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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Shiyankovskii, Serguey V. and Terentieva, Julia G.(1996) 'Critical behaviour of the cholesteric to nematic transition in an electric field', *Liquid Crystals*, 21: 5, 645 – 650

To link to this Article: DOI: 10.1080/02678299608032876

URL: <http://dx.doi.org/10.1080/02678299608032876>

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Critical behaviour of the cholesteric to nematic transition in an electric field

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(Received 9 February 1996; accepted 29 April 1996)

This work is devoted to a self-consistent account of concentration-uniformity distortion in nematic–cholesteric mixtures in an electric field. In so far as the dielectric anisotropy of the components may differ both in absolute value and in sign, we take into account the fact that the local value of $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ may depend on the local concentration of the components. The occurrence of concentration heterogeneity has the following consequences: (a) the critical field slightly increases, (b) the cholesteric–nematic transition remains as a second-order phase transition, but the critical behaviour of the pitch transforms from logarithmic to inverse power. It was shown that when the applied field increases, the periodicity of the structure is divided into two regions: a quasi-nematic region (when the director is parallel with the external field) and a crest in the concentration wave. When \mathbf{E} goes to \mathbf{E}_c , the crest of the concentration wave is nearly constant and the quasi-nematic region grows. When the dielectric anisotropies of the components are equal, the concentration wave causes enrichment with chiral dopant of regions where the director is rapidly rotating. When $\Delta\varepsilon$ of the chiral component has a higher value than $\Delta\varepsilon$ of the nematic component, the extent of this effect also intensifies the effect of stratification of the system. Conversely, when $\Delta\varepsilon^N > \Delta\varepsilon^{Ch}$, both of the mechanisms compete and the structure of the crest becomes more complex.

1. Introduction

The distortion of the cholesteric helical pitch under an external field (electric or magnetic) has been well studied; de Gennes was the first to describe theoretically the unwinding of the helical pitch [1]. At a certain critical field \mathbf{E}_c , the pitch diverges to infinity logarithmically and the cholesteric to nematic phase transition occurs.

The influence of an external field on cholesteric pitch has been confirmed well from a number of experimental studies (beginning with [2, 3]). However, it is necessary to note that almost all of these were carried out, not on pure cholesteric samples (a pure cholesteric pitch P_0 is about 0.1–0.5 μ and requires a critical field 10^5 V cm⁻¹), but on nematic samples doped with a small amount of cholesteric (this gives P_0 about 10–50 μ and critical fields of 10^3 V cm⁻¹). In view of this, we raise a question: is the critical behaviour of a nematic–cholesteric mixture the same as for a pure cholesteric (as described by de Gennes)? Some experiments, e.g. [3], show that the helical pitch can increase up to five times. But even a simple estimate shows that this requires a critical field approaching $(\mathbf{E} - \mathbf{E}_c)/\mathbf{E}_c \approx 10^{-10}$. It is also worth noting that all the experimental measurements involved a great

many errors in the vicinity of \mathbf{E}_c , and so this leaves the question open regarding the critical behaviour of mixtures.

The first theoretical investigation of a heterogeneous system (elongated ferroelectric particles suspended in a nematic or cholesteric phase) in a magnetic field was carried out by Brochard and de Gennes [4]. But some approximations such as (a) that the interaction with the external field is dominant for the particles and (b) the polarity of the structure, are not valid for normal nematic–cholesteric mixtures, for which we suppose another mechanism for the homogeneous distortion.

It is well known that regions (A) where the molecules are oriented along the external field \mathbf{E} (figure 1) grow as \mathbf{E} increases. Director rotation $d\phi/dz$ becomes non-uniform, and one could suppose that with chiral dopants the enrichment of regions involving rapid rotation of the director (B) decreases the free energy.

The unwinding of the nematic–cholesteric mixture by a magnetic field was studied in [5]. For the case where both components have equal diamagnetic anisotropies, it was shown that, assuming the twisting power depends on dopant concentration, a spatial concentration wave occurs. The resulting concentration heterogeneity has the following consequences: (a) the critical field slightly increases, (b) the cholesteric–nematic transition remains

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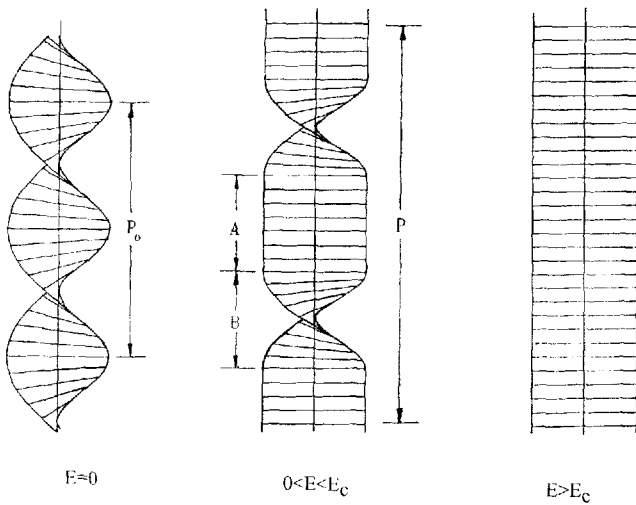


Figure 1. Cholesteric pitch under external fields with different values, applied perpendicular to the cholesteric axis.

as a second-order phase transition, but the critical behaviour of the pitch always transforms from logarithmic to inverse power.

This work is devoted to a self-consistent account of concentration-uniformity distortion in an electric field. In so far as dielectric anisotropy of the components may differ both in absolute value and in sign, we take into account the fact that the local value of $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ may depend on the local concentration of the components. The results of this work also describe the systems in a magnetic field under conditions where the diamagnetic characteristics of the components are appreciably different.

2. Free energy of a nematic-cholesteric mixture

Let $c = c_0 + \Delta c(z)$, where c_0 is the averaged cholesteric component concentration and $\Delta c(z)$ is a small deviation, which satisfies the condition

$$\int_0^p \Delta c(z) dz = 0 \quad (1)$$

The averaged free energy density of the nematic-cholesteric mixture is

$$\bar{f} = \frac{1}{2p} \int_0^p \left[K_{22} \left(\frac{\partial \varphi}{\partial z} - \beta \right)^2 - \frac{\Delta \epsilon}{4\pi} \mathbf{E}^2 \sin^2 \varphi + f_{\text{mic}} \right] dz \quad (2)$$

where the first term corresponds to the elastic part of free energy, the second describes external field effects and the third takes into account the intermolecular interaction and entropy term. One can expand the last

term over $\Delta c(z)$:

$$f_{\text{mic}} = f^{(0)} + f^{(1)} \Delta c(z) + \frac{1}{2} f^{(2)} (\Delta c(z))^2 + \frac{1}{2} \alpha \left[\frac{d(\Delta c(z))}{dz} \right]^2 + \dots \quad (3)$$

where

$$f^{(i)} \equiv \frac{\partial^i f_{\text{mic}}}{\partial c^i}$$

To calculate $f^{(i)}$ one can use, for instance, the Maier-Saupe model as developed in [6].

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

The macroscopic part of the free energy also depends on the chiral component concentration. As we considered a small concentration deviation, we neglect the higher powers of $\Delta c(z)$ in β and $\Delta \epsilon$:

$$\beta = \beta_0 + \beta_c \Delta c(z)$$

$$\Delta \epsilon = \Delta \epsilon^0 [1 - g \Delta c(z)]$$

If the linear dependence for β and $\Delta \epsilon$ is valid for all values of concentration, one can find parameters β_c and g

$$\beta_c \equiv \frac{\beta_0}{c_0}; \quad g \equiv \frac{\Delta \epsilon^N - \Delta \epsilon^{\text{Ch}}}{\Delta \epsilon^0} \quad (4)$$

$\Delta \epsilon^N$ and $\Delta \epsilon^{\text{Ch}}$ are the dielectric anisotropies of the nematic and cholesteric components, respectively, and $\Delta \epsilon^0$ is the dielectric anisotropy of the homogeneous mixture.

Insofar as we are interested in the behaviour of the system near the cholesteric to nematic phase transition, let us calculate the averaged free energy density of the system relative to the free energy of the nematic phase f_N

$$\begin{aligned} \Delta \bar{f} &= \bar{f} - f_N \\ &= \frac{K_{22}}{2P} \int_0^p \left[b \Delta c(z)^2 + \left(\frac{\partial \varphi}{\partial z} - \beta_0 - \beta_c \cdot \Delta c(z) \right)^2 - \beta_0^2 \right. \\ &\quad \left. + \left(h \frac{\pi}{2} \right)^2 \beta_0 \cos^2 \varphi + g \cdot \Delta c(z) \sin^2 \varphi \right] dz \quad (5) \end{aligned}$$

where

$$f_N = \frac{1}{2} K_{22} \beta_0^2 - \frac{\Delta \varepsilon^2}{4\pi} \mathbf{E}^2$$

$$h^2 = \frac{\mathbf{E}^2}{\mathbf{E}_0^2}, \quad \mathbf{E}_0^2 = \frac{2\pi^2 \beta_0 K_{22}}{\Delta \varepsilon^0}, \quad b = \frac{f^{(2)}}{K_{22}}$$

\mathbf{E}_0 is a critical field for a homogeneous mixture such as that studied by de Gennes.

To obtain the minimum value of Δf , we first minimize this functional over $\varphi(z)$ and $\Delta c(z)$ under the condition (1) and a fixed helical pitch P , and then find the minimum of $\Delta f(P)$. The solution of the Euler variation equations

$$-\beta_0^2 \left(\frac{\pi}{2} h\right)^2 (1 - g \Delta c(z)) 2 \sin \varphi \cos \varphi$$

$$= \frac{\partial^2 \varphi}{\partial z^2} - \beta_c \frac{\partial(\Delta c(z))}{\partial z} - 2\beta_c \left(\frac{\partial \varphi}{\partial z} - \beta_c \Delta c(z)\right)$$

$$- g \beta_0^2 \left(\frac{\pi}{2} h\right)^2 \sin^2 \varphi - 2b \Delta c(z) + L = 0 \quad (6)$$

where L is the Lagrange factor, gives the following expressions for the free energy density:

$$\Delta \bar{f} = h^2 - \frac{h}{48k^4(1-\delta)} \left\{ g^2 \delta h^2 \pi^2 \left[6(1-\delta)^{1/2} \frac{\theta(k)}{K(k)} k \right. \right.$$

$$\left. - 2hk^2 \theta(k) + hk^2 - h\theta^2(k) + 4h\theta(k) - h \right]$$

$$+ g\delta(1-\delta)^{1/2} h \pi^2 k \frac{6}{K(k)}$$

$$\times \left[-hk^2 - 4h\theta(k) + 2h + 2 \frac{k}{K(k)} \right]$$

$$+ 12k^2 \left[8\theta(k) \left(\frac{(1-\delta)^{1/2}}{E(k)} k - (1-\delta)h \right) \right.$$

$$\left. + 4h(1-\delta) - h\delta \frac{\pi^2}{K^2(k)} \right\} \quad (7)$$

and helical pitch:

$$\frac{P}{P_0} = \frac{4(1-\delta)^{1/2} k K(k)}{h}$$

$$\times \left\{ \frac{1}{1 + h \frac{\pi^2}{8k^2} \delta g \frac{1}{K(k)} \left[k + \frac{1}{2} hgE(k) \right]} \right\} \quad (8)$$

where $P_0 = 2\pi/\beta_0$.

Here we wrote $\theta(k) = E(k)/K(k)$, where $K(k)$, $E(k)$ are

the first and second elliptic integrals. The parameter $\delta = K_{22} \beta_c^2 / (b + K_{22} \beta_c^2)$ characterizes the ability of the system to disturb the concentration homogeneity. The case where $\delta = 0$ corresponds to a uniform concentration and the results of our calculations coincide with those of de Gennes. To find the minimum $\Delta f(P)$, we can use the condition $d(\Delta f(k))/dk$ due to the monotonic dependence of $P(k)$. The solution of this equation is

$$h = \frac{k}{12(1-\delta)^{1/2} E^2(k) \theta(k) 4E(k)(1-\delta) + \frac{\delta \pi^2}{K(k)}}$$

$$\times \{ -48E^2(k) \theta(k) k(1-\delta) + 3g\delta \theta(k) k \pi^2 [4\theta(k) + k^2 - 2] 4\pi^2 + g^2 \delta k [3\theta^2(k) k^2 + 2\theta(k) - k^2 + 2] \pi^2 \} \quad (9)$$

and gives the extreme value of the free energy (7) and the implicit pitch dependence $P(h)$ as $P(k)$ and $h(k)$.

3. Results and discussion

For the homogeneous mixture ($\delta = 0$), expressions (7-9) are identical to the results of de Gennes and give logarithmic dependence for $P(h)$: $P \sim -\log(1-h)$, because $P \sim K(k)$, and $1-h \sim 1-k^2$. The appearance of the concentration inhomogeneity becomes appreciable only in the vicinity of the critical field and causes two effects. First, it slightly changes the critical field

$$h_c \equiv h(k=1) = (1-\delta)^{-1/2} \left(1 + \delta \frac{g(g+3)\pi^2}{48(1-\delta)} \right) \quad (10)$$

Second, the critical behaviour changes according to

$$1 - \frac{h}{h_c} = \frac{\delta \pi^2 (g+2)^2}{16K(k)} + 0.96(1-k^2) \quad (11)$$

When $k \rightarrow 1$, the first term becomes dominant because it goes to unity more slowly than the second. Finally the critical behaviour becomes inverse power, $P \sim (h_c - h)^{-1}$.

The dependencies $P(h)$ in the vicinity of h_c are depicted in figure 2 on a logarithmic scale; therefore when $\delta = 0$ it is represented by a straight line. The transition to the inverse power dependence (curves +, \circ , Δ , \times) is characterized by deviation from the straight line, which takes place when two terms in (11) become approximately equal. For the systems with a higher ability to disturb the concentration homogeneity, the transition from logarithmic to inverse power critical behaviour occurs earlier.

In order to find out the cause that leads to change in the critical behaviour we analysed the structure of a concentration wave that can be presented in parametric form:

$$z(\varphi, k) = 4(1-\delta)^{1/2} F(\varphi, k) E(k)$$

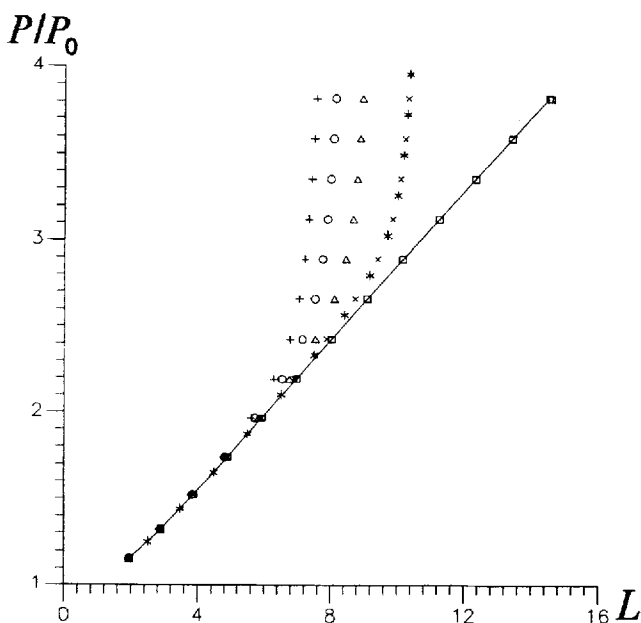


Figure 2. Cholesteric pitch dependencies $P(h)$ near the critical field h_c , where $L = -\ln(1 - h/h_c)$, $\delta = 0.0005$. For $g = -2$ the $P(h)$ dependency becomes logarithmic. + + + + $g = 2.0$; ○ ○ ○ ○ $g = 1.0$; Δ Δ Δ Δ $g = 0.0$; × × × × $g = -1.0$; □ □ □ □ $g = -2.0$; **** $g = -3.0$.

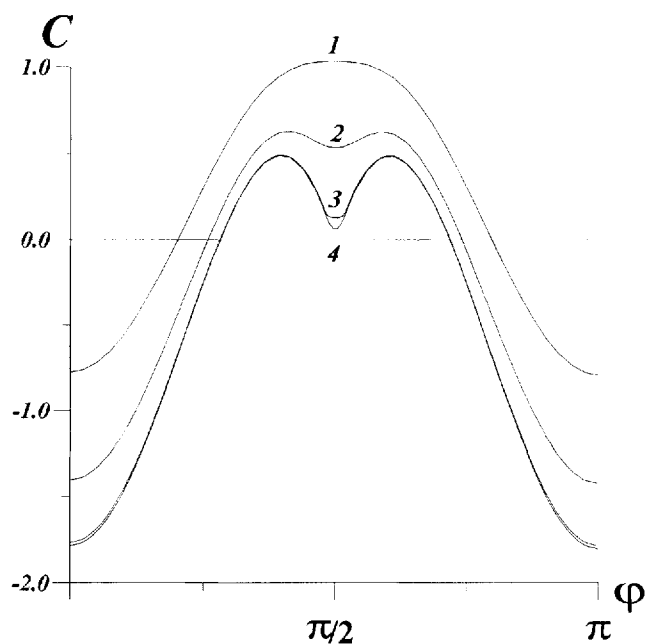


Figure 3. Concentration wave $C(\varphi)$ near the critical field for different values of h ; $\delta = 0.0005$, $g = -2.0$, $m = 1 - k^2$. (1) $m = 0.1$, $h = 0.8586$, $P/P_0 = 1.154$; (2) $m = 0.03$, $h = 0.9795$, $P/P_0 = 1.581$; (3) $m = 10^{-5}$, $h = 0.9973$, $P/P_0 = 1.9657$; (4) $m = 10^{-8}$, $h = 0.0000443$, $P/P_0 = 4.48$.

$$\tilde{C}(\varphi) = \left\{ 4(1 - k^2 \sin^2 \varphi)^{1/2} - \pi \right. \\ \left. \times \left[(\theta(k) - 1) + k^2 \sin^2 \varphi g \frac{k}{E(k)} + \frac{2k}{K(k)} \right] \right\} \\ \times \frac{\pi}{8kE(k)}$$

where φ is the angle between the applied field direction and the normal to the director and

$$\tilde{C} = \frac{\Delta C}{C_0 \delta \pi}$$

The function $z(\varphi, k)$ is nearly independent of g when α is small. That is why all the qualitative features of the concentration wave can be described with the function $C(\varphi)$ depicted in figure 3 for different h . It is seen that when $k \rightarrow 1$ the period of structure is divided into two regions: a quasi-nematic region (when the director is parallel with the external field, $\varphi \approx \pi/2$) and a crest in the concentration wave ($|\varphi| < \pi/2$). When k increases, the crest of the concentration wave remains nearly constant and the quasi-nematic region grows $P \sim \ln(1 - k)$, therefore

$$C(\pi/2) \approx -A/p \sim \ln^{-1}(1 - k)$$

where A is an integral surplus of the cholesteric component in the crest.

When the dielectric anisotropies of the components are equal, the concentration wave with chiral dopants causes enrichment of regions of rapid director rotation. When $g > 0$ the difference between the dielectric anisotropies of the components also enriches these regions and intensifies the effect of stratification of the system (figure 4, curves +, ○ and figure 5). Conversely, if the chiral component has a higher dielectric anisotropy than the nematic ($g < 0$), then both mechanisms compete and the structure of the crest becomes more complex (figure 4, curves Δ, ×, □). When $g = -1/\pi$, the crest becomes twin-peaks. When $g = -\pi/4$, in the middle of the crest, a region impoverished in cholesteric component appears ($C(\varphi) < 0$). When $g = -2$, then $A = 0$ (figure 6) and a shift of the crests does not lead to a change of the cholesteric component concentration in the quasi-nematic region. Probably this is the reason for that system's critical behaviour when $P(h)$ becomes logarithmic again (figure 2, curve □). It is necessary to note that, although in this case the two mechanisms compensate each other, the system remains inhomogeneous (figure 4, curve ×) and the critical field is larger than unity (10). When $g < -2$ (figure 2, curve *) the electrostatic mechanism becomes dominant and the chiral dopants enrich the regions where the director is

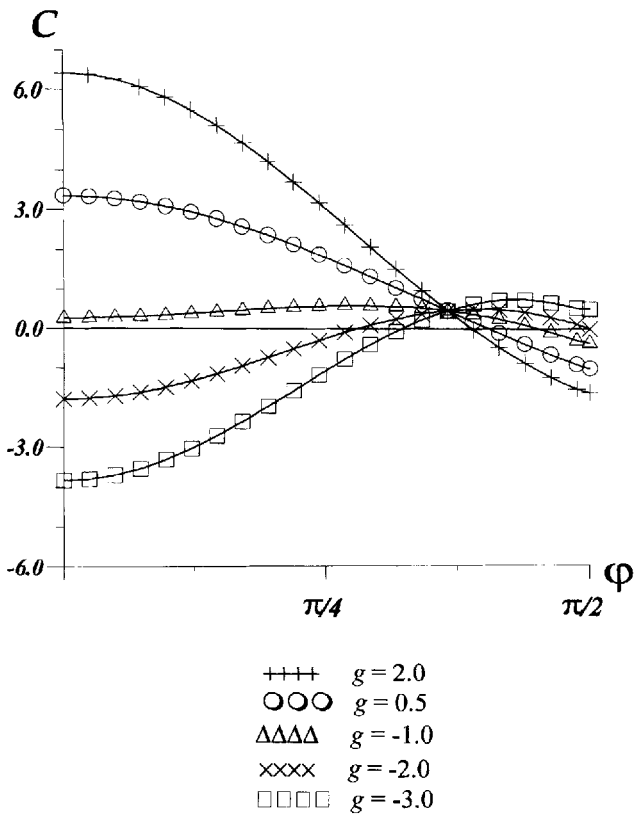


Figure 4. Concentration function for different g , where $C = \Delta C / (C_0 \delta \pi)$; $\delta = 0.0005$, $m = 1 - k^2 = 10^{-8}$, $h = 0.0000443$.

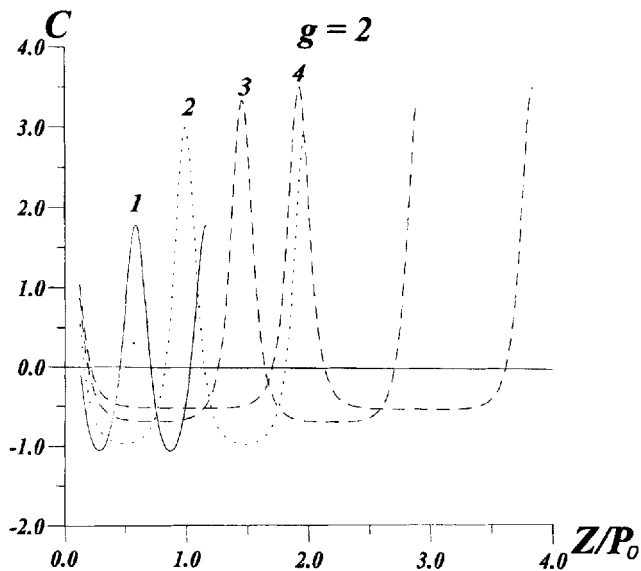


Figure 5. Concentration wave $C(z)$ for $g = 2.0$ in the vicinity of the critical field. Nematic specimen enrichment when the director is along the field. (1) $m = 10^{-1}$; (2) $m = 10^{-3}$; (3) $m = 10^{-5}$; (4) $m = 10^{-7}$.

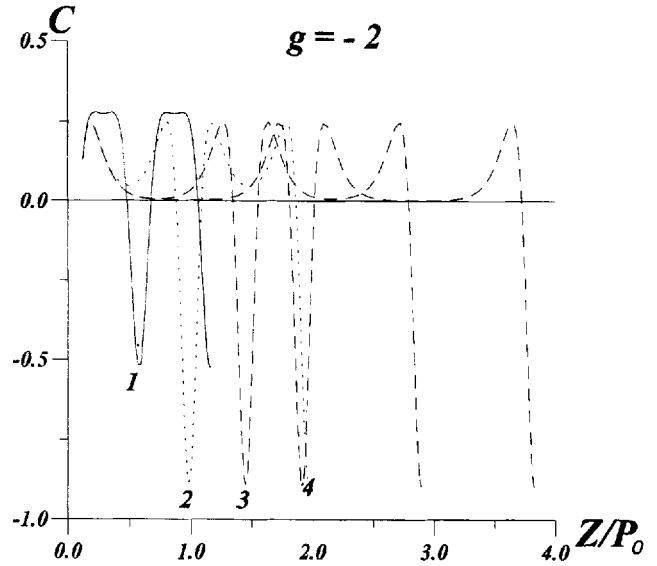


Figure 6. Concentration wave $C(z)$ for $g = -2.0$ in the vicinity of the critical field. Values of m are the same as in figure 5.

oriented along the field (figure 4, curve \square). Finally, the most general impression of the concentration wave behaviour for different g that one could obtain is shown in figure 7.

The concentration wave amplitude and the region with inverse power behaviour are determined by the parameters δ and g . Therefore, it is useful to do experimental work on thermotropic mixtures with dopants of high helical twisting power and large differences in the dielectric anisotropies of the components.

It should be noted that the results obtained are valid only for a free helical structure which is not affected by any boundary constraints. In mixtures with fixed boundary conditions some other effects may appear [7], and the occurrence of the concentration inhomogeneity

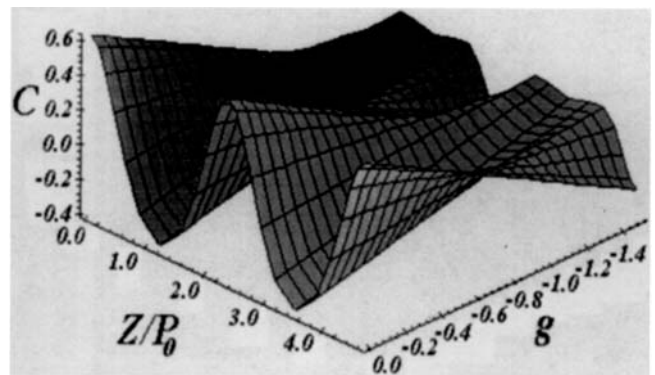


Figure 7. Concentration wave $C(z)$ structures in the vicinity of the critical field for variable g parameter values, $m = 10^{-5}$.

seems to be interesting and will be a problem for our future study.

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