Nematic-cholesteric mixture in a magnetic field: A change in the critical behavior

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This work is devoted to the self-consistent account of possible concentration-uniformity distortion, when an external magnetic (or electric) field is applied perpendicular to the cholesteric axis in a nematic-cholesteric mixture. It is shown that this effect changes the critical value of the external field, when the helical pitch diverges to infinity, and the critical behavior from logarithmic to an inverse power.

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I. INTRODUCTION

The influence of an external magnetic [1] or electric [2] field on a cholesteric pitch has been studied quite well. de Gennes was the first to study this problem theoretically [3] and now it is a classical one. The main results of his work are the following:

(1) The pitch P should increase with an increase in the magnetic field H applied perpendicular to the cholesteric axis.

(2) There is critical value of external field H_c, when the pitch P diverges to infinity and the phase transition of second order takes place.

(3) The critical behavior $P(H)$ is logarithmic:

$$P(H)/P_0 \approx \frac{2}{\pi^2}\ln\left[\frac{16}{1-(H/H_c)^2}\right].$$

The distortion of a helix by an external field has had good confirmation in a number of experimental works (beginning with Refs. [4,5]) almost all of which was carried out on nematic samples doped with a small amount of cholesteric. But it is worth noting that, so far as all experimental measurements had a great many errors in the vicinity of H_c, it leaves the question open regarding the critical behavior of the mixtures.

Figure 1 shows that regions (A) where molecules oriented along the magnetic field H grow as H increases. Director rotation $d\varphi/dz$ becomes nonuniform, and one could suppose that the enrichment of the director rapid rotation regions (B) with chiral dopants decreases the free energy.

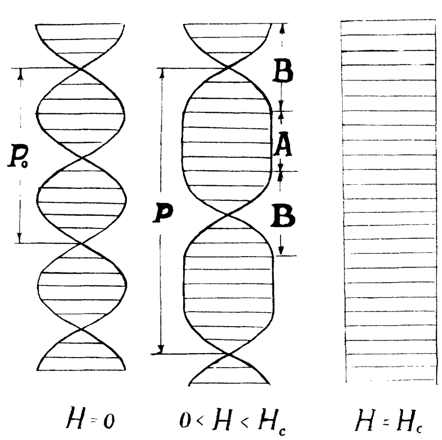

FIG. 1. Schematic representation of director rotation.

That is why this work is devoted to the self-consistent account of possible concentration-uniformity distortion. As will be shown below, this effect changes the critical behavior of the system.

II. HELIX DISTORTION IN AN INHOMOGENEOUS NEMATIC-CHOLESTERIC MIXTURE

Let $c(z)=c_0+\tilde{c}(z)$, where c_0 is the averaged concentration, $\tilde{c}(z)$ is a small deviation, which satisfies the condition

$$\int_0^P \tilde{c}(z)dz=0\ . \tag{1}$$

To consider the concentration distortion effect we represent the free-energy density as a sum of two terms, $f=f_{\rm mic}+f_{\rm mac}$, where $f_{\rm mic}$ takes into account the intermolecular interaction and entropy term and $f_{\rm mac}$ includes the elastic energy and external field effect

$$f_{\rm mac}=\frac{1}{2}\left[K_{22}\left[\frac{d\varphi}{dz}-\beta\right]^2-\frac{\Delta\chi}{4\pi}H^2\sin^2\varphi\right], \tag{2}$$

where $\Delta\chi$ is the magnetic anisotropy.

One can expand $f_{\rm mic}$ over $\tilde{c}(z)$,

$$f_{\rm mic}=f_0+f_1\tilde{c}(z)+\tfrac{1}{2}f_2[\tilde{c}(z)]^2+\tfrac{1}{2}g\left[\frac{d\tilde{c}(z)}{dz}\right]^2+\cdots, \tag{3}$$

where

$$f_i=\left.\frac{\partial^i f_{\rm mic}}{\partial c^i}\right|_{c=c_0}.$$

To calculate f_i one can use, for instance, the Maier-Saupe model as it has been developed in [6].

Since the characteristic length of concentration heterogeneity is about the helical pitch, the gradient term is negligible because the coefficient $g\approx\xi^2 f_2$ (where ξ is about intermolecular distances). The coefficient f_2 must be positive to ensure that the uniform concentration minimizes the free energy.

The macroscopical part of the free energy depends on the chiral dopant concentration through K_{22}, $\Delta\chi$, and β, but $\beta(c)$ gives the main contribution. Therefore, we assume that K_{22} and $\Delta\chi$ are constants and β is proportional to the dopant concentration

$$\beta=\beta_c c(z)=\beta_0+\beta_c\tilde{c}(z), \quad \beta_0=\beta_c c_0 .$$

So the averaged free-energy density is

$$\bar{f}=f_0+\frac{1}{2P}\int_0^P\left\{f_2[\tilde{c}(z)]^2+K_{22}\left[\frac{d\varphi}{dz}-\beta_0-\beta_c\tilde{c}(z)\right]^2 -\frac{\Delta\chi}{4\pi}H^2\sin^2\varphi\right\}dz . \quad (4)$$

To obtain the minimum value of $\bar{f}$ we minimize at first this functional over $\varphi(z)$ and $\tilde{c}(z)$ under condition (1) and fixed helical pitch P, and then we find the minimum of $\bar{f}(P)$. The Euler variation equations are the following:

$$\frac{\mathcal{H}^2}{2}\sin(2\varphi)=\frac{d^2\varphi}{dz^2}-\beta_c\frac{d\tilde{c}(z)}{dz}, \quad \mathcal{H}^2=\frac{\Delta\chi H^2}{4\pi K_{22}} ,$$
$$K_{22}\beta_c\left[\frac{d\varphi}{dz}-\beta_0-\beta_c\tilde{c}(z)\right]+\mathcal{L}-f_2\tilde{c}(z)=0 , \quad (5)$$

where $\mathcal{L}$ is the Lagrange factor.

The solution of variation equations gives

$$\bar{f}=f_0+\frac{\mathcal{H}^2}{4(2-\delta)}\left\{\frac{1}{k\mathcal{K}(k)}\left[\frac{\mathcal{E}(k)}{k}(1-\delta)(2-\delta)-\pi\beta_0\frac{\sqrt{1-\delta}}{\mathcal{H}}\right]+\beta_0^2\frac{1-\delta}{\mathcal{H}^2}-\frac{(1-\delta)}{k^2}+\frac{\pi^2\delta(1-\delta)}{4k^2\mathcal{K}^2(k)}\right\}, \quad (6)$$

where

$$P=2k\frac{\sqrt{1-\delta}}{\mathcal{H}}\mathcal{K}(k), \quad \delta=\frac{K_{22}\beta_c^2}{K_{22}\beta_c^2+f_2} , \quad (7)$$

$\mathcal{K}(k)$ and $\mathcal{E}(k)$ are the first and the second elliptic integrals.

To minimize $\bar{f}(P)$ we use the condition $d\bar{f}(P)/dk=0$, because P is a monotonic function of k. This condition gives the implicit dependence $P(H)$ as $P(k)$ and $H(k)$, $0\le k\le 1$,

$$h=H/H_c=k\frac{2-\delta}{2W(k,\delta)},$$
$$p=P/P_0=(1-\delta)\frac{4}{\pi^2}\mathcal{K}(k)W(k,\delta) , \quad (8)$$

where

$$P_0=2\pi/\beta_0, \quad H_c=\frac{\pi}{(2-\delta)}\beta_0\left[\frac{4\pi K_{22}}{\Delta\chi(1-\delta)}\right]^{1/2} \quad (9)$$

and

$$W(k,\delta)=\mathcal{E}(k)(2-\delta)/2 +\delta\left[\frac{\pi^2}{4\mathcal{K}(k)}\frac{2-\delta}{1-\delta}-\frac{1-k^2}{2}\frac{\mathcal{K}^2(k)}{\mathcal{E}(k)}\right] . \quad (10)$$

III. RESULTS AND DISCUSSION

First of all, we should note that the account of concentration heterogeneity slightly increases the critical field according to (9). The parameter δ characterizes the ability of the system to disturb the concentration homogeneity. Figure 2 shows the helical pitch dependence on the magnetic field under different δ. A case when $\delta=0$ corresponds to uniform concentration and our calculations coincide with de Gennes's results (curve 1). Curves 2 ($\delta=0.05$) and 3 ($\delta=0.1$) show that when $1-h \gg \delta$, the influence of concentration heterogeneity is negligible. Nevertheless, these curves have another asymptotic when $h\rightarrow 1$. Due to the second term in $W(k,\delta)$ [Eq. (10)],

$$1-h\sim\frac{\delta}{\mathcal{K}(k)} ,$$

and the dependence of $p(h)$ becomes an inverse power

$$p\sim\frac{\delta}{1-h} .$$

Therefore, even for very small δ, the logarithmic behavior, which has been predicted for a pure cholesteric, has to transform into an inverse power for a nematic-cholesteric mixture. This transformation is caused by the concentration wave and occurs when

$$H\ge H_c(1-2\delta), \quad P\ge P_0\frac{2}{\pi^2}\ln(4/\delta) . \quad (11)$$

Figure 3 shows the spatial distribution of concentration, which is given by

$$\tilde{c}(z)=c_0\frac{\pi\delta}{W(k,\delta)}\left\{dn\left[\frac{z}{P_0W(k,\delta)}\right]-\frac{\pi}{2}\mathcal{K}(k)\right\}, \quad (12)$$

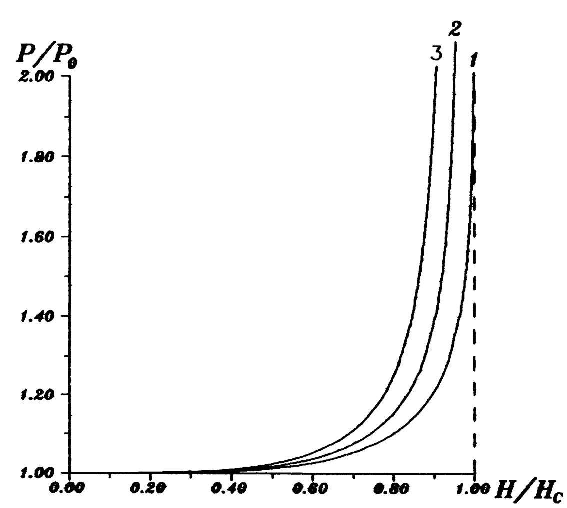

FIG. 2. Helical pitch P dependence on magnetic-field H in normalized form under different δ: (1) $\delta=0$; (2) $\delta=0.05$; (3) $\delta=0.1$.

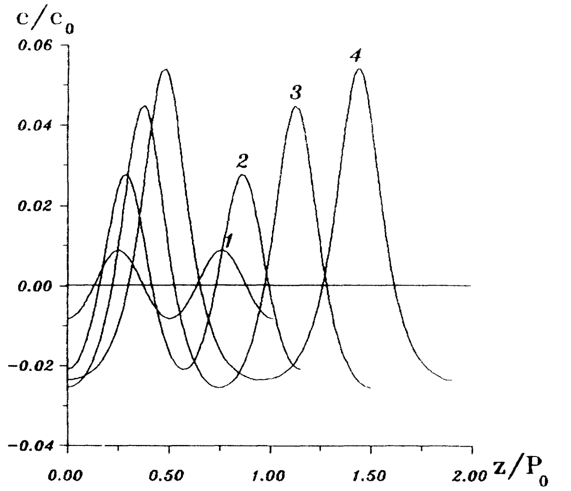

FIG. 3. Concentration waves for $\delta = 0.05$ under different magnetic fields: (1) $h = 0.485$; (2) $h = 0.797$; (3) $h = 0.919$; (4) $h = 0.947$.

where $dn[\ ]$ is a Jacobian elliptic function. If $h < 1 - 5\delta$, the concentration wave is sinusoidal (curve 1), and when $h \to 1$ it transforms into a set of constant shaped peak spaced in a half of a pitch (curves 2–4). The maximum peak amplitude

$$\tilde{c}_{\max} = c_0 \frac{\pi\delta}{(1-\delta)(2-\delta)} \tag{13}$$

remains rather small, so the transaction of series (3) is valid. In a critical region where the inverse power behavior $P(H)$ occurs, concentration peaks have been formed and scatter, keeping their shape.

The concentration wave amplitude (13) and the region with inverse power behavior (11) are determined by the parameter δ (7). The estimations in the framework of the Maier-Saupe model [6] show that $f_2 \cong (10-0.01) n k_B T$, where n is molecular density. To get the maximum amplitude effect, optical active dopants (OAD's) with high helical twisting power [for instance, derivatives of benzylidene-1-menthon (DBLM) with $\beta_c \approx 0.24\ \mathrm{nm}^{-1}$ [7] or chiral biaryls with $\beta_c \approx 0.4\ \mathrm{nm}^{-1}$ [8]] should be used. In this case, $\delta \cong 0.1-0.001$ for mixtures with common thermotropic nematics ($n = 2\times 10^{21}\ \mathrm{cm}^{-3}$, $K_{22} = 4\times 10^{-7}$ dyne), and this is sufficient for experimental observation. We suppose that different behaviors of mixtures DBLM+N-(4′-methoxybenzylidene)-4-(n-butyl)aniline and DBLM+N-(4′-butyloxybenzylidene)-4-(n-butyl)aniline in a magnetic field [9] may be caused by the concentration distortion effect. The parameter δ may be greater than 0.1 in thermotropic mixtures with a saturated concentration of OAD (when $f_2 \to 0$) or in lyotropic mixtures with low n, but these cases will be considered in another paper because the expansion (3) becomes invalid.

IV. CONCLUSIONS

The influence of an external magnetic (or electric) field on a cholesteric pitch is usually studied in nematic-cholesteric mixtures. Therefore, the possibility of concentration inhomogeneity is considered in this paper. The calculated dependence $P(H)$ [Eq. (8), Fig. 2] shows that concentration distortion is significant near the cholesteric-nematic transition and causes two effects: (1) the critical field H_c slightly increases (9), and (2) the cholesteric-nematic transition remains as the second-order phase transition, but the critical behavior of pitch always transforms from logarithmic to inverse power [Eqs. (8)–(10)].

The concentration wave amplitude (13) and the region with inverse power behavior (11) are determined by the parameter δ (7). Therefore, the experimental observation is useful to carry on in thermotropic mixtures with high helical twisting dopants or in lyotropic mixtures.

The electric-field effect gives the same results (with substitution $H \to E$, $\Delta\chi \to \Delta\epsilon$) if $\Delta\epsilon \ll \epsilon$. In the opposite case, the electric field becomes inhomogeneous and requires another consideration.

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[1] E. Sackmann, S. Meiboom, and L. Snyder, J. Am. Chem. Soc. **89**, 5981 (1967).
[2] J. J. Wysocki, J. Adams, and W. Haas, Phys. Rev. Lett. **20**, 1024 (1968).
[3] P. G. de Gennes, Solid State Commun. **6**, 163 (1968).
[4] R. B. Meyer, Appl. Phys. Lett. **14**, 208 (1969).
[5] G. Durand, L. Leger, F. Rondelez, and M. Veyssie, Phys. Rev. Lett. **22**, 227 (1969).
[6] Yu. G. Terentieva and S. V. Shiyanovskii, Zh. Eksp. Teor. Fiz. **102**, 1189 (1992) [Sov. Phys. JETP **75**, 645 (1992)].
[7] I. B. Nemchenok, A. V. Tolmachev, L. A. Kutulya, and V. G. Tishchenko, Zh. Fiz. Khim. **60**, 635 (1986).
[8] G. Gottarelli, M. Osipov, and J. P. Spada, J. Phys. Chem. **95**, 3879 (1991).
[9] Yu. A. Grinchenko and A. V. Tolmachev, Ukr. Fiz. Zh. **33**, 374 (1988).