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Tiezheng Qian

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TIEZHENG QIAN*

Department of Physics, University of California, Berkeley, CA 94720, USA

PING SHENG

Department of Physics, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

We show that the competition between the correlation of liquid crystalline order and the orienting effect of applied field is crucial in determining the characteristic behaviour of local ordering in the boundary layer, close to the substrates with strong anchoring. The equilibrium states for the low and the high field are found to be distinct. In particular, varying the field strength can induce a phase transition, across which the order parameter configuration changes continuously from one to the other of the two limiting equilibrium states.

1. Introduction

Long-range deformations of nematic liquid crystals (LCs) can be described by a spatially varying unit vector $\mathbf{n}$, the local axis of uniaxial orientational ordering. Based on this viewpoint, Oseen, Zocher, and Frank developed a continuum elastic theory [1–3], which has been successfully used for decades in explaining various field-induced effects. In particular, the Fréedericksz transition (FT), first detected optically by Fréedericksz in 1927 [4] and then explained by Zocher using the continuum theory [2], is now a well-understood field-induced phenomenon which has found applications in various LC display devices [5]. On the other hand, there have been increasing experimental evidence to show that substrate–LC interactions, strong fields, and severe geometric confinements can result in short range variations of liquid crystalline order (LCO), described by a traceless symmetric tensor $\overset{\leftrightarrow}{Q}$, which incorporates the local axis/axes of uniaxial/biaxial symmetry as well as the degree of local orientational ordering [6]. The Landau–de Gennes (LdG) phenomenological theory [7] based on the order parameter $\overset{\leftrightarrow}{Q}$, developed almost twenty years ago by de Gennes [6], has proven to be successful in explaining and predicting various LCO-involved phenomena, such as surface wetting [8], surface-induced bulk alignment [9, 10], and defect core structure [11],

all involving the fast spatial variations of LCO. Recently, it has been observed that polyimide-coated substrates can induce a boundary layer of strong biaxial character, which can only be described by the tensor order parameter [10]. In addition, the prediction of the bulk orientational state through the LdG theory shows good agreement with experiment. The use of the tensor order parameter is therefore not only necessary but also sufficiently accurate.

With regard to the behaviour of LCO in the short-range distortions of LCs, the core structure of nematic defects, which can not be represented by the director field $\mathbf{n}(\mathbf{r})$, constitutes an important object for study. It has been predicted that strong biaxial ordering exists in the core region, away from which uniaxial ordering is gradually restored towards that in an undistorted system [11]. This 'biaxial escape' phenomenon has also been found in extremely thin hybrid cells which impose severe geometric confinement [12, 13]. In particular, it has been shown that as the cell thickness is varied, there exists a second order phase transition through which the equilibrium state changes continuously from the configuration characterized by a spatially rotating director (in thick cell) to that by a predominant biaxial ordering (in thin cell) [12, 13].

The purpose of this paper is to show the existence of a field-induced configurational transition which manifests predominant biaxial ordering as well as biaxial escape in the boundary layer close to the substrate. Consider a

*Author for correspondence.

semi-infinite LC sample on the substrate under homogeneous alignment conditions. Applying a vertical electric/magnetic field leads to a spatial variation of the order parameter in a boundary layer which takes the field coherence length ξ as the characteristic thickness. A spatially rotating director is always obtained from the Frank theory. However, the corresponding order parameter configuration is not stable when the field strength is large enough to make ξ comparable to the LC correlation length Δ. In fact, the high field equilibrium state is found to be characterized by three spatially varying eigenvalues, i.e. three spatially varying diagonal elements of $\vec{Q}(z)$ in the local principal system, while the principle axes show no rotation at all. With the limiting equilibrium states at low and high field strength found to be distinct, a phase transition between the two is therefore inevitable as the field strength is varied. In particular, symmetry consideration shows that there exist two low-field stable configurations which are degenerate and characterized by the spatially rotating director. This is simply a manifestation of the spontaneous symmetry breaking. However, the two-fold degeneracy vanishes as the field strength is increased to a second order phase transition point, above which there exists only one single equilibrium state, which must be invariant under the same symmetry transformation as that associated with the low-field degeneracy. This transition is intrinsically different from the conventional FT, if triggered in LC cells by varying the applied voltage. While the former involves only the ordering state in the boundary layers of characteristic thickness Δ, the latter changes the alignment state throughout the cell. A brief discussion is presented on the hydrodynamic effect corresponding to the symmetry breaking and restoration in field-induced equilibrium states.

2. The model

We consider a semi-infinite LC sample on a substrate with proper alignment conditions. The system is in the half space $z \geqslant 0$ with the substrate defined at the $z = 0$ plane. The LdG free energy density is given by

$$f = \frac{1}{2}(\alpha Q_{ij}^2 + L_1 Q_{ij,k}^2 + L_2 Q_{ij,j} Q_{ik,k})$$
$$- \beta Q_{ij} Q_{jk} Q_{ki} + \gamma (Q_{ij}^2)^2. \tag{1}$$

Here α, L_1, L_2, β, and γ are phenomenological constants, the indices i, j, k run from 1 to 3 with the correspondence $1 \leftrightarrow x$, $2 \leftrightarrow y$, $3 \leftrightarrow z$, summation over repeated indices is implied, and comma in the subscript means derivative with respect to the spatial coordinate that follows. Substituting $\vec{Q} = S(3\mathbf{nn} - I)/2$ into equation (1) yields

the familiar expression

$$f^U = a(T - T^*)S^2 - BS^3 + CS^4 + \frac{3}{4}\left(L_1 + \frac{1}{6}L_2\right)[\nabla S]^2$$
$$+ \frac{3}{8}L_2[\mathbf{n} \cdot \nabla S]^2 + \frac{9}{4}S^2 \left\{ \left(L_1 + \frac{1}{2}L_2\right)[\nabla \cdot \mathbf{n}]^2 \right.$$
$$+ L_1[\mathbf{n} \cdot \nabla \times \mathbf{n}]^2 + \left(L_1 + \frac{1}{2}L_2\right)[\mathbf{n} \times \nabla \times \mathbf{n}]^2 \right\}$$
$$+ \frac{3}{2}L_2 S[\nabla \cdot \mathbf{n}][\mathbf{n} \cdot \nabla S] + \frac{3}{4}L_2 S[\mathbf{n} \times \nabla \times \mathbf{n}] \cdot \nabla S$$

$$\tag{2}$$

where $a(T - T^*) = 3\alpha/4$, T^* is the supercooling temperature, $B = 3\beta/4$, and $C = 9\gamma/4$. Here the Frank elastic energy density for the spatial variation of $\mathbf{n}$ is expressed in the usual form of $[\nabla \cdot \mathbf{n}]^2$ (splay), $[\mathbf{n} \cdot \nabla \times \mathbf{n}]^2$ (twist), and $[\mathbf{n} \times \nabla \times \mathbf{n}]^2$ (bend), with the respective elastic constants given by $K_{splay} = 9/2S^2(L_1 + 1/2L_2)$, $K_{twist} = 9/2S^2 L_1$, and $K_{bend} = 9/2S^2(L_1 + 1/2L_2)$.

We choose the LC correlation length

$$\Delta = \left[\frac{(3L_1/4 + L_2/2)C}{B^2}\right]^{1/2}$$

defined from f^U in equation (2), as the length unit. For uniform substrates, the order parameter depends on the coordinate z only, i.e. $Q_{ij} = Q_{ij}(z)$. We assume a fixed boundary condition at $z = 0$: $\vec{Q}(0) = S_b(3\mathbf{xx} - I)/2$ where S_b is the uniaxial orientational order parameter in bulk. This is the homogeneous alignment modelled in [12]. In the presence of an electric field $\mathbf{E}$ applied perpendicular to the substrate, the field-induced free energy density is

$$f_F = \frac{1}{8\pi}\mathbf{D} \cdot \mathbf{E} \tag{3}$$

where $\mathbf{D} = \overleftrightarrow{\epsilon}\mathbf{E}$ is the electric displacement field and $\overleftrightarrow{\epsilon}$ is the local dielectric tensor, given by $\overleftrightarrow{\epsilon} = 1/3(\epsilon_\parallel + 2\epsilon_\perp) + 2/3\epsilon_a^m \overleftrightarrow{Q}$ with ϵ_a^m being the maximum dielectric anisotropy. For simplicity, we first discuss the case of positive, small ϵ_a^m, i.e. $\epsilon_a^m/\epsilon_\parallel \ll 1$. In this limit, the electric field is almost uniform, regardless of the $\overleftrightarrow{\epsilon}$ variation.

The total free energy $F[\vec{Q}(z)] = \int dz(f + f_F)$, written in the dimensionless form as

$$\bar{F} = \frac{F}{\Delta B^4/C^3} = \int d\zeta(f + f_F) \tag{4}$$

is given by

$$f = \left(t + \frac{1}{4}\right)\left(\frac{2}{3}\bar{Q}_{ij}^2\right) - \frac{4}{3}\bar{Q}_{ij}\bar{Q}_{jk}\bar{Q}_{ki} + \left(\frac{2}{3}\bar{Q}_{ij}^2\right)^2$$
$$+ \frac{2}{3 + 2\rho}\bar{Q}_{ij,k}^2 + \frac{2\rho}{3 + 2\rho}\bar{Q}_{ij,j}\bar{Q}_{ik,k} \tag{5}$$

and

$$f_{\mathrm{F}} = -\frac{\epsilon_a^m E^2 C^2}{12\pi B^3}\bar{Q}_{33} \tag{6}$$

where $\zeta = z/\Delta$, $\bar{Q}_{ij} = CQ_{ij}/B$, $\rho = L_2/L_1$, and $t = (T - T_{\mathrm{IN}})/4(T_{\mathrm{IN}} - T^*)$, with $T_{\mathrm{IN}} = T^* + B^2/4aC$ being the isotropic–nematic transition temperature.

3. Field-induced phase transition

The equilibrium state is given by the order parameter configuration which minimizes the free energy functional $\bar{F}$. Using a finite difference scheme, we transform $\bar{F}$ into a multi-variable function and apply the modified Newton method to find the optimal configurations for both stable and metastable states.

3.1. *Semi-infinite system*

For the semi-infinite system modelled in §2, the field-induced bulk state is uniaxial, with $\mathbf{n} = \mathbf{z}$, and the spatial variation of the order parameter only exists close to the substrate. The characteristic length of the boundary layer is the field coherence length

$$\xi(E) = \left(\frac{4\pi K}{\epsilon_a E^2}\right)^{1/2} \tag{7}$$

where K is given by the elastic constant K_{splay} or K_{bend}, and $\epsilon_a = S_b \epsilon_a^m$ is the dielectric anisotropy $\epsilon_\parallel - \epsilon_\perp$. For a weak field, ξ is much larger than the LC correlation length Δ. As a result, the local ordering is approximately given by $\overleftrightarrow{Q} = S_b(3\mathbf{nn} - I)/2$, where S_b is the uniaxial orientational order parameter minimizing $a(T - T^*)S^2 - BS^3 + CS^4$, and the LC deformation is essentially long-range, described by the spatially varying $\mathbf{n}(\mathbf{r})$ according to the Frank theory. Under the homogeneous alignment condition specified by fixed $\overleftrightarrow{Q}(0)$, only $Q_{11}, Q_{22}, Q_{33} = -Q_{11} - Q_{22}$, and $Q_{13} = Q_{31}$ do not vanish, and the director rotation is reflected by $|Q_{13}(z)|$, which first increases from zero at $z = 0$ to its maximum value $3S_b/4$ somewhere in the boundary layer, and then decreases back to zero as $z \to \infty$. Note that the free energy functional and the boundary condition are both invariant under the x-reversal transformation:

$$Q_{11}(z) \to Q_{11}(z), \quad Q_{22}(z) \to Q_{22}(z), \quad Q_{13}(z) \to -Q_{13}(z). \tag{8}$$

Accordingly, there always exist two degenerate stable configurations as long as $Q_{13} \neq 0$, and each state with either $Q_{13} \geq 0$ or $Q_{13} \leq 0$ is a result of the spontaneous symmetry breaking when minimizing F. For a field strength that is large enough, we find that the maximum value of $|Q_{13}|$ decreases continuously with increasing E until $E = E_B$, at which the two degenerate states merge

into one single equilibrium state with $Q_{13}(z) = 0$ throughout the sample. The x-reversal symmetry is thus restored at $E = E_B$, above which Q_{13} vanishes and the single equilibrium state, specified by the three non-zero components Q_{11}, Q_{22}, and Q_{33}, is x-reversal invariant. That means a second order phase transition occurs at the critical field E_B. In fact, the x-reversal symmetric state exists as a metastable state in a wide range of $E(<E_B)$. Below but not far away from E_B, as E increases, the two degenerate equilibrium states with decreasing $|Q_{13}|$ become closer and closer to the metastable symmetric state. The second order phase transition is indeed marked by the point where the two degenerate states become identical and merge with the symmetric state simultaneously. In figure 1, the maximum $|\bar{Q}_{13}|_{\mathrm{max}}$ is depicted as a function of $\varepsilon = \epsilon_a^m E^2 C^2/12\pi B^3$. The critical field E_B is obtained from the dimensionless parameter $\varepsilon_B = \epsilon_a^m E_B^2 C^2/12\pi B^3$ recorded at the transition point. We find $\varepsilon_B = 0.904$ at $t = -1.0$ for $L_2/L_1 = 1$. The energy difference between the stable $|Q_{13}| \neq 0$ states and the metastable x-reversal invariant state is depicted as a function of $\varepsilon(<\varepsilon_B)$ in figure 2. Assuming $S_b \simeq 0.6$ and $B/C \simeq 1/2$, we have $\xi(E_B) \simeq 1.5\Delta$. The predominant boundary layer biaxial ordering at the transition point is depicted in figure 3.

The second order phase transition originates from the competition between local ordering and elastic distortion. Comparing with the high-field configurations, optimal $\overleftrightarrow{Q}(z)$ for low field exhibits a spatial rotation of the principal axes but a better local orientational ordering. With the LC correlation length $\Delta \ll \xi$ for small E, the local ordering is approximately preserved as in the undistorted system, leaving the local director spatially rotated from $\mathbf{x}$ to $\mathbf{z}$ by the applied field. Increasing $\mathbf{E}$
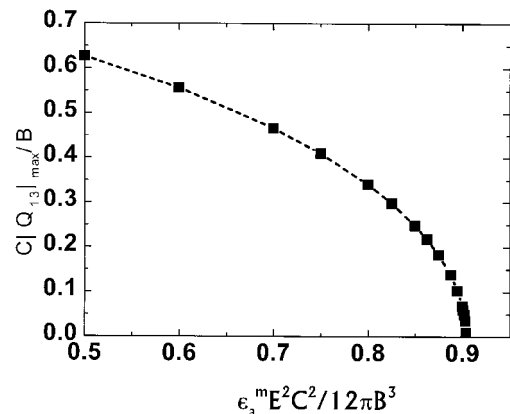

Figure 1. Variation of the maximum $|Q_{13}|_{\mathrm{max}}$ (in units of B/C), plotted as a function of $\varepsilon = \epsilon_a^m E^2 C^2/12\pi B^3$. The second order transition occurs when $|Q_{13}|_{\mathrm{max}}$ meets zero at $\varepsilon = \varepsilon_B$. For $\varepsilon > \varepsilon_B$, $|Q_{13}|_{\mathrm{max}} \equiv 0$. The dashed line represents a square root dependence on $\varepsilon_B - \varepsilon$, showing the mean-field behaviour of a second order phase transition.
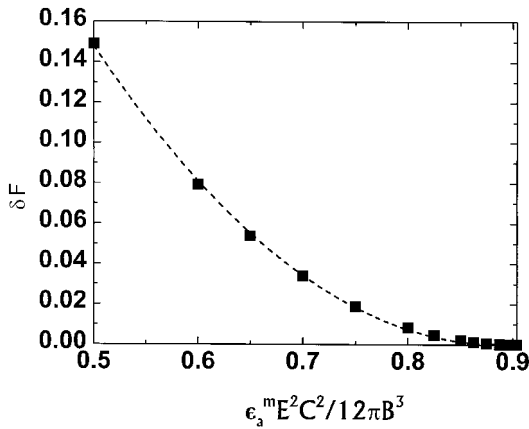
Figure 2. Variation of the dimensionless energy difference between the stable $|Q_{13}| \neq 0$ states and the metastable x-reversal invariant state, plotted as a function of ε in the range of $\varepsilon < \varepsilon_B$. the dashed line delineates a quadratic dependence on $\varepsilon_B - \varepsilon$, showing the mean-field behaviour of a second order phase transition.
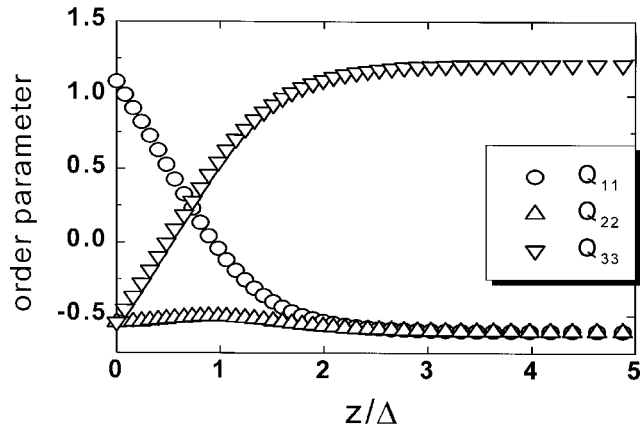
Figure 3. Spatial variation of the three non-vanishing order parameter components (in units of $B/C \simeq 0.5$) in the equilibrium state at the transition point.

leads to a thinning boundary layer, within which the elastic energy increases as $1/\xi$ while the ordering energy decreases as ξ, approximately. As E approaches E_B, it becomes more favourable in total energy to sacrifice the local ordering in the boundary layer, with the elastic energy being lowered at the same time. This is actually achieved by a boundary layer order parameter configuration in which the eigenvalues of biaxial $\overleftrightarrow{Q}(z)$ experience a spatial variation such that the maximum eigenvalue changes from the xx component at $z = 0$ to the zz component at $z \to \infty$, as depicted in figure 3, while the principal axes show little or no rotation at all. This scenario has been called 'eigenvalue exchange', which was first discussed in extremely thin cells [12, 13]. It is interesting to note that as a result of the LdG functional form governing the competition between local ordering

and elastic distortion, the symmetric configuration still exists as a metastable state below the second-order phase transition point. This boundary layer phenomenon is different from a 'standard' second order phase transition below which the symmetric state is unstable.

3.2. Liquid crystal cell

Now we show the realizability of the field-induced configurational transition in a LC cell with two substrates imposing the same homogeneous alignment. We consider nematics of positive, large dielectric anisotropy, i.e. $\epsilon_a/\epsilon_\parallel \sim 1$. In the presence of an applied voltage V, the field-induced free energy is given by

$$\int_0^d -\frac{1}{8\pi} \mathbf{D} \cdot \mathbf{E} \, dz = -\frac{1}{8\pi} \frac{V^2}{\int_0^d dz/\epsilon_{33}} \qquad (9)$$

where $\mathbf{E} = E(z)\mathbf{z}$ is the electric field, satisfying $V = \int_0^d E(z) \, dz$ (d is the cell thickness), and $\mathbf{D}$ is the electric displacement field, with $D_z = \epsilon_{33}(z)E(z)$ being uniform along the z direction. The FT first occurs due to the field-induced alignment of bulk director as V is raised to V_F. Two stable configurations exist after the FT, leading to a multi-domain structure in the cell. Further increase in V aligns the central part of the cell uniformly in the z direction. At sufficiently high V, ξ approaches Δ, and the configurational transition occurs at a critical voltage V_B as the two degenerate stable states (distinguished from each other only in the two boundary layers near $z = 0$ and $z = d$) merge into one single equilibrium state, leaving the cell in a single-domain structure. This second order phase transition in the LC cell is intrinsically different from the FT because the former involves only the short range variation of LCO in the boundary layer set by the LC correlation while the latter changes the alignment state throughout the cell. In this sense, the configurational transition is a true boundary layer phase transition (BLPT). In essence, the BLPT is caused by competition between the lengths Δ and ξ while the FT is caused by that between ξ and d. Accordingly, V_B is proportional to d and the critical field E_B is independent of d, while V_F is independent of d and E_F is inversely proportional to d. Here E_B or E_F refers to the average field strength V_B/d or V_F/d, respectively, since $\mathbf{E}$ is in general not uniform due to the large anisotropy. For the 4-n-pentyl-4′-cyanobiphenyl (5CB), $a = 0.065 \, \text{J cm}^{-3} \, \text{K}$, $B = 0.53 \, \text{J cm}^{-3}$, $C = 0.98 \, \text{J cm}^{-3}$, $L = 4.5 \times 10^{-14} \, \text{J cm}^{-1}$, and $\rho \simeq 1$, with $\Delta = 40 \, \text{Å}$. Taking $\epsilon_\parallel = 20$ and $\epsilon_\perp = 5$, as for materials of large dielectric anisotropy (5CB has $\epsilon_a \simeq 15$), we find $V_B = 11.9 \, V_0$ at $t = -1.0$ for a cell with $d = 20\Delta$. Here V_0 is given by $(4\pi K_{\text{splay}}/\epsilon_a)^{1/2} \simeq 0.25$ volt, on the same order as V_F, thus $V_B \simeq 3$ volt, with $\xi(E_B) \simeq 1.6\Delta$. For $V \propto d$ in the $d \gg \Delta$

regime, it is readily seen that the BLPT can be induced by applying a modest voltage (~ 30 volt) to a cell of thickness $\sim 1\,\mu$m.

4. Concluding remarks

The results presented in this paper only serve to illustrate the possible field-induced phase transition associated with boundary layer liquid crystalline ordering. The vertically applied field plus the homogeneous alignment condition considered here by no means exhaust all possibilities. For example, a similar situation can be discussed for the external field applied parallel to the substrate under homeotropic alignment conditions. In this case, two-fold degeneracy exists in the low field regime while the high field equilibrium state is single, characterized by a predominant biaxial ordering close to the surface. Consequently, a BLPT is inevitable as the field strength is varied. It is also of interest to study the configurational transition for substrates under planar alignment conditions [†], which makes the system symmetric under continuous rotation about the substrate normal, provided the applied field is vertical. In addition, it is more realistic to use a proper surface potential form instead of the fixed alignment condition since the surface anchoring can be broken by the strong field near the transition point.

In the regime of $V > V_F$ and $\xi \ll \Delta$, switching off the holding voltage applied to LC cells can give rise to fast rotation of the directors in the boundary layers. Due to the coupling between the orientational and the translational degrees of freedom, dynamical backflow is induced by the temporarily rotating directors. This phenomenon has been intensively studied by using the Ericksen–Leslie (EL) hydrodynamic theory [14] based on the director description [15]. With negligible inertial effect, the instantaneous fluid flow just after switching off the voltage is determined by the starting director configuration. For the cells considered in this paper, there exist two stable states at a certain holding voltage; they start to relax by inducing their respective flow fields which are of the same magnitude but in opposite

directions. In this regime, switching off higher holding voltage induces large flow field. We have generalized the EL theory to take into account the dynamic effect of LCO [16]. We find that the starting flow field does not fully increase with the switched off voltage. In fact, the flow field decreases continuously in magnitude with the increasing switched off voltage as the starting state approaches the configurational transition point. This is physically understood as the hydrodynamic effect due to symmetry breaking and restoration in field-induced equilibrium states. Work in this direction will be published elsewhere.

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†A unrubbed polyimide-coated substrate imposes such an alignment condition [10].

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