

Substrate-Induced Orientational Order in the Isotropic Phase of Liquid Crystals

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Nematic order induced near a solid boundary in an otherwise isotropic liquid crystal is studied theoretically, at temperatures just above the bulk nematic-isotropic phase transition. Three distinct regimes are found, depending on the strength of orientational torques at the boundary: (i) strong orientational order, (ii) strong orientational order followed by a first-order transition to a state of weak orientational order as temperature is raised, and (iii) a state of weak orientational order.

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It is well known that in the ordered phases of liquid crystals, the orientation of and textures in the order parameter of a thin liquid-crystal film are influenced very importantly by orientational torques experienced by the molecules at the solid boundary of the supporting substrate.¹ This paper discusses the nature of orientational order induced by a solid boundary by such torques, in a liquid crystal that is otherwise isotropic by virtue of being at a temperature above (but near) the bulk ordering temperature T_c^∞ for ordering into a nematic phase described by the order parameter Q .

We find that a rich variety of behaviors are possible, depending on the strength of the orientational torques, which are described by a parameter V , within the framework of a model we have used previously.² More specifically, right at T_c^∞ the pinning force localized at the *boundary* drives a transition of the *entire* bulk liquid to the nematic phase (although the bulk coherence length ξ remains finite). At T_c^∞ the free energies of the isotropic and nematic phases are exactly equal, so that an arbitrarily weak perturbation "triggers" the phase transition. Thus the pinning force can fix the director of the molecules in the nematic phase. Above T_c^∞ we find there is a critical value V_c of the parameter V . For $V > V_c$, we have strong orientational order near the surface which extends at distance still substantially longer than the coherence length $\xi(T)$ but remains finite. For $V < V_c$, however, we still have strong orientational order just above T_c^∞ , but there is a discontinuous (first order) jump to a state of weak orientational order³ at a temperature $T_c^s > T_c^\infty$. There is a critical temperature T_c^s in the phase diagram, at which the magnitude of the jump ΔQ in the order parameter between strong and

weak states vanishes, for $V = V_c$.

We assume the free-energy density of liquid crystal is given by the Landau-Ginzburg functional:

$$F_L = U(Q) + \frac{1}{2}D \left(\frac{dQ}{dz} \right)^2, \quad (1)$$

where

$$U(Q) = \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4.$$

Here Q is the spatial coverage of the Legendre polynomial $P_2(\cos\theta)$ with θ the angle between the long axis of the molecule and the director. Equation (1) is an approximation: The order parameter Q is in fact a tensor, and there are two gradient terms which differ for homeotropic and planar geometries. As a consequence of this approximation, we only consider the case when the substrate enforces a pinning of the molecules along the z axis normal to the interface,² where Eq. (1) is valid and $0 < Q < 1$. The mean-field theory provides an adequate description of the isotropic-to-nematic phase transition in the bulk material, in the sense that classical exponents are found⁴; we employ the mean field theory in the present study. The coefficient A depends strongly on temperature, $A = a(T - T^*)$. By virtue of the term proportional to B in Eq. (1), the bulk transition is first order, at the temperature $T_c^\infty = T^* + 2B^2/9aC$. Just below T_c^∞ , the order parameter assumes the value $Q_c = 2B/3C$.

Other authors have studied orientational order near surfaces and interfaces in ferromagnets or antiferromagnets,⁵ ferroelectrics,^{6,7} or in ferromagnets subject to strong pinning at an interface.⁸ In these cases, symmetry arguments require $B = 0$, while the striking effects reported here all have their origin in

the influence of the BQ^3 term. Sheng⁹ explored aspects of the behavior of the order parameter in a thin film with the functional of Eq. (1) as the basis, but imposed the boundary condition on the order parameter $Q(z=0)=1$ on one side, a condition difficult to achieve even with very strong orientational pinning. [In our view,² the first layer of molecules is bonded tightly to the substrate, and is thus indeed fully oriented. However, the functional in Eq. (1) describes the liquid outside this first layer; our parameter V (defined below) is then a measure of the influence of the solid layer on the nearby liquid.]

We start from Eq. (3.5) of Ref. 2,

$$AQ - BQ^2 + CQ^3 - D \frac{d^2Q}{dz^2} = V\delta(z), \quad (2)$$

which is just the Euler-Lagrange equation which results from Eq. (1), with a pinning term $VQ\delta(z)$ added to the free-energy density to describe the orientational torque, short ranged in character, exerted on the molecules very near the first adsorbed

layer. Equation (2) implies that we consider the case where we can neglect long-range alignment forces (van der Waals interactions) which may exist and can either reinforce or conflict with the direct surface effects.¹⁰ The first integral of Eq. (2) reads

$$U(Q) = \frac{1}{2}D(dQ/dz)^2 \quad (3a)$$

with the boundary condition

$$U(Q(0)) = V^2/8D. \quad (3b)$$

Equation (3b) is a quadratic equation in the order parameter at the interface $Q(0)$, and then admits either one or three positive solutions. In the latter case, the physical solution is the one which minimizes the total free energy $F = \int_0^\infty F_L dz - VQ(0)$. We find that the stable solution is the largest value of $Q(0)$, since F is dominated by the driving term $-VQ(0)$, i.e., the strong state is always favored. This strong-state solution, however, ceases to exist, and a first-order transition to the weak state appears when $U(Q(0))$ becomes smaller than the secondary minimum of $U(Q)$. This determines the equation of the line of first-order transition:

$$V^2 = \frac{D}{6C^3} [B^2 - 2A_s C + B(B^2 - 4A_s C)^{1/2}] [6A_s C - B^2 - B(B^2 - 4A_s C)^{1/2}], \quad V < V_c \quad (4)$$

with $A_s = a(T_c^s - T_c^\infty)$. In particular, the asymptotic limit as $V \rightarrow 0$ is $T_c^s - T_c^\infty = V^2(4Q_c^2 aD)^{-1}$ so that the line of the first-order transition is parabolic near T_c^∞ . This line ends once $U(Q)$ becomes a monotonic function of Q , when the minimum and maximum of U vs Q merge into an inflection point at $Q = Q(0)$. This determines the location of the critical point:

$$T_c - T_c^\infty = \frac{B^2}{36aC}, \quad V_c = \left[\frac{DB^4}{24C^3} \right]^{1/2}. \quad (5)$$

The profile $Q(z)$ is obtained by integrating Eq. (3). We obtain

$$Q = Q_c \{1 - [1 - Q_c/Q(0)]e^{-z/\xi_0}\}^{-1} \quad (6)$$

at $T = T_c^\infty$, with $\xi_0 = \xi(T_c^\infty) = (2D/C)^{1/2}/Q_c$, and

$$Q = \frac{4A\alpha Q(0)e^{-z/\xi}}{2[\alpha + \frac{1}{3}BQ(0)e^{-z/\xi}]^2 - ACQ(0)^2 e^{-2z/\xi}} \quad (7)$$

at $T > T_c^\infty$, with $\xi = (D/A)^{1/2}$ the bulk correlation length and

$$\alpha = A - \frac{BQ(0)}{3} + \sqrt{A \left[A - \frac{2}{3}BQ(0) + \frac{1}{2}CQ(0)^2 \right]^{1/2}}.$$

As $z \rightarrow \infty$, Eq. (6) gives $Q \rightarrow Q_c$ at $T_c = T_c^\infty$, so that the bulk liquid has undergone a first-order transition to the nematic phase as a result of the breaking of symmetry induced by the pinning force. At $T > T_c^\infty$, the liquid remains in the isotropic phase far from the interface, and the asymptotic behavior of Eq. (7) is $Q = Q(0)(2A/\alpha)e^{-z/\xi}$ when $z \rightarrow \infty$. In the limit $Q(0) \ll 1$, Eq. (7) reduces to

the simple form

$$Q(z) = (V\xi/2D)e^{-z/\xi} \quad (8)$$

obtained by linearizing Eq. (2).¹¹ The term weak refers to a state where Eq. (8) describes both the dependence of Q on V and on z . At $T < T_c^s$ (the strong case), where $Q(0)$ is large, the variations

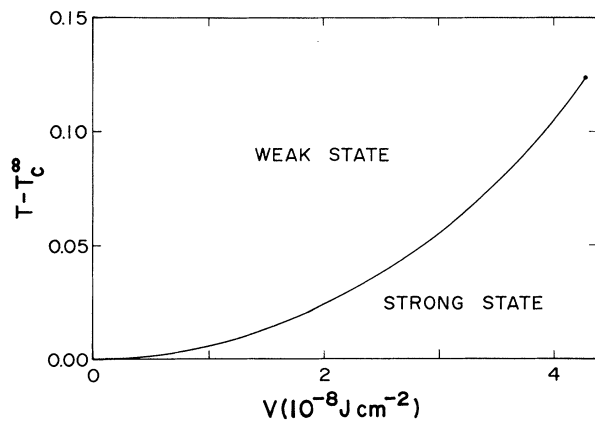


FIG. 1. Phase diagram in the V - T plane, for MBBA near the interface of a solid. The solid line is the line of first-order transitions, calculated from Eq. (4), ending at the critical point $V_c = 4.27 \times 10^{-8} \text{ J cm}^{-2}$, $T_c - T_c^\infty = 0.125 \text{ K}$.

$Q(z)$ are highly nonexponential near the interface; in particular, a broad plateau in the variations $Q(z)$ is observed, for such values of z where Q is in the vicinity of the minimum of $U(Q)$ located at $Q = [B + (B^2 - 4AC)^{1/2}]/(2C)$, which, according to Eq. (3a), corresponds to a minimum of dQ/dz . It can be shown that the width of this plateau varies like $\ln(T - T_c^\infty)$.

We illustrate these results in Figs. 1 to 3 by explicit calculations for the liquid-crystal *p*-methoxybenzylidene-*p*-(*n*-butyl)aniline (MBBA), using the appropriate parameters²: $a = 6.27 \times 10^{-2} \text{ J cm}^{-3} \text{ K}^{-1}$, $T^* = 314 \text{ K}$, $B = 0.47 \text{ J cm}^{-3}$, $C = 0.79 \text{ J cm}^{-3}$, and $D = 4.43 \times 10^{-13} \text{ J/cm}$. Then $T_c^\infty \sim 315 \text{ K}$. The numbers give $V_c = 4.27 \times 10^{-8} \text{ J cm}^{-2}$, $T_c - T_c^\infty = 0.125 \text{ K}$ for the critical point of the diagram displayed in Fig. 1. In Fig. 2, we present $Q(0)$ calculated as a function of T , for values of V in the range of $10^{-8} \text{ J cm}^{-2}$, which makes evident discontinuous jumps between strong and weak states for $V < V_c$. Note that in the strong case $Q \sim Q_c \approx 0.4$. Very strong pinning indeed would be required to achieve a state with $Q(0) = 1$, as assumed by Sheng.

In Fig. 3, we show how the profiles $Q(z)$ vary as a function of temperature for a typical value of $V = 3.5 \times 10^{-8} \text{ J cm}^{-2}$, in which case $T_c^s = 0.08 \text{ K}$. At $T > T_c^s$, the weak state is observed, characterized by an exponential decay of Q vs z , with healing length controlled by the bulk coherence length, ξ , equal to 266 \AA at T_c^∞ . At $T < T_c^s$, in the strong state, $Q(z)$ decays more slowly and a plateau is observed as one approaches T_c . This is a crossover ef-

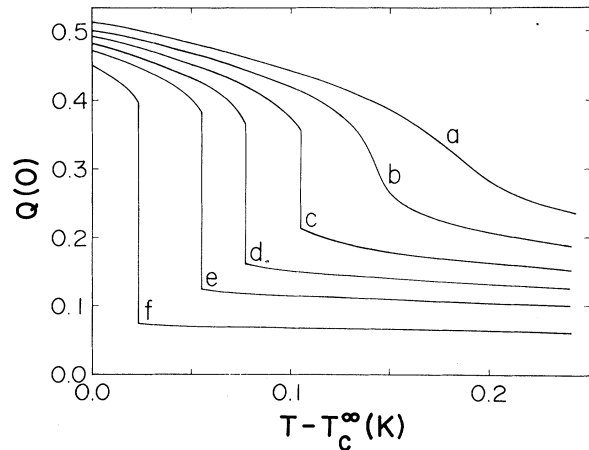


FIG. 2. The orientational order parameter at the interface, $Q(0)$, as a function of temperature, for six values of the pinning parameter V . Curves f through a are computed for the following values: $3.0, 3.4, 3.6, 4.0, 4.5,$ and $5.0 \times 10^{-8} \text{ J/cm}^2$, respectively.

fect between the behavior of $Q(z)$ at T_c^∞ which tends asymptotically to $Q = Q_c$ at $z \rightarrow \infty$ (curve a), and the behavior of the disordered state at $T > T_c^\infty$, where at large distance from the surface, we recover the exponential decay $Q \propto e^{-z/\xi}$.

Orientalional order near the interface, above T_c^∞ , may be studied by optical experiments. Indeed, Miyano¹² has observed substrate-induced orientational order above T_c^∞ in a liquid crystal, by studying birefringence. Light reflected from a transparent substrate, incident on the interface from the substrate side, would be a particularly appropriate

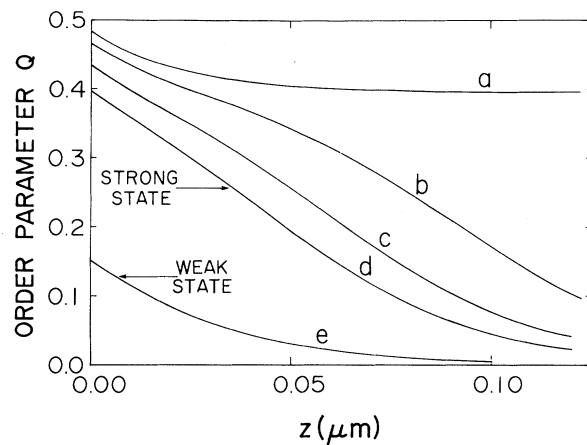


FIG. 3. The order parameter Q as a function of distance z from the interface, for a pinning force $V = 3.5 \times 10^{-8} \text{ J cm}^{-2}$, at different temperatures $T - T_c^{(\infty)} = 0, 2, 5, 7,$ and $10 \times 10^{-2} \text{ K}$ (curves a through e , respectively).

probe if the angle of incidence is greater than the critical angle for total internal reflection. Then the optical field is evanescent on the liquid-crystal side, and the measurement is particularly sensitive to the state of the liquid crystal near the solid boundary. To be more specific, one may envision a prism with the bottom coated by a metal film. Then coupling to surface polaritons in the metal film, in the Kretschmann geometry used in attenuated total reflection experiments, produces a characteristic reflectivity dip controlled by the frequency of the surface polariton, for angles of incidence beyond the critical angle.¹³ A liquid crystal placed below the metal film will shift the frequency of the surface polariton and hence the position of the dip; by monitoring the temperature variation of the dip position above T_c^∞ , one may explore the substrate-induced orientational order as a function of temperature, and a first-order jump in the order parameter such as that displayed in Fig. 1 should be readily observable. We will be eager to see further optical studies of solid-liquid-crystal interfaces.

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³The definition of the terms strong and weak orientational order will be clear from our subsequent discussion.

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