ϵ_x.

A. Cholesteric pitch depending on concentration and temperature

We first show the pitch of a cholesteric phase. Figure 1 shows the cholesteric pitch p^*/p_0, Eq. (41), plotted against the temperature τ at $\phi_P = 0.1$ for $\epsilon_n = 0.3$, $n_L = 2$, and $n_P = 50$. The chiral interaction parameter ϵ_x is changed. At the dotted line the CIT takes place and the pitch becomes infinity. Depending on the chiral interaction parameter ϵ_x, we find three types of temperature-dependent pitch. As shown in Eq. (42), the value of Q^* decreases with increasing S_P/S_L for $\epsilon_x < \epsilon_n$ at a constant ϕ_P. For a weak chiral coupling ($\epsilon_x = 0.1$) between a polymer and a liquid crystal, the pitch increases with increasing temperature and disappears at the CIT. On the other hand, for a strong chiral coupling, or $\epsilon_x > \epsilon_n$ ($\epsilon_x = 0.6$), the pitch decreases with increasing temperature. On decreasing temperature, the pitch becomes almost independent of temperature. When $\epsilon_x = \epsilon_n$ ($\epsilon_x = 0.3$), the pitch is a constant.

Figure 2 shows the orientational order parameters (left) and the ratio (S_P/S_L) (right), plotted against temperature with $\epsilon_n = 0.3$ and $\phi_P = 0.1$. We have the first-order CIT at $\tau \simeq 1.04$, where the orientational order parameters jump and increase with decreasing temperature. The value of the ratio S_P/S_L decreases with decreasing temperature and becomes almost a constant. As shown in Eq. (42), the temperature dependence of the pitch strongly depends on the sign of $\epsilon_x - \epsilon_n$ and S_P/S_L.

Figure 3 shows the cholesteric pitch p^*/p_0, Eq. (41), plotted against the polymer concentration at $\tau = 0.95$ for
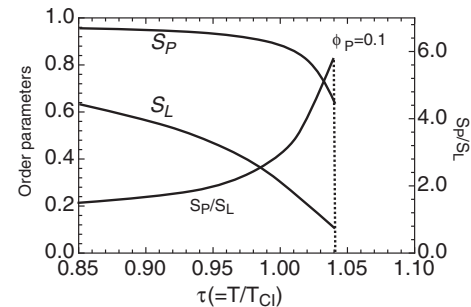

FIG. 2. Orientational order parameters (left) and the ratio (S_P/S_L) (right), plotted against temperature with $\epsilon_n = 0.3$ and $\phi_P = 0.1$. The order parameters decrease with increasing temperature and we have the first-order CIT at $\tau \simeq 1.04$.
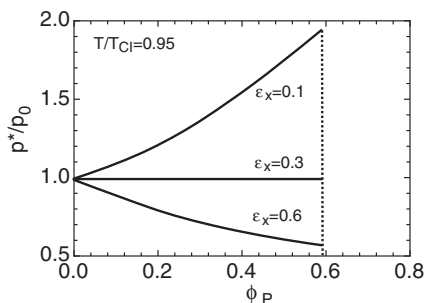
FIG. 3. Cholesteric pitch $p^*/p_0 (= Q_0/Q^*)$ plotted against the polymer concentration for the various values of ϵ_x with $\epsilon_n = 0.3$ and $\tau = 0.95$.

FIG. 5. Orientational order parameters S_P, S_L, and the ratio S_P/S_L, plotted against the polymer concentration ϕ_P for $\tau = 0.9$ in Fig. 4.

$\epsilon_n = 0.3$, $n_L = 2$, and $n_P = 50$. At the dotted line the CIT takes place. When $\epsilon_x > \epsilon_n$, the pitch decreases with increasing ϕ_P, because of the strong chiral coupling between a polymer and a liquid crystal. When the chiral coupling parameter is weak, $\epsilon_x < \epsilon_n$, the helical pitch increases with ϕ_P and unwinds at the CIT. These numerical results are consistent with the experimental results.[2, 8, 11–13] The pitch strongly depends on the chiral interaction parameter ϵ_x between a polymer and a liquid crystal.

B. Phase separations

In this subsection we show the phase behaviors of mixtures of a polymer and a cholesteric liquid crystal. The equilibrium free energy is calculated by substituting Q^* into Eq. (38). The coexistence (binodal) curve can be calculated from the standard common-tangent construction in the free energy (Eq. (1)) to find coexisting phases of different concentrations. We here take $\chi/v_{LL} = 0.1$. The binodal curves are also obtained by solving the two-phase coexistence conditions: the chemical potentials μ_L and μ_P of coexisting phases have to be equal to each other.

Figure 4 shows the phase diagram on the temperature-concentration plane for $\epsilon_n = 0.3$, $\epsilon_x = 0.2$, $n_L = 2$, and $n_P = 10$. Solid curves show the binodal line and the dotted line shows the CIT. The CIT temperature decreases with increasing polymer concentrations because of dilution. Below $\tau < 1$, we have the phase separation (Ch+I) between a cholesteric (Ch) and an isotropic (I) phase. The CIT line is hidden inside the binodal lines. With decreasing temperature,

the width of the two-phase region becomes wide. At the low polymer concentrations, we have the stable cholesteric phase.

Figure 5 shows the orientational order parameters S_P of the polymer and S_L of the liquid crystal, plotted against the polymer concentration at $\tau = 0.9$ in Fig. 4. The orientational order parameters decrease with increasing the concentration of polymer chains and we have the first-order CIT at $\phi_P \simeq 0.19$. The orientational order of the polymer is higher than that of the liquid crystal, because of the coupling between the polymer and liquid crystal. For a weak coupling, or smaller values of ϵ_n, the orientational order S_P has smaller values than that of S_L and the binodal curve of the cholesteric phase in Fig. 4 shifts to the lower concentrations.

Figure 6 shows the cholesteric pitch p^*/p_0, Eq. (41), plotted against the volume fraction of polymers for various temperatures in Fig. 4. As shown in Eq. (42), the value of Q^* decreases with increasing ϕ_P for $\epsilon_x < \epsilon_n$, or the pitch increases with increasing ϕ_P. Figure 7 shows the twist elastic constant K_{22} plotted against the volume fraction of polymers for various temperatures. The elastic constant decreases with the increasing polymer concentration. The value of K_{22} increases with decreasing temperature at a fixed ϕ_p. When $(a/k_BT)K_{22} = 0.5$, by taking $k_BT \simeq 1$ kcal/mol and $a \simeq 15$ Å, we can estimate $K_{22} \sim 10^{-6}$ dyn, which is the correct order of magnitude of the elastic constant.[3] Our numerical results are consistent with the experimental observations.

C. Polymer-induced cholesteric phases

When the nematic coupling between a polymer and a liquid crystal is strong, the phase behaviors are drastically
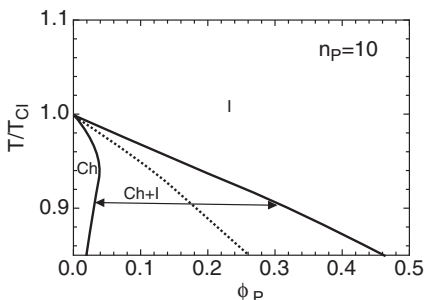

FIG. 4. Phase diagram on the temperature-concentration plane for $\epsilon_n = 0.3$, $\epsilon_x = 0.2$, $n_L = 2$, and $n_P = 10$. Solid curves show the binodal line and the dotted line shows the cholesteric-isotropic phase transition.
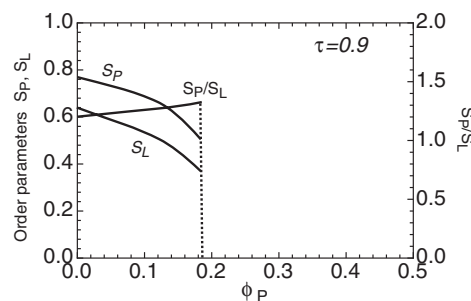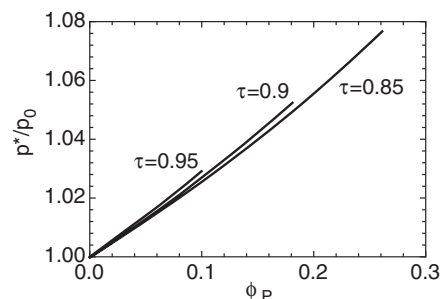

FIG. 6. Cholesteric pitch p^*/p_0, Eq. (41), plotted against the volume fraction of polymers for various temperatures in Fig. 4.
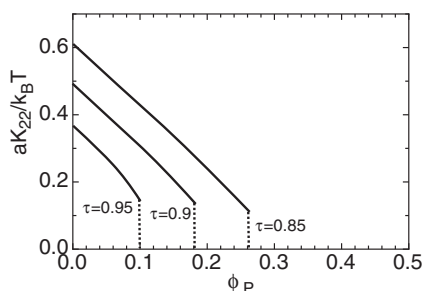
FIG. 7. Twist elastic constant K_{22} plotted against the volume fraction of polymers for various temperatures in Fig. 4.
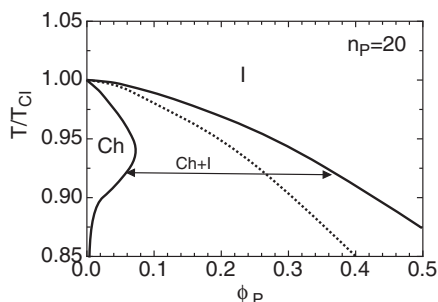

FIG. 9. Phase diagram on the temperature-concentration plane for $\epsilon_n = 0.3$, $\epsilon_x = 0.2$, $n_L = 2$, and $n_P = 50$. Solid curves show the binodal line and the dotted line shows the cholesteric-isotropic phase transition. The strong anisotropic coupling between a polymer chain and a liquid crystal induces the cholesteric phase at high temperatures.

changed. On increasing the molecular weight of a polymer chain, this anisotropic coupling becomes dominant. The anisotropic coupling between a polymer and a liquid crystal has been widely studied in nematic and smectic A phase in polymer and liquid crystal mixtures. It has been recognized that smectic A and nematic phases can be induced in a nematic liquid crystal mixture by strong mesogenic interactions.[26–29]

Figure 8 shows the phase diagram on the temperature-concentration plane for $n_P = 20$. Solid curves show the binodal line and the dotted line shows the CIT. We have the phase separation (Ch+I). On increasing the molecular weight of the polymer, the anisotropic coupling between a polymer and a liquid crystal becomes strong and the CIT line shifts to higher temperatures and the binodal line of the cholesteric phase shifts to higher concentrations, compared to $n_P = 10$ (Fig. 4).

Figure 9 shows the phase diagram on the temperature-concentration plane for $n_P = 50$. Solid curves show the binodal line and the dotted line shows the CIT. We find that the CIT temperature increases from $\tau = 1$ with increasing ϕ_P and has a maximum as a function of ϕ_P. The cholesteric phase is stabilized by the anisotropic coupling between a polymer chain and a liquid crystal.[53] The binodal lines of the phase separation (Ch+I) merge, or exhibit azeotropes, at which the two equilibrium isotropic and cholesteric phases have the same composition, while the cholesteric-isotropic phase separation (Ch+I) appears at high polymer concentrations. At the lower temperatures of the polymer induced-cholesteric phase, we have the phase separation between two cholesteric phases (Ch$_1$+Ch$_2$) with different polymer concen-

trations. In this figure we have calculated with $\epsilon_n = 0.3$. When the nematic interaction is weak, for example, $\epsilon_n = 0.1$, such induced-cholesteric phase does not appear and we only have the cholesteric-isotropic phase separations, where the CIT temperature decreases from $\tau = 1$ with increasing ϕ_P, as shown in Fig. 4.

Figure 10 shows the cholesteric pitch p^*/p_0, Eq. (41), plotted against the temperature for various values of the polymer concentration ϕ_P in Fig. 9. As shown in Eq. (42), for $\epsilon_x < \epsilon_n$, the pitch increases with increasing ϕ_P. Figure 11 shows the twist elastic constant K_{22} plotted against the volume fraction ϕ_P for various temperatures in Fig. 9. At low temperatures ($\tau < 1$), the value of K_{22} decreases with the increasing polymer concentration ϕ_P. This is similar to Fig. 7. At high temperatures ($\tau > 1$), however, the K_{22} has a maximum as a function of ϕ_P due to the appearance of polymer-induced cholesteric ordering.

In our theory, there are two important molecular parameters to understand cholesteric behaviors in the liquid crystal/polymer mixtures: one is the nematic interaction ϵ_n and the other is the chirality parameter ϵ_x between a polymer and a liquid crystal. The chiral interaction ϵ_x depends on the helical configuration between a polymer and a liquid crystal. The phase diagrams including the CIT and binodal curves are almost independent of the chiral interaction parameter ϵ_x, because the contribution of the chirality in the free energy is small (order of $Q(\ll 1)$), although, the pitch strongly depends on ϵ_x. The larger values of ϵ_x correspond to the smaller pitch,

FIG. 8. Phase diagram on the temperature-concentration plane for $\epsilon_n = 0.3$, $\epsilon_x = 0.2$, $n_L = 2$, and $n_P = 20$. Solid curves show the binodal line and the dotted line shows the cholesteric-isotropic phase transition.
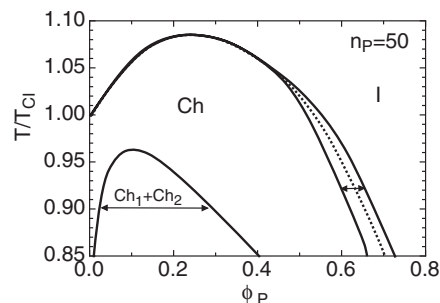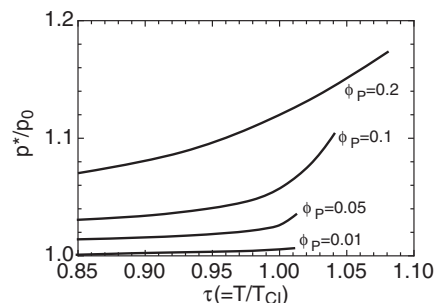

FIG. 10. Cholesteric pitch p^*/p_0, Eq. (41), plotted against the temperature for various of the polymer concentration ϕ_P in Fig. 9
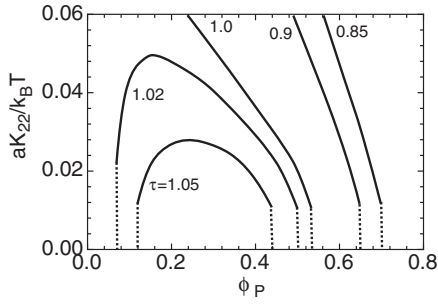
FIG. 11. Twist elastic constant K_{22} plotted against the volume fraction of polymers for various temperatures in Fig. 9.

FIG. 12. Ratio S_P/S_L of two orientational order parameters plotted against the reduced-temperature for various values of ϵ_n with $\phi_P = 0.01$.

where the pitch decreases with increasing temperature and polymer concentration.

IV. MIXTURES OF A NEMATIC LIQUID CRYSTAL AND A CHIRAL DOPANT

Our theory presented in Sec. III can describe mixtures of a non-chiral nematic liquid crystal ($i = L$) and a chiral dopant ($i = P$). In this section we focus on the pitch of the mixtures. It is well known that when a non-chiral nematic liquid crystal phase is doped with a low concentration of a chiral molecule, a chiral nematic phase is formed with a helical pitch, which is inversely proportional to the concentration of the chiral dopant.[3] This chiral nematic phase is induced by a chiral coupling between the liquid crystal and dopant. In Sec. III, we have considered the chiral coupling between two constituent molecules and then our theory can give the underlying physics of the chiral coupling.

For non-chiral nematic liquid crystal molecules ($i = L$), we can take $U_{LL,1} = 0$ in Eq. (4), or $c_{LL} = 0$ in Eq. (27). Then the cholesteric pitch (or the wave number Q of the cholesteric pitch) is given as a function of the volume fraction ϕ_P of the chiral dopant:

$$Q = \frac{2\epsilon_n \alpha_x \left(\frac{S_P}{S_L}\right)\phi_P}{1 - \left[1 - 2\epsilon_n\left(\frac{S_P}{S_L}\right)\right]\phi_P}, \tag{47}$$

where $\alpha_x (\equiv c_{LP}/v_{LP})$ shows the strength of the chirality of dopants ($\epsilon_n \alpha_x = c_{LP}/v_{LL}$).

When $\phi_P \ll 1$, we find

$$Q/\phi_P \simeq H_{TP} + H_{TP}\left(1 - \frac{H_{TP}}{\alpha_x}\right)\phi_P + \cdots, \tag{48}$$

where

$$H_{TP} \equiv 2\epsilon_n \alpha_x \frac{S_P}{S_L} \tag{49}$$

is called the helical twisting power of a chiral dopant.[1,3] The larger values of H_{TP} correspond to the smaller pitch. For $H_{TP} > 0$, the wave number Q of the twist pitch linearly increases with increasing ϕ_P at dilute solutions, which is consistent with the experiments.[1,53–55] The temperature and concentration dependences of H_{TP} are given through the ratio S_P/S_L.

Figure 12 shows the ratio S_P/S_L of two orientational order parameters plotted against the reduced-temperature for various values of ϵ_n with $\phi_P = 0.01$. The other parameters are
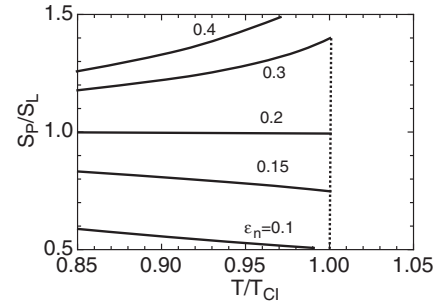
the same with Fig. 4. We find that the temperature dependence of H_{TP} has three types. When $\epsilon_n = 0.3$ and 0.4, or a strong coupling between a nematic liquid crystal and a chiral dopant, the value of S_P/S_L is larger than unity and increases with increasing temperature because of the anisotropic coupling between a liquid crystal and a chiral dopant. The value of H_{TP} increases with increasing temperature. On the other hand, for a weak coupling $\epsilon_n = 0.1$ and 0.15, the ratio of two order parameters decreases with increasing temperature. In this case, the polymer chains are weakly oriented due to the weak anisotropic coupling with liquid crystal molecules. The H_{TP} decreases with increasing temperature. When $\epsilon_n = 0.2$, the value S_P/S_L is independent of temperature and the helical twisting power becomes a constant. When $S_P/S_L \simeq 1$, $\alpha_x = 1$, and $d_0 = 0.004$ μm, we can estimate the helical twisting power HTP $= H_{TP}/d_0 \simeq 100$ (μm^{-1}), which is consistent with the magnitude of the helical twisting power in nematic liquid crystals K15 induced by TADDOL dopants.[56] The temperature dependence of the helical twisting power is determined by the nematic interaction parameter ϵ_n between a liquid crystal and a chiral dopant.

Using the twist elastic constant (Eq. (45)) of the pure nematic liquid crystal, we find that the helical twisting power can be expressed as

$$H_{TP} = \frac{c_{LP}S_P}{aK_{22}^{\circ}/k_BT} \simeq \frac{c_{LP}}{aK_{22}^{\circ}/k_BT}, \tag{50}$$

for $S_P \simeq 1$. The helical twisting power is inversely proportional to the twist elastic constant K_{22}°[57–60] and the sign of H_{TP} depends on the values of c_{LP} and S_P. Note that the positive values of c_{LP} correspond to an attractive chiral interaction between a nematic liquid crystal and a dopant. The sophisticated calculations of HTP have been studied by many authors.[57–61] Following the simulation of Allen,[58] the parameter c_{LP} in our model corresponds to the difference $\Delta\mu$ in the chemical potentials between mirror image forms of a dopant, where $\Delta\mu$ changes the sign as a function of twist angle between the symmetry axes of two ellipsoids. Due to the surface chirality model developed by Ferrarini et al., the term $c_{LP}S_P$ can correspond to the chirality order parameter, which describes the coupling between the chiral surface of the molecule and its orientational ordering.[60]

As shown in Fig. 13, when Q/ϕ_P is plotted against ϕ_P, using Eq. (48), the intercept corresponds to H_{TP} and the slope
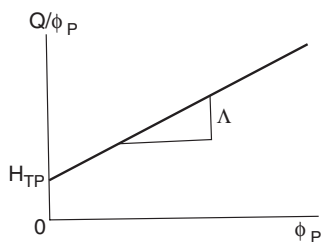
FIG. 13. Wave number Q/ϕ_P plotted against ϕ_P for $H_{TP} > 0$ (see Eq. (48)). When $H_{TP} < 0$, the slope becomes negative.

(Λ) shows the value

$$\Lambda = H_{TP}\left(1 - \frac{H_{TP}}{\alpha_x}\right), \tag{51}$$

yielding

$$\alpha_x = \frac{H_{TP}}{1 - \Lambda/H_{TP}}. \tag{52}$$

Using Eq. (49), we have

$$\epsilon_n = \frac{H_{TP}}{2\alpha_x(S_P/S_L)} \simeq \frac{H_{TP}}{2\alpha_x}. \tag{53}$$

for $S_P/S_L \simeq 1$. Then if we experimentally observe H_{TP} and Λ, the strength of chirality c_{LP} (or α_x) and the nematic interaction ϵ_n can be determined from Eqs. (52) or (50) and (53). When $\Lambda \simeq 0$, we have $\alpha_x \simeq H_{TP}$ and the value of ϵ_n is of the order of unity.

V. SUMMARY

We have presented a mean field theory to describe phase behaviors in mixtures of a polymer and a cholesteric liquid crystal. Our main original contribution is to taking into account the chiral coupling between a polymer and a liquid crystal. As the results, we obtain analytical expressions of the pitch of the cholesteric phase and the twist elastic constant as a function of orientational order parameters of a polymer and a liquid crystal.

The pitch of the cholesteric phase depends on the chiral interaction parameter ϵ_x and the nematic parameter ϵ_n and is given as a function of temperature and concentration through the ratio of orientational order parameters in the form S_P/S_L. When $\epsilon_x > \epsilon_n$ ($\epsilon_x < \epsilon_n$), the pitch decreases (increases) with increasing the polymer concentration and temperature. We also find isotropic-cholesteric and cholesteric-cholesteric phase separations on the temperature-concentration plane. We demonstrate that a strong coupling between a polymer and a liquid crystal can stabilize cholesteric phases.

Our theory can apply to mixtures of a non-chiral nematic liquid crystal and a chiral dopant. We have derived the pitch as a function of the concentration of chiral dopants and the orientational order parameters, and the chiral interaction parameters. We have shown that these chiral interaction parameters can be determined by experiments. We find that the HTP is given as a function of a ratio of orientational order parameters in the form S_P/S_L, which depends on temperature and concentration. For a strong (weak) nematic coupling between a nematic liquid crystal and a chiral molecule, the HTP increases (decreases) with increasing temperature. Our theory is consistent with some experimental observations.

In this paper we have considered the equilibrium properties of cholesteric phases in mixtures of a liquid crystal and a polymer. The kinetics of the phase ordering process is also important. Luca and Rey have used a model based on the Landau-de Gennes theory to understand the structure formation process of the twisted polywood architecture ubiquitously found in biological fibrous composites.[32,33] They found that the phase ordering process is slowed by an increase in chirality, linked to a biaxiality. We hope that our theory will be applied to understand the kinetics of phase separations including cholesteric phases in mixtures of a liquid crystal and a polymer.

We here do not take into account biaxiality[42,62] of a cholesteric phase and also neglect excluded volume interactions, which are important for long rodlike molecules.[51] This entropic contribution affects the temperature dependence of a cholesteric pitch.[43] The theory can be extended to nematic and cholesteric liquid crystal mixtures, binary mixtures of cholesteric liquid crystals, cholesteric liquid crystalline polymers, and lyotropic cholesteric phases.

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