

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

Natasha Kotheekar and D. W. Allender

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

R. M. Hornreich

Physics of Complex Systems, Weizmann Institute of Science, 76100 Rehovot, Israel

(Received 4 January 1995; revised manuscript received 30 June 1995)

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.

PACS number(s): 61.30.Gd, 64.70.Md, 68.45.-v

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 cell 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.

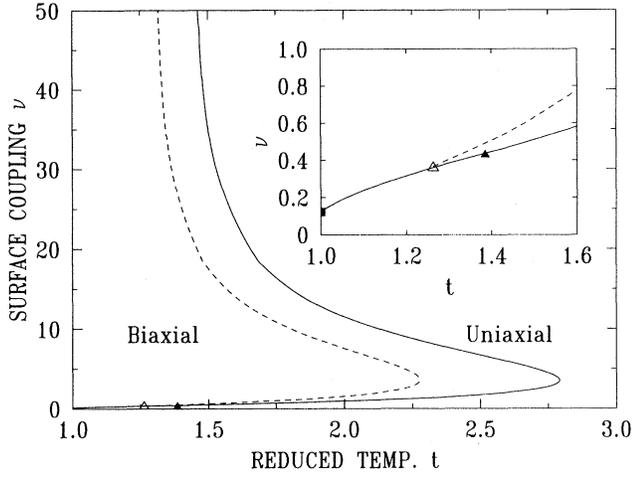


FIG. 1. Phase diagram for $L = \infty$. Shown is the continuous transition boundary between the uniaxial and the biaxial surface layer obtained from the Landau formulation (solid line). Also shown is the BKT boundary (dashed line) between the two layers. The bulk transition occurs at $t = 1$. Inset represents an enlargement of the lower interaction strength region of the graph. Shown is the mean-field tricritical point (filled triangle) and the BKT tricritical point (open triangle). The transition from the uniaxial to the biaxial surface region changes from second order to first order via the tricritical point with decreasing surface coupling (ν). The prewetting (first order) transition boundary between the two surface layers ends on the bulk transition line (filled square).

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 $\epsilon_{ij}^D(\mathbf{r})$ as [17]

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

and the bulk free energy density as [17]

$$g_b[\epsilon] = \frac{1}{2} [a\epsilon_{ij}^2 + c_1\epsilon_{ij,k}^2 + c_2\epsilon_{ij,i}\epsilon_{kj,k}] - \beta\epsilon_{ij}\epsilon_{jk}\epsilon_{ki} + \gamma(\epsilon_{ij}^2)^2. \quad (2)$$

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 (β, γ, 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]

$$\begin{aligned} \mu_{ij} &= s^{-1}\epsilon_{ij}, & s &= \beta/\sqrt{6}\gamma, & \frac{1}{4}t &= (3\gamma/\beta^2)a, \\ f &= (36\gamma^3/\beta^4)g, & \frac{1}{4}\xi^2 &= (3\gamma/\beta^2)c_1, & \rho &= c_2/c_1. \end{aligned} \quad (3)$$

Here t is the reduced temperature and the bulk nematic-

isotropic transition occurs at $t = 1$. The parameter ξ is the correlation length.

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

$$\mu_{ij}(\zeta) = \frac{1}{\sqrt{6}} \begin{pmatrix} -\mu + \eta & 0 & 0 \\ 0 & -\mu - \eta & 0 \\ 0 & 0 & 2\mu \end{pmatrix}, \quad (4)$$

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

$$\begin{aligned} f_b &= \frac{1}{4}t\mu^2 + \frac{1}{12}t\eta^2 - \mu^3 + \mu\eta^2 + \mu^4 \\ &+ \frac{2}{3}\mu^2\eta^2 + \frac{1}{9}\eta^4 + \frac{1}{4}\left(1 + \frac{2}{3}\rho\right)\mu'^2 + \frac{1}{12}\eta'^2, \end{aligned} \quad (5)$$

where primes denote differentiation with respect to ζ . We shall concentrate on the case $\rho = 1$ since the ratios 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

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

where $L = L'/\xi$. Here ν 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/cm² 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

$$F[\mu]/\xi = F_b[\mu]/\xi + F_s[\mu]/\xi = \int_{-L}^L d\zeta f_b + F_s. \quad (7)$$

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

$$\mu'(-L) = 4\nu/\sqrt{6}\left(1 + \frac{2}{3}\rho\right), \quad \eta'(-L) = 0; \quad (8)$$

$$\mu'(L) = -4\nu/\sqrt{6}\left(1 + \frac{2}{3}\rho\right), \quad \eta'(L) = 0. \quad (9)$$

Numerical results for the thermodynamic boundaries separating the different states in the surface coupling (ν)-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 (ν)–reduced temperature (t) plane for different values of film thickness ($L = \infty, 4.8,$ 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 ξ . 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

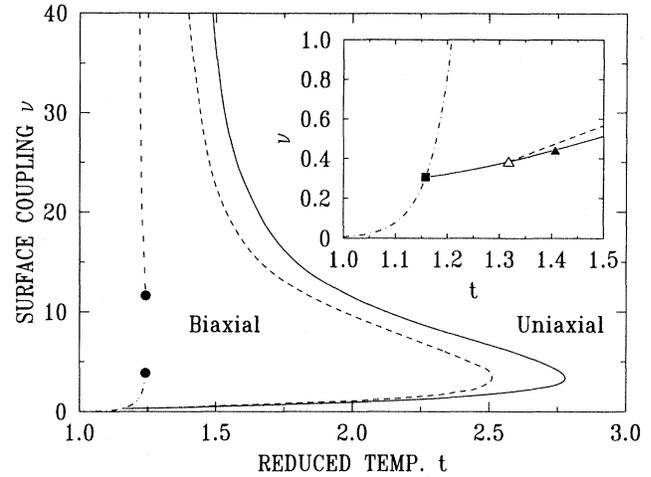


FIG. 2. Phase diagram for $L = 4.8$. Shown are the continuous transition boundaries obtained from Landau theory and BKT formulation as in Fig. 1. Also shown are the two branches of the bulk transition boundary (dotted-dashed line) ending in critical points (filled circles). Inset represents an enlargement of the lower interaction strength region of the graph showing the mean-field and BKT tricritical points as well as the point of intersection of the prewetting line with the bulk transition line (filled square) which moves to higher temperatures as well as higher surface couplings with decreasing film thickness.

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

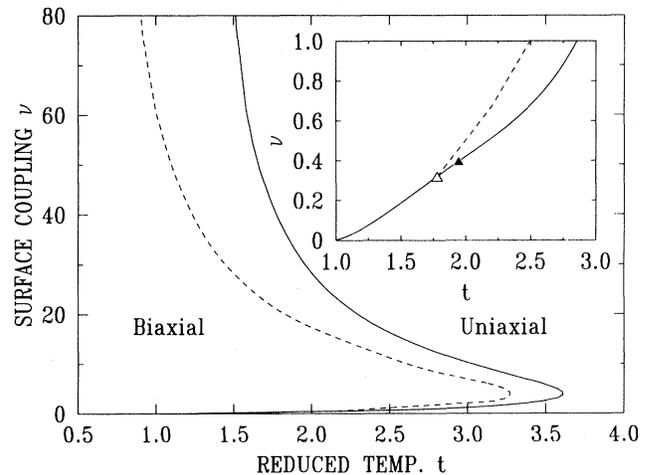


FIG. 3. Phase diagram for $L = 1$. Shown is the single transition boundary from the uniaxial surface layer to the bulk obtained from Landau theory and BKT formalism, respectively. Inset shows an enlargement of the lower interaction strength region of the graph. The transition from the uniaxial surface region to the bulk changes from second order to first order via a tricritical point with decreasing surface coupling.

fluctuations. The order in the surface biaxial layer has the same symmetry as the two-dimensional XY model. The continuous phase transition, which describes symmetry breaking within the bounding plane, is therefore in principle described by the Berezinskii-Kosterlitz-Thouless (BKT) mechanism [20,21]. The BKT fluctuations 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 methods. 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 surface 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 uniaxially 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.

This work has been supported in part by ALCOM Grant No. DMR89-20147 and the Basic Research Foundation, administered by the Israeli Academy of Arts and Sciences, Israel. We acknowledge helpful discussions with E.C. Gartland regarding the use of COLNEW.

-
- [1] J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl.* **1**, 1 (1982).
 [2] P. Sheng, *Phys. Rev. Lett.* **37**, 1059 (1976).
 [3] K. Miyano, *Phys. Rev. Lett.* **43**, 51 (1979).
 [4] P. Sheng, *Phys. Rev. A* **26**, 1610 (1982).
 [5] M.M. Telo de Gama, *Mol. Phys.* **52**, 611 (1984).
 [6] A. Mauger *et al.*, *Phys. Rev. Lett.* **53**, 2485 (1984).
 [7] A. Poniewierski and T.J. Sluckin, *Mol. Cryst. Liq. Cryst.* **111**, 373 (1984).
 [8] A.K. Sen and D.E. Sullivan, *Phys. Rev. A* **35**, 1391 (1987).
 [9] T.J. Sluckin and A. Poniewierski, *Phys. Rev. Lett.* **55**, 2907 (1985); in *Fluid Interfacial Phenomena*, edited by C.A. Croxton (Wiley, New York, 1985), p. 215.
 [10] A. Poniewierski and T.J. Sluckin, *Mol. Cryst. Liq. Cryst.* **2**, 281 (1987).
 [11] M. M. Telo de Gama and P. Tarazona, *Phys. Rev. A* **41**, 1149 (1990).
 [12] M. M. Telo de Gama *et al.*, *Mol. Phys.* **71**, 801 (1990).
 [13] M.P. Allen, *Mol. Phys.* **68**, 181 (1989).
 [14] N. Kotheke, D.W. Allender, and R.M. Hornreich, *Phys. Rev. E* **49**, 2150 (1994).
 [15] R.M. Hornreich, E.I. Kats, and V.V. Lebedev, *Phys. Rev. A* **46**, 4935 (1992).
 [16] R. Seiden *et al.* (unpublished).
 [17] P.G. deGennes, *Mol. Cryst. Liq. Cryst.* **12**, 193 (1971).
 [18] H. Grebel *et al.*, *Phys. Rev. A* **28**, 1114 (1983).
 [19] U. Ascher, J. Christiansen, and R.D. Russel, *ACM Trans. Math. Software* **7**, 209 (1981).
 [20] J.M. Kosterlitz and D.J. Thouless, *J. Phys. C* **5**, 1224 (1972).
 [21] J.M. Kosterlitz and D.J. Thouless, *J. Phys. C* **6**, 1181 (1973).
 [22] W. Chen *et al.*, *Phys. Rev. Lett.* **62**, 1860 (1989).