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Phase transitions in finite-thickness nematic liquid-crystal films: Planar anchoring

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Phase transitions in finite-thickness nematogenic materials bounded by two planar surfaces and characterized by identical surface interactions linearly proportional to the order parameter have been studied theoretically by solving the coupled nonlinear Euler-Lagrange equations. The surface interaction was assumed to favor molecular orientation in the surface plane with no rubbed or preferred direction. The related problem of a semi-infinite film having a single surface has been studied previously at temperatures above the bulk nematic-isotropic phase transition point \( T_{NI} \). For that geometry and physically relevant elastic constants, it was shown that, in addition to the bulk transition, there is a second transition at higher temperatures between biaxial and uniaxial ordering of the surface layer when the strength of the surface coupling is not too weak. It is shown here that this double phase transition reduces to a single one for sufficiently thin layers.

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Theoretical studies of nematic liquid-crystal films have been of long standing interest due to their applications in displays [1] in addition to their role as model systems for the study of phase transitions and critical phenomena [2–9]. A surface may strongly affect the degree and direction of nematic order of the region it bounds, resulting in deviations from the equilibrium order of an unbounded (infinite) sample domain. For example, at temperatures above the bulk nematic-isotropic transition \( (T_{NI}) \), there is local ordering of the liquid-crystal molecules in the vicinity of an interface due to interaction potentials which transmit the aligning action of the substrate into the bulk. The orientational ordering near such an interface is restricted to a boundary layer as the magnitude of the order decays with distance from the surface.

Several authors have investigated the effects of confinement of nematic liquid crystals (NLC’s) for different geometries and surface potentials [4,10–13]. In particular, it was shown by Sheng [4], who used the Landau-de Gennes theory to treat the case of a confined liquid-crystal sample between two parallel plates with homeotropic boundary conditions and a surface interaction potential linear in the order parameter, that the bulk-transition temperature shifts upward as the film thickness is reduced. Also, if the liquid-crystal cell thickness is comparable with or thinner than the boundary layer thickness, the bulk transition between the isotropic and nematic phases disappears. Similar modifications of the phase diagram are expected to occur when the surface aligning mechanism is other than homeotropic.

The purpose of this work is to study, above \( T_{NI} \), the effect of finite thickness on the phase diagram of NLC’s when the surface interaction favors planar anchoring, i.e., molecular orientation parallel to the surface but without any preferred direction in this plane. A surface of this type may be modeled by a surface potential that is linear or quadratic in the nematic order parameter by appropriately choosing the parameters appearing in the potential. In earlier work, phase transitions in semi-infinite nematogenic materials bounded by a single flat surface and characterized by a preferential planar surface interaction linear [14] and/or quadratic [15,16] in the order parameter were studied theoretically at temperatures above \( T_{NI} \). It was found, for physically relevant elastic constants, that there is at most one additional phase transition above and distinct from the bulk phase transition, depending upon the strength of the surface coupling (see Fig. 1). For weak surface coupling, no surface phase transition occurs and a uniaxial surface layer having the director normal to the surface remains the stable state until \( T_{NI} \) is reached. However, as the linear surface interaction coupling is increased, there is a prewetting transition from a uniaxially ordered surface layer to a biaxially ordered one as the temperature is reduced towards \( T_{NI} \). On further increasing the surface coupling, this transition boundary becomes second order via a tricritical point. Eventually, the second-order transition boundary becomes asymptotically independent of the surface coupling. It was also shown that the mean-field continuous transition boundary is suppressed due to Berezinskii-Kosterlitz-Thouless (BKT) fluctuations.

Here we consider the case of a NLC bounded by two planar surfaces. We shall show, for the case in which the surface interactions are identical and linear in the order parameter, that the two successive phase transitions occurring with decreasing temperature in the semi-infinite case (first between two surface states, then to the bulk ordered state) reduce to a single one when the layer is sufficiently thin. Typical phase diagrams, showing the effects of film thickness on the bulk phase transition as well as the boundary layer phase transition, will be given.

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We consider a NLC cell of width $2L'$ and large cross-section area $A$ sandwiched between two identically treated substrates situated at $z = \pm L'$, where $z$ is the coordinate normal to the surfaces. Within the Landau–de Gennes formalism, the nematic tensor order parameter may be expressed in terms of the dielectric tensor $\epsilon_{ij}(r)$ as [17]

$$\epsilon_{ij} = \epsilon_{ij}^0 - \frac{1}{3} \text{Tr}(\epsilon^0) \delta_{ij}$$

and the bulk free energy density as [17]

$$g_b[\epsilon] = \frac{1}{2} \left[ \alpha \epsilon_{ij}^2 + c_1 \epsilon_{ij,k}^2 + c_2 \epsilon_{ij} \epsilon_{k,l} \right] - \beta \epsilon_{ij} \epsilon_{jk} \epsilon_{ki} + \gamma (\epsilon_{ij}^2)^2.$$  

Here $\epsilon_{ij,k} \equiv \partial \epsilon_{ij}/\partial x_k$ and a sum is implied over repeated indices. The coefficient $a$ is regarded as (linearly) temperature dependent whereas the other coefficients ($\beta, \gamma, c_1$, and $c_2$) are taken to be constant in the temperature region of interest.

The expression for $g_b$ can be simplified by setting [18]

$$\mu_{ij} = s^{-1} \epsilon_{ij}, \quad s = \beta/\sqrt{6\gamma}, \quad \frac{1}{4} t = (3\gamma/\beta^2)a,$$

$$f = (3\epsilon_{ij}/\beta^4)g, \quad \frac{1}{4} \xi^2 = (3\gamma/\beta^2)c_1, \quad \rho = c_2/c_1.$$  

Here $t$ is the reduced temperature and the bulk nematic-isotropic transition occurs at $t = 1$. The parameter $\xi$ is the correlation length.

The scaled nematic order parameter $\mu_{ij}$ can be written in its principal axis system as a function of two scalar functions $\mu(\zeta)$ and $\eta(\zeta)$ as

$$\mu_{ij}(\zeta) = \frac{1}{\sqrt{6}} \begin{pmatrix} -\mu + \eta & 0 & 0 \\ 0 & -\mu - \eta & 0 \\ 0 & 0 & 2\mu \end{pmatrix},$$

where $\zeta = z/\xi$. Substituting Eq. (4) into Eq. (2) using Eq. (3), the corresponding reduced bulk free energy density becomes

$$f_b = \frac{1}{4} t \mu^2 + \frac{1}{12} t \eta^2 - \mu^3 + \mu^2 + \mu^4 + \frac{2}{3} \eta^2 \mu^2 + \frac{1}{3} \eta^4 + \frac{1}{4} \left( 1 + \frac{2}{3} \rho \right) \mu^4 + \frac{1}{12} \eta^2,$$

where primes denote differentiation with respect to $\zeta$. We shall concentrate on the case $\rho = 1$ since the ratio between the bend and the twist elastic constants ($K_{33}/K_{22}$) is typically of order 1–2 and Landau–de Gennes theory predicts $K_{33}/K_{22} = 1 + \rho/2$.

To obtain the total scaled free energy per unit area, the expression for the total bulk free energy needs to be supplemented by a surface contribution $F_s$ which, to lowest order in the reduced nematic order parameter, may be written as

$$F_s/\xi = \frac{4}{\sqrt{6}} \nu \mu(-L) + \frac{4}{\sqrt{6}} \nu \mu(L),$$

where $L = L'/\xi$. Here $\nu$ is proportional to the strength of the surface interaction; planar boundary conditions are obtained by requiring that $\nu > 0$. Note that for $\rho = 1$, $\nu = 1.0$ corresponds to a surface interaction strength of 1.5 ergs/cm$^2$ and the scaled film thickness $L = 1$ corresponds to a real film thickness of approximately 79 Å. The total scaled free energy per unit area in the $x$-$y$ plane is thus given by

$$F[\mu]/\xi = F_b[\mu]/\xi + F_s[\mu]/\xi = \int_{-L}^{L} d\zeta f_b + F_s.$$  

The functions $\mu(\zeta)$ and $\eta(\zeta)$ are determined by minimizing $F$ for any particular set of parameters. Formally, this is done by solving the coupled nonlinear Euler-Lagrange equations (see [14]) obtained from the Landau–de Gennes free energy density expression Eq. (5) subject to the boundary conditions

$$\mu'(-L) = 4\nu/\sqrt{6} \left( 1 + \frac{2}{3} \rho \right), \quad \eta'(-L) = 0;$$

$$\mu'(L) = -4\nu/\sqrt{6} \left( 1 + \frac{2}{3} \rho \right), \quad \eta'(L) = 0.$$  

Numerical results for the thermodynamic boundaries separating the different states in the surface coupling ($\nu$)-temperature ($T$) phase space were obtained by employing a computer software code COLNEW [14,19]. Transitions from the biaxial to the uniaxial surface layer above $T_{NI}$
can be either second or first order, depending upon the strength of surface coupling [14]. On the other hand, transitions from the bulk state to either the biaxial or the uniaxial surface layer are more subtle. For semi-infinite thickness, this transition occurs at $t = 1$ but is first order for the bulk to uniaxial case and second order for the bulk to biaxial transition. This is explained by the fact that the uniaxial surface layer only partially wets the surface while the biaxial layer wets the surface completely. However for finite thickness, both uniaxial and biaxial surface layers only partially wet the surface and the transition from the bulk state is always first order.

The results of our calculations are summarized graphically in Figs. 1–3. These are phase diagrams in the interaction strength ($\nu$)–reduced temperature ($t$) plane for different values of film thickness ($L = \infty, 4.8, \text{and } 1$, respectively). The insets in these figures are the corresponding enlargements of the low interaction-strength regions of these graphs. For a semi-infinite film, the bulk phase transition occurs at $T_{Ni}$ for all surface couplings [14]. This transition shifts to higher temperatures as the film thickness is reduced because of the ordering field exerted by the bounding walls. Although this field is short-range and is exerted directly only on those molecules adjacent to the walls, intermolecular interactions cause it to influence the bulk, particularly when the film thickness is small and comparable with the correlation length $\xi$. In contrast to the bulk transition, the surface layer transition from the biaxial surface state to the uniaxial surface state has a smaller shift to only slightly higher temperatures since the surface behavior of the confined NLC depends only very weakly on the film thickness. Consequently, the point of intersection of the prewetting transition line and the bulk $Ni$ transition line shifts to higher surface couplings as well as to higher temperatures.

On further reducing the film thickness it is found that, at $L = 4.85$, the bulk transition is significantly modified. At this critical film thickness, the bulk transition disappears at $\nu = 15.3$. Below $L = 4.85$ (see Fig. 2), the bulk transition boundary splits into two branches terminating in critical points. Thus, there is an intermediate range of surface couplings for which there is no bulk transition but only a continuous surface transition. The two critical points move apart as $L$ is further reduced, increasing the range of surface couplings for which only a continuous phase transition occurs. At $L = 4.55$ the upper branch of the bulk transition disappears entirely. The lower branch of the bulk transition continues to shrink as $L$ reduces further. Eventually, it merges with the prewetting transition line at $L = 3.38$. Below $L = 3.38$ there is only one transition, from the uniaxially ordered surface layer to the bulk (see Fig. 3). This transition is first order for weak surface couplings and becomes second order via a tricritical point as the surface coupling is increased. An interesting point to note here is that even for extremely thin films of the NLC, the surface phase transition never disappears for any surface coupling. This feature can be easily understood since the surface phase transition here occurs between two surface states having different symmetries. While such transitions may be of either first or second order, there must always be a transition of some sort. The line of transitions cannot terminate in a critical point.

Finally, the continuous transition boundary determined from Landau theory is not the true thermodynamic boundary since the mean-field solution neglects
fluctuations. The order in the surface biaxial layer has
the same symmetry as the two-dimensional XY model.
The continuous phase transition, which describes sym-
metry breaking within the bounding plane, is there-
fore in principle described by the Berezinskii-Kosterlitz-
Thouless (BKT) mechanism [20,21]. The BKT fluctu-
ations lead to a suppression of the mean-field solution
and result in a shift of the continuous transition boundary
to lower temperatures [14]. It is found that a greater
suppression of the mean-field boundary occurs for very
thin films. The dashed lines in the phase diagrams (1–
3) represent the BKT boundaries. The BKT phase
boundary can possibly be detected experimentally by
evanescent-wave ellipsometry [22] or by inelastic light
scattering [15].

In summary, we have calculated the thermodynamic
phase diagram for a finite thickness film of NLC above
its bulk transition temperature for the case of planar
boundary conditions and an interaction potential that
is linear in the order parameter. The Euler-Lagrange
equations have been solved exactly by numerical meth-
ods. It is found that while the bulk transition shifts to
higher temperatures as the film thickness is reduced, the
surface layer transition is fairly robust to changes in film
thickness. There is also a critical thickness for all sur-
f ace couplings at which the bulk transition disappears.
Consequently, for sufficiently thin samples of nematic,
the double phase transition obtained for the semi-infinite
case reduces to a single one. For weak surface coupling,
there is a single first-order phase transition from a uni-
axially ordered surface layer to a biaxially ordered one
as the temperature is reduced. This transition becomes
second order via a tricritical point as the surface coupling
is increased.

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