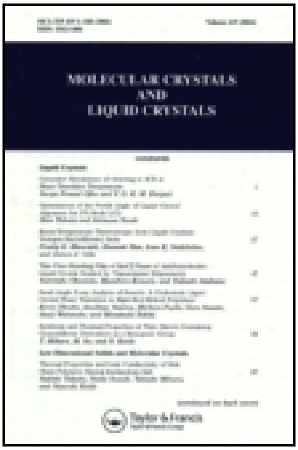

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Phase Transitions in a Cholesteric Close to a Disordering Surface

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Phase Transitions in a Cholesteric Close to a Disordering Surface

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The thermodynamic behaviour of a semi-infinite cholesteric sample close to a disordering surface is analyzed within the frame of the Landau-Ginzburg-de Gennes theory. In particular, the effect of the boundary on the field-induced cholesteric-nematic phase transition is considered. The appearance of a nematic layer on the top of the cholesteric bulk phase is predicted and an experiment which could possibly demonstrate this phenomenon is proposed.

Keywords: Phase transitions; Surface effects

INTRODUCTION

Surface properties of cholesterics are important not only for fundamental studies but also for technological applications. The latter have been of considerable interest since the supertwist configuration was proposed for a liquid crystal cell[1]. The response of a cholesteric to an external field, combined with proper boundary conditions, plays a crucial rôle in the operation of such a cell. In particular, when the electric field is parallel to the helix axis and perpendicular to the boundary, a generalized Fréedericksz transition may occur. This effect was studied theoretically assuming strong anchoring conditions[2]. A Landau-Ginzburg-de Gennes theory was developed for the analysis of surface interactions and field effects for the case of the electric field being perpendicular to the helix axis, with an ordering boundary[3]. It was assumed that the cholesteric wave vector is not affected by the presence of surface and external field. Consequently, these results apply only to the case of a weak field, below the threshold value required for a field-induced cholesteric-nematic phase transition.

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In the present work we concentrate on *the influence of a disordering surface with its normal along the helix axis on the field-induced cholesteric-nematic phase transition.* Recently, the bulk phase diagram of a cholesteric liquid crystal in a field applied perpendicular to the helix axis was examined by Seidin *et al.*[4]. The transitions between the cholesteric, nematic and the so-called undulating state[4] were analyzed. In this work we study how the presence of the disordering boundary influences the topology of the bulk phase diagram. Because of considerable numerical difficulties the undulating state[4] is not taken into account and we concentrate on the surface effects on the field-induced cholesteric-nematic phase transition. In real systems there are agents like, for example, concentration of the chiral compound, which change the characteristics of this transition[5]. Therefore, it seems important to investigate how the proximity of the disordering surface affects the unwinding of the cholesteric helix.

A semi-infinite cholesteric sample bounded by a disordering surface with its normal along the helix axis can be described by the tensor order parameter[6]

$$\boldsymbol{\mu} = -\frac{\mu_0(\zeta)}{\sqrt{6}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \frac{\mu_2(\zeta)}{2\sqrt{2}}\left[e^{ik\zeta/2}\begin{pmatrix} 1 & i & 0 \\ i & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + c.c.\right]. \quad (1)$$

Here ζ is a normalized coordinate in the direction of the wave vector of reduced magnitude κ[6], μ_0 and μ_2 are scalar amplitudes to be determined by a minimization of the free energy and *c.c.* denotes complex conjugate. κ is often called chirality since it is related to the concentration of a chiral dopant in the cholesteric material. For the usual cholesteric bulk phase μ_0 and μ_2 are constants. Here we introduce a one-dimensional spatial dependence as we shall consider surface-induced disordering due to the presence of the confining plane at $\zeta = 0$.

For the sake of simplicity, we assume that the cholesteric wave vector is not affected by the proximity of the boundary. This approximation seems to be reasonable as the typical cholesteric pitch is about 10 – 50 μm[7] and the thickness of the interface is 100–1000 Å[8].

The total free energy per unit area of the semi-infinite cholesteric sample, in suitably normalized units[6], is given by

$$f = \int_0^\infty \mathrm{d}\zeta \left[\frac{1}{4}t\mu_0^2 + \frac{1}{4}(t-\kappa^2)\mu_2^2 + \left(1+\frac{2}{3}\rho\right){\mu_0'}^2 + {\mu_2'}^2 \right.$$
$$\left. \mu_0^3 - 3\mu_0\mu_2^2 + (\mu_0^2+\mu_2^2)^2\right] + \frac{1}{2}w\left[\mu_0^2(\zeta=0) + \mu_2^2(\zeta=0)\right]. \quad (2)$$

Here prime denotes differentiation with respect to ζ, t is the reduced temperature, ρ is a ratio of elastic constants and w is the surface coupling strength. The last term of Eq. (2) mimics the presence of a disordering boundary[9].

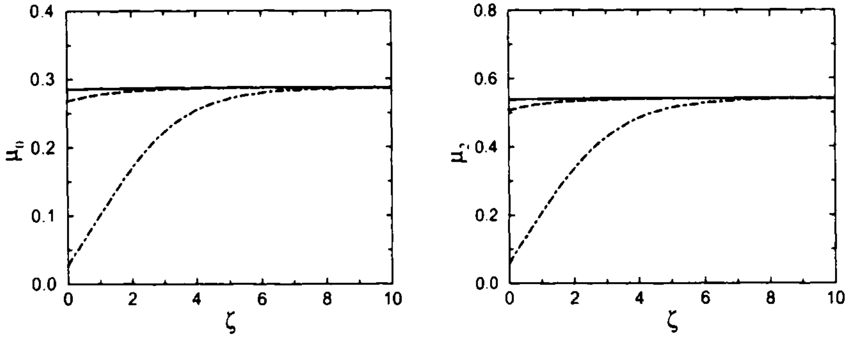

FIGURE 1 The profiles of the scalar amplitudes $\mu_0$and μ_2 for the fixed values of parameters $\kappa = 0.4 \sqrt{6}$, $l = 1.4$, $c = 1$. The *solid*, *dashed* and *dotted-dashed*lines correspond to the surface coupling $w = 0.01$, $w = 0.1$ and $w = 5$, respectively

The equilibrium profiles of the amplitudes $\mu_0(\zeta)$ and $\mu_2(\zeta)$ are determined by a minimization of the free energy functional (2) which yields the Euler-Lagrange equations

$$\left(1 + \frac{2}{3}\rho\right) \mu_0'' = \frac{1}{2}\left[\frac{1}{2}t\mu_0 + 3\mu_0^2 - 3\mu_2^2 + 4(\mu_0^2 + \mu_2^2)\mu_0\right], \tag{3}$$

$$\mu_2'' = \frac{1}{2}\left[\frac{1}{2}(t - \kappa^2)\mu_2 - 6\mu_0\mu_2 + 4(\mu_0^2 + \mu_2^2)\mu_2\right]. \tag{4}$$

with the boundary conditions

$$\left(1 + \frac{2}{3}\rho\right) \mu_0'(\zeta = 0) = \frac{1}{2}w\mu_0(\zeta = 0). \quad \mu_2'(\zeta = 0) = \frac{1}{2}w\mu_0(\zeta = 0). \tag{5}$$

$$\mu_0'(\zeta = \infty) = 0. \qquad \mu_2'(\zeta = \infty) = 0. \tag{6}$$

In order to solve the boundary value problem defined by Eqs. (3)-(6) the Euler-Lagrange equations (3)-(4) were first linearized in the bulk in order to obtain the asymptotic boundary conditions. The latter were used to solve the Euler-Lagrange equations with the help of a standard relaxation method.

As a result we obtained the profiles $\mu_0(\zeta)$ and $\mu_2(\zeta)$ for fixed values of temperature t, chirality κ, elastic constant ρ and surface coupling strength w. While the first two of these parameters may be easily adjusted in an experiment, it is difficult to control the elastic constant ρ. However, it turns out that the results do not exhibit a strong dependence on its value. We could verify this behavior by performing calculations for various values of $c = 1 + 2\rho /3$, within the range of $c = 0.1 \ldots 10$. In the following we shall assume that $c = 1$, i.e., $\rho = 0$.

Let us now focus our attention on the profiles of the scalar amplitudes for various values of the surface coupling strength. As one can infer from Fig. 1, the cholesteric order may be significantly reduced at the surface. The profiles $\mu_0(\zeta)$ and $\mu_2(\zeta)$ increase monotonically to the bulk values of the scalar amplitudes. However, within the frame of our model, where the cholesteric wave vector q_c stays constant throughout the sample, and for the considered values of the chirality κ, we do not observe any surface-induced disordering transition[10]. Namely, the surface order parameters $\mu_0(0)$ and $\mu_2(0)$ always exhibit a discontinuity at the cholesteric-isotropic phase transition, irrespectively of the value of the surface coupling strength. A continuous evolution can be reproduced in our model only in the limit of the vanishing chirality.

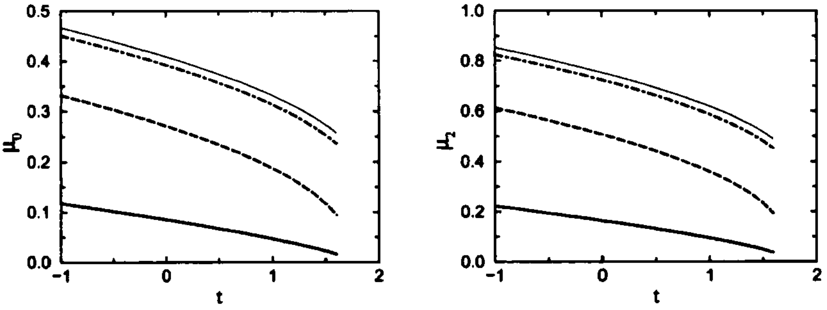

FIGURE 2 The temperature dependence of the surface order parameters $\mu_0(0)$, $\mu_2(0)$ for different values of the surface coupling: *dotted-dashed* line $w = 0.1$, *dashed* line $w = 1$ and *solid* line $w = 5$. For comparison, the bulk order parameters $\mu_0(\infty)$, $\mu_2(\infty)$ are given by the *thin* solid line

In Fig. 2 the temperature dependence of the surface order parameters is plotted for different values of the surface coupling w. The transition at the surface is first order and takes place at the same temperature as in the bulk. Namely, the jump in the bulk order parameter is always followed by a corresponding jump of the surface order parameter. Only in the limit $w \to \infty$ the amplitudes $\mu_0(\zeta)$, $\mu_2(\zeta)$ continuously approach zero at the bulk transition temperature.

We shall now investigate the influence of the disordering surface on the field-induced cholesteric-nematic phase transition. For materials characterized by a positive dielectric anisotropy the application of an electric (or magnetic) field perpendicular to the axis of the helix results in the unwinding of the helix[7]. Therefore, the assumption that the cholesteric wave vector is constant, is no longer valid and the calculations become much more extended. Hence, we disregard the biaxiality of the order parameter, in order to be able to concentrate on the effects related to the change in the cholesteric pitch. We shall work with the uniaxial order parameter $\mu = {}^{1/2}\, S\, (3\, \mathbf{n} \otimes \mathbf{n} - \mathbf{1})$. In the considered geometry, $\mathbf{n}$ is a planar director field, $\mathbf{n}(\zeta) = \hat{\mathbf{x}} \cos\theta(\zeta) + \hat{\mathbf{y}} \sin\theta(\zeta)$. Both the director angle θ and the scalar order parameter S, which measures the degree of orientational order, depend on the normalized[4] coordinate ζ. The total free energy of the cholesteric phase, bounded by a disordering surface in the presence of an electric field applied perpendicular to the helix axis, is then

$$
\begin{aligned}
f = \int_0^\infty \mathrm{d}\zeta \left\{ \frac{1}{2} t S^2 - \frac{1}{3} S^3 + \frac{1}{4} S^4 - tS \left(\frac{1}{3} + \cos\theta \right) - \frac{1}{l} q_0 S^2 \theta' \right. \\
\left. \frac{1}{2l^2} S^2 \theta'^2 + \frac{1}{2l^2} S'^2 \right\} + \frac{1}{2l} w S^2(0),
\end{aligned} \tag{7}
$$

where e is the reduced electric field, $q_0 = \kappa / \sqrt{6}$ and 2 l gives the cholesteric pitch. If the field $c = 0$ then we get $l = l_0 \equiv \pi / q_0$. However, for $e > 0$ and in the presence of the disordering surface one expects $l > l_0$. The Euler-Lagrange equations which result from a minimization of the functional (7) read

$$
S\theta'' = 2 q_0 l S' - 2\theta' S' + e l^2 \sin\theta, \tag{8}
$$

$$
S'' = S\theta'^2 - 2 l q_0 S \theta' + l^2 \left[tS - S^2 + S^3 - e \left(\frac{1}{3} + \cos\theta \right) \right]. \tag{9}
$$

with the boundary conditions at the surface

$$
S(\zeta = 0) = wl. \quad \theta(\zeta = 0) = 0, \tag{10}
$$

while in the bulk

$$
S(\zeta = 2) = 0. \quad \theta(\zeta = 2) = 2\pi. \tag{11}
$$

In the Eqs. (8)-(11) we have fixed the upper integration limit at $\zeta_{\max} = 2$. In this way, we assume that the surface influences only the first one of the cholesteric "unit cells".

We solved the equations of motion (8)-(11) numerically using a standard relaxation method in order to obtain the equilibrium profiles of S and θ . Finally, the phase diagram was determined. We stress once more that we were interested *only* in the influence of the surface on the field-induced cholesteric-nematic transition. Therefore, the cholesteric-paranematic and nematic-paranematic transition line is given only approximately by the analytical solution[11].

Returning to the results of our calculations, let us discuss the phase diagram for a comparably small chirality parameter $q_0 = 0.1$. Here, the influence of the surface results in shifting the second order transition line towards lower fields (with respect to the value calculated in the bulk, see Fig. 3). This means that for certain

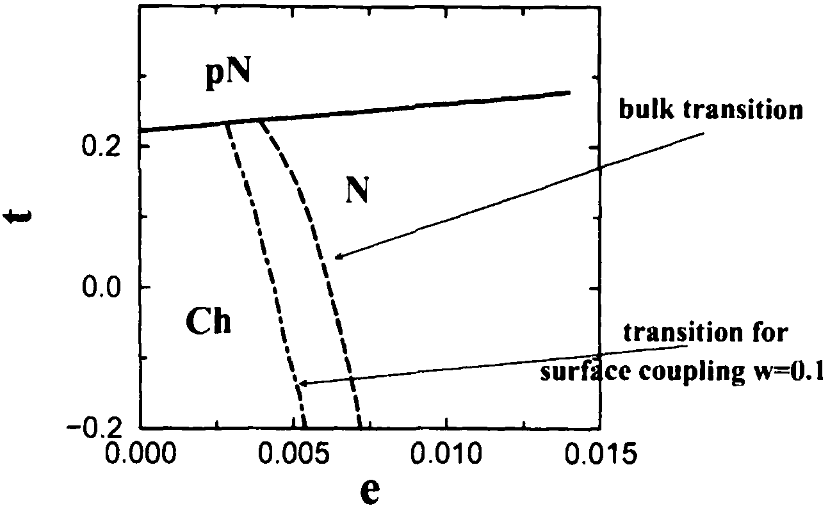

FIGURE 3 Phase diagram for chirality parameter $q_0 = 0.1$ and surface coupling $w = 0.1$. The *dotted-dashed* line denotes the transition from cholesteric to nematic. For comparison, the cholesteric-nematic bulk transition is given by the *dashed* line

values of the field e, a nematic layer appears between the solid substrate and the bulk cholesteric. The thickness of this layer should be larger than $2l$.

Within the range of the parameters that we have studied the tricritical point, which was predicted to appear in the bulk samples, was not observed. This is illustrated in Fig. 4 where the phase diagram for chirality parameter $q_0 = 0.4$ and surface coupling $w = 0.1$ is given. The cholesteric-nematic transition is not only shifted towards lower fields, as in the case of $q_0 = 0.1$ previously discussed, but the first order transition line is replaced by a second order one.

Finally, we discuss the shape of the profiles $\theta(\zeta)$ and $S(\zeta)$ in the cholesteric phase, close to the cholesteric-nematic field-induced phase transition (see Fig. 5). S, which measures the degree of nematic ordering, decreases significantly in the vicinity of the boundary. The presence of the external field is clearly manifested in the profile of θ – it is no longer a linear function of ζ as in the case of an ordinary cholesteric.

We would like to propose an experiment which could possibly demonstrate the surface-induced nematic layer. The cholesteric sample should be contained between two glass plates in a wedge geometry. This is a well-known experimental technique for cholesteric liquid crystals[7]. In order to obtain a surface that prefers the isotropic phase, the glasses should be evaporated with SiO[12].

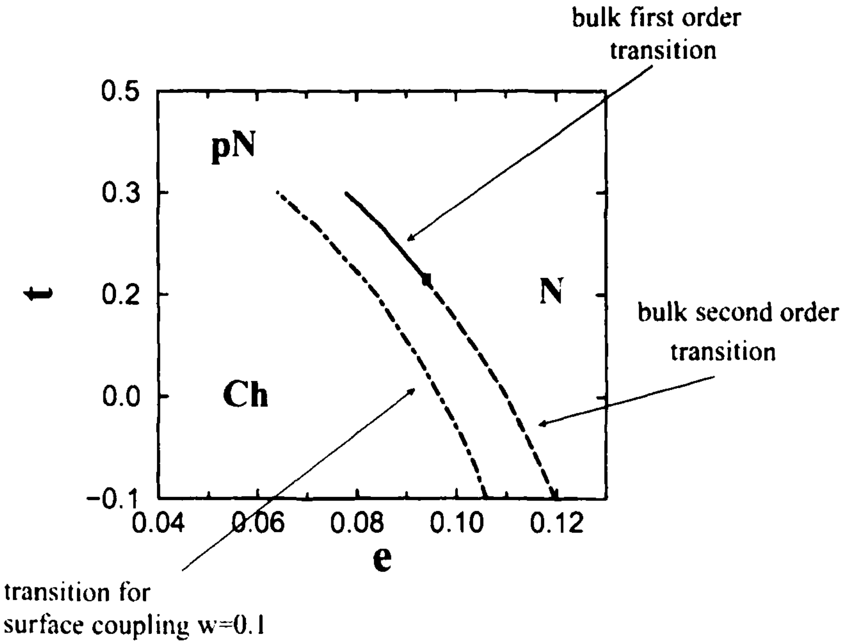

FIGURE 4 Phase diagram for chirality parameter $q_0 = 0.4$ and surface coupling $w = 0.1$. The *dotted-dashed* line denotes the second order transition from cholesteric to nematic. For comparison, the cholesteric-nematic bulk transition is given. The *thin dashed* line is the approximate boundary of the paranematic state

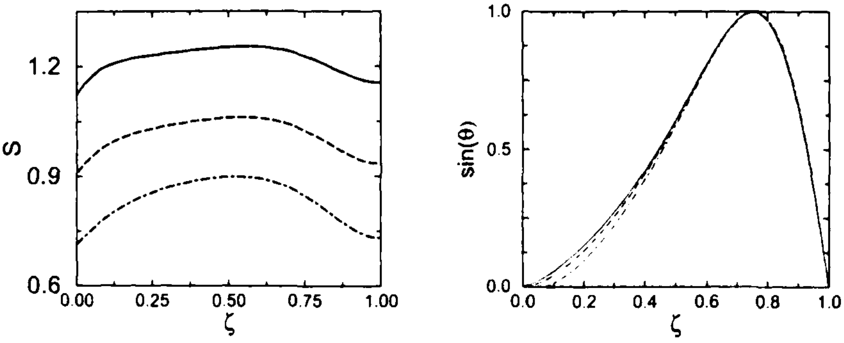

FIGURE 5 The profiles of order parameters S and θ for chirality $q_0 = 0.4$ taken at the cholesteric-nematic transition (dotted line in Fig. 4). The *solid* line corresponds to $t = -0.1$ and e 0.001, the *dashed* one to $t = 0.15$, $e = 0.0088$ and the *dotted-dashed* line to $t = 0.3$ and $e = 0.0072$

A wedge prepared in such a way can now be filled with the cholesteric material. In order to obtain the proper orientation of the helix axis with respect to the plates the field should be applied already in the isotropic phase. We stress that the wedge angle is of the order ~ 1° and we could, approximately, assume that the axis of the helix is perpendicular to both plates. Tuning properly the field it should be possible to observe *simultaneously* both the reflections stemming from the nematic[13] and the Grandjean-Cano lines[14] typical for a cholesteric. If the experiment confirmed the presence of the surface-induced nematic layer, more detailed calculations should be performed, which then would take into account the fact that the cholesteric pitch now has to adjust itself to the distance between the plates.

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