Novel Surface Phase Transition in Nematic Liquid Crystals: Wetting and the Kosterlitz-Thouless Transition

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The growth of nematic films near a wall close to the nematic-isotropic transition is studied for planar boundary conditions. If the nematic phase wets the wall, near the onset of bulk nematic behavior the nematic film near the wall is in a Kosterlitz-Thouless low-temperature phase. The transition to this phase can be a defect-unbinding transition or a first-order transition, or two transitions may occur. A surface phase diagram is drawn as a function of temperature, bulk ordering field, and surface ordering field.

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There has been considerable interest over the last few years in the development of surface order in nematic liquid crystals, and in particular in the question of whether the order near an interface might differ quantitatively or qualitatively from the order in the bulk.[1-7] This interest arises both from the relevance of surface nematic order to visual display systems and for fundamental reasons connected with the resurgence of interest in surface phase transitions and wetting phenomena.[8-10]

We have studied the development of nematic order at a wall-nematogen interface as the temperature is reduced towards the bulk nematic-isotropic (N-I) phase transition at T_{NI}. Other investigators have considered this problem for homeotropic (director normal to the wall) or homogeneous (director given by an easy axis in the plane of the wall) boundary conditions.[1,2,4,5,11] We study here the case of planar boundary conditions (the directions in the plane of the wall form a degenerate set of easy axes), which, although experimentally somewhat exotic and hard to achieve, provides a surface phase diagram with some qualitatively new features which are of particular interest in the more general context of the statistical mechanics of surfaces.

The simplest nematic order parameter is a traceless symmetric tensor which, in the coordinates of its principal axes, may be written as

$$Q_{ij}=\tfrac{1}{2}\langle 3n_in_j-\delta_{ij}\rangle = \begin{pmatrix} -\frac{1}{2}Q+P & 0 & 0 \\ 0 & -\frac{1}{2}Q-P & 0 \\ 0 & 0 & Q \end{pmatrix}, \quad (1)$$

where $\hat{\mathbf{n}}$ is a molecular orientation. At the N-I transition there is a first-order phase transition between an isotropic phase ($Q=P=0$) and a uniaxial nematic phase ($Q\neq 0, P=0$). However, this phase transition is affected by magnetic fields.[12,13] In the context of this work it is useful to recall that if the nematogen has negative diamagnetic anisotropy, and the magnetic field is in the z direction, the high-temperature (paranematic, P) phase has a small but nonzero $Q<0$, whereas the low-temperature (N) phase has a broken symmetry in the x-y plane and is biaxial ($Q\neq 0, P\neq 0$). The temperature of the phase transition is increased by the applied field, but the transition remains first order until at a critical field there is a tricritical point beyond which the transition is continuous.

We consider the surface phase diagram of such a system placed in the region $z>0$, with an extra surface ordering field also providing a degenerate set of easy axes in the x-y plane. From an experimental point of view we are interested in the case of zero bulk field. However, consideration of the more general phase diagram provides both a context in which the results may be interpreted and an example of a system with interesting surface behavior.[11,14] Surface order may usefully be discussed in terms of the parameters

$$\Gamma_Q=-\int_0^\infty Q(z)\,dz, \quad (2a)$$

$$\Gamma_P=\int_0^\infty P(z)\,dz. \quad (2b)$$

As discussed elsewhere[5,6,8-11,15] the development of surface order is closely related to the question of whether the nematic wets the wall. Complete wetting of the wall by the nematic phase corresponds to $\Gamma_P, \Gamma_Q \to \infty$ as $T \to T_{NP}^+$, and complete wetting of the wall by the paranematic (isotropic) phases corresponds to $\Gamma_P, \Gamma_Q \to -\infty$ as $T \to T_{NP}^-$ (T_{NI}^-).

We have used mean-field theory, supplemented by

general arguments on the way in which mean-field theory results are affected by fluctuations. At zero field we find the following, depending on the strength of the surface field: (a) Γ_Q remains finite and $\Gamma_P=0$ as $T\rightarrow T_{NI}^+$. (b) $\Gamma_Q\rightarrow\infty$, $\Gamma_P\rightarrow\infty$ as $T\rightarrow T_{NI}^+$; there is a first-order phase transition at $T_S>T_{NI}$ at which there are discontinuities in Γ_Q and Γ_P, and for $T>T_S$, $\Gamma_P=0$. (c) $\Gamma_Q\rightarrow\infty$, $\Gamma_P\rightarrow\infty$ as $T\rightarrow T_{NI}^+$; there is a continuous surface phase transition at $T_{S1}>T_{NI}$ above which $\Gamma_P=0$, followed by a first-order surface phase transition at T_{S2} ($T_{S1}>T_{S2}>T_{NI}$). (d) $\Gamma_Q\rightarrow\infty$, $\Gamma_P\rightarrow\infty$ as $T\rightarrow T_{NI}^+$; there is merely a continuous surface phase transition at T_S above which $\Gamma_P=0$. The first-order transitions are the boundary transitions predicted by Sheng,[1,2] now recognized as prewetting transitions.[5,6,11,14,15] Fluctuations cause all the continuous transitions to be defect-unbinding transitions of the type first discussed by Kosterlitz and Thouless.[16,17]

In a finite bulk field the N phase always wets the wall sufficiently close to the tricritical point. This follows by noting that[18] near a critical point wetting always occurs because $\sigma_{12}\sim(T_c-T)^{\mu}$ and $\sigma_1-\sigma_2\sim(T_c-T)^{\beta_1}$ with $\mu>\beta_1$ (where β_1 is a surface exponent); near a three-dimensional tricritical point $\mu=2$, $\beta_1=\frac{1}{2}$.[9,10,15]

The form of surface field that we have chosen always implies some extra order at the wall. We choose this form because it allows us to examine the qualitatively new features of the surface phase diagram, (c) and (d) above. A slightly different form allows the further possibility that $\Gamma_Q=0$, $\Gamma_P=0$, as $T\rightarrow T_{NI}^+$. This corresponds to complete wetting by the isotropic phase and has been observed for 5CB (4-*n*-pentyl-4′-cyanobiphenyl) on walls coated with parylene and polyimide.[19] In this case the P phase completely wets the wall near the tricritical point.

These ideas may be described within Landau–de Gennes theory as follows.[12,20,21] The free energy per unit volume of a nematogenic system may be written as

$$\mathcal{F}=\mathcal{F}_0+\tfrac{1}{2}AQ_{ij}Q_{ij}-\tfrac{1}{3}BQ_{ij}Q_{jk}Q_{ki}+\tfrac{1}{4}C(Q_{ij}Q_{ij})^2-\tfrac{1}{2}\chi_A H_iH_jQ_{ij}+\mathcal{F}_G, \tag{3a}$$

$$\mathcal{F}_G=\tfrac{1}{2}L_1(\partial Q_{ij}/\partial x_k)\partial Q_{ij}/\partial x_k+\tfrac{1}{2}L_2(\partial Q_{ij}/\partial x_j)\partial Q_{ik}/\partial x_k, \tag{3b}$$

where **H** is the magnetic field, χ_A is the anisotropic part of the magnetic susceptibility (assumed negative here), $A=A'(T-T^*)$, and L_1 and L_2 are effective elastic constants. Following Fan and Stephen[12] we find it convenient to deal with a nondimensional version of Eqs. (3).

Defining $\eta=-CQ/B$, $p=-CP/B$, and $F=C^3\mathcal{F}/B^4$, one obtains

$$F=F_0+F_u+F_G, \tag{4a}$$

$$F_u=\tfrac{3}{4}t\eta^2+\tfrac{1}{4}\eta^3+\tfrac{9}{16}\eta^4-h\eta+p^2(t-\eta+\tfrac{3}{2}\eta^2)+p^4, \tag{4b}$$

where $t=AC/B^2$ is the nondimensional temperature, and $h=-\frac{1}{2}\chi_A H^2C^2/B^3$ is a dimensionless ordering field.[22] With this free energy the N-I transition takes place at $t_{NI}=\frac{1}{27}$, and the tricritical point occurs at $t_c=\frac{7}{96}$, $h_c=\frac{1}{64}$. The phase transition can also be formally extended to $t<0$, where both biaxial and uniaxial phases are only metastable (the stable phase is a large-positive-Q uniaxial phase).[12,13] The P phase becomes unstable along the line $\eta=\frac{1}{9}[-1+(1-18t)^{1/2}]$. The experimentally relevant $h=0$ case has $\eta=0$ for $t>t_{NI}$ and $\eta=\frac{1}{12}[1+(1-24t)^{1/2}]$ for $t<t_{NI}$.

In the presence of a surface one must minimize a surface free-energy functional of the profiles $\eta(z)$,$p(z)$:

$$\Phi\{\eta(z),p(z)\}=\frac{1}{\xi_1}\int_0^{\infty}dz\left[F_u(\eta,p)-F_{\infty}+\xi_1^2\left(\frac{d\eta}{dz}\right)^2+\xi_2^2\left(\frac{dp}{dz}\right)^2\right]-h_1\eta(z=0), \tag{5}$$

where $\xi_1=[(\frac{3}{2}L_1+L_2)C/2B^2]^{1/2}$ and $\xi_2=(L_1C/B^2)^{1/2}$ are correlation lengths, $F_{\infty}=F(\eta(\infty),p(\infty))$ is the bulk free-energy density far into the bulk fluid, and h_1 is a dimensionless surface contact potential. The planar boundary conditions are imposed by the condition $h_1>0$. We have taken the simplest form of the surface free energy consistent with the phenomena under discussion. More generally we expect terms quadratic in the surface order parameters.

The Euler-Lagrange equations resulting from Eq. (5) are only readily solvable in the case $\xi_2=0$. In this case, however, the theory strongly resembles the theory of Cahn,[18] and possesses a solution in closed form. We find that $\Gamma_P=0$ if $\eta(z=0)<\eta_c=\frac{1}{3}[1-(1-6t)^{1/2}]$, and that when $\eta(z)>\eta_c(t)$, $p(z)=[\frac{1}{2}(\eta-\frac{3}{2}\eta^2-t)]^{1/2}$. The surface phase diagram possesses features predicted by Cahn,[18] in particular, a first-order wetting transition at P-N coexistence (in this case wetting by the nematic phase). The transition takes place at decreasing temperatures as the surface field h_1 is increased, and is accompanied by a first-order prewetting line away from P-N coexistence, along which there is a discontinuity in Γ_Q and Γ_P, and

which terminates at a surface critical point. For sufficiently large h_1 the wetting transition can occur in the unphysical region ($h < 0, t < \frac{1}{27}$) or even be preempted by the loss of stability of the P phase.

These features are general to wetting phase diagrams. The novel feature of this surface phase diagram is the additional presence of a line of continuous surface phase transitions at $\eta(z=0)=\eta_c$, at which Γ_P becomes nonzero. This phase transition corresponds to the breaking of the surface symmetry in the x-y plane. As h_1 is increased this line may terminate (a) at a surface critical end point on the prewetting line (which may or may not be in the physical region), or (b) at the limit of stability of the P phase. The topology of the phase diagram in t-h-h_1 space is shown in Fig. 1. If the surface energy includes terms quadratic in η a third possibility is that the line terminates on the P-N coexistence curve.

Experimental interest is concentrated on the zero-external-field ($h=0$) case. Inspection of Fig. 1 shows that in this case the surface phase diagram is governed by whether the prewetting line or the continuous-surface-phase-transition line crosses the $h=0$ line. We find that (a) for $h_1 < h_{11}=0.0118$, there is no surface phase transition, only a bulk phase transition at T_{NI}; this is the regime in which the nematic only partially wets the wall. The wetting regimes are as follows: (b) For $h_{11} < h_1 < h_{12}=0.0161$ there is a first-order surface phase transition; (c) for $h_{12} < h_1 < h_{13}=0.0241$, as T is decreased there is successively a continuous and a first-order surface phase transition; and (d) for $h_1 > h_{13}$ there is a continuous surface phase transition at a temperature above T_{NI}.

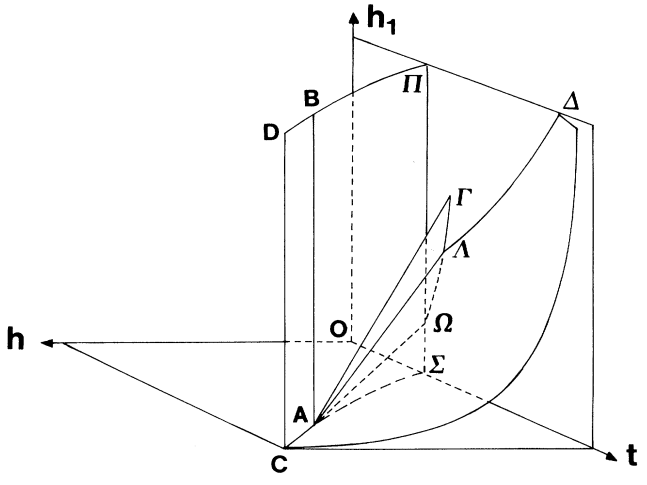

FIG. 1. Surface and bulk transitions of the system in the space of temperature (t), bulk field (h), and surface field (h_1). AC is a line of bulk continuous transitions, A is the tricritical point, and ΣA is a line of bulk first-order transitions. C$A\Sigma$O is the $h_1=0$ plane (no surface coupling). A$\Gamma\Lambda\Omega$ is a sheet of first-order surface transitions, and AC$\Delta\Lambda$ is a sheet of surface Kosterlitz-Thouless transitions. Points with Greek letters lie in the plane $h=0$.

The qualitative structure of the phase diagram remains unaffected by relaxation of the $\xi_2=0$ approximation. A stability analysis of the $\Gamma_P=0$ solutions (for which the approximation is exact) shows that the continuous surface transition now occurs as $\eta(z=0) > \eta_c$. The $\xi_2=0$ approximation underestimates the N-I surface tension; relaxing it pushes all features of the phase diagram towards the tricritical point, and hence increases h_{11}, h_{12}, h_{13}. The continuous transition is third order in the $\xi_2=0$ approximation, but becomes second order otherwise.

However, the mean-field picture gives a qualitatively incorrect picture of the surface phase close to complete wetting by the N phase. For all $T > T_{NI}$ the surface layer in which $p(z)\neq 0$ is not macroscopically thick. The nematic director in this region is constrained to lie in the plane of the surface. The surface biaxial layer therefore has the symmetry of the two-dimensional X-Y model, which has algebraic but no true long-range order in its low-temperature phase. The scale of the decay of directional order will be roughly the thickness of the nematic film; as coexistence is approached this diverges, achieving full long-range order in the saturated film at coexistence. We expect that the continuous phase transition will not be a true ordering transition, but rather a defect-unbinding transition.[16,17] The relevant defects are disclination lines in the director field, which lies in the x-y plane[23] (the director is a function of x and y, but not of z). In practice, even the saturated film (at or below T_{NI}) will exhibit a pattern of disclination lines pinned to surface imperfections (the Schlieren texture). In the unsaturated film these defects are equilibrium phenomena, however. An analogous phenomenon has been noted for nematic films between plates.[24] At the defect-unbinding transition there will be a jump of $8/\pi$ in the surface elastic constant K, where the fluctuation energy of surface director fluctuations is

$$H_s = \tfrac{1}{2} K \int (\nabla_{11}\phi)^2 \, dx \, dy, \tag{6}$$

with $\phi(x,y)$ the angle between the director at (x,y) and the x axis.[25] This jump should be observable, for instance, in light-scattering measurements.

A good candidate for the experimental realization of the phenomena that we describe is the 5CB–liquid-gallium interface. This interface imposes planar boundary conditions on the 5CB.[26] The nematic phase strongly wets the interface with respect to its vapor,[26] which suggests that it may also do so with respect to the isotropic phase.

Finally, we note that related phenomena occur in other areas of statistical mechanics. In the theory of

magnetism, under some circumstances there can be a surface transition which occurs above the critical point and marks the onset of surface order.[8,15] The line of surface Kosterlitz-Thouless transitions in the system that we discuss is an example of a line of such transitions. We might ask whether this line meets the bulk second-order P-N line above t_c at a special or surface-bulk transition. The form of surface interaction that we take in Eq. (5) prohibits this, but a surface energy term quadratic in the surface order parameters allows this; such a term may also affect the order of the wetting transitions and give rise to a phase diagram slightly more complicated than Fig. 1. The surface defect-unbinding transition always occurs if the nematic wets the wall unless it is preempted by the Sheng transition. An analogous surface transition also occurs in ^{4}He films adsorbed at a wall, either from the vapor or from a ^{3}He-rich ^{3}He-^{4}He mixture; the jump in the surface elastic constant corresponds to the jump in superfluid density associated with the sudden onset of third sound.[27]

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