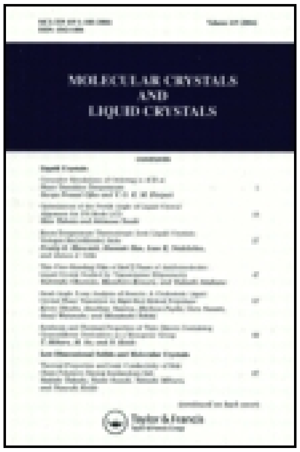

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Wetting and Capillary Condensation in Liquid Crystal Systems

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WETTING AND CAPILLARY CONDENSATION IN LIQUID CRYSTAL SYSTEMS*

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Abstract We discuss, using general principles, the growth of a nematic wetting layer at a surface in an isotropic fluid close to the nematic-isotropic transition. The effect of competition between the nematic anchoring at a wall and at the incipient isotropic surface can lead to effects which are particular to systems with orientational order. Such effects also change the Kelvin equation which governs the shift in the nematic-isotropic phase transition in a finite geometry.

1. INTRODUCTION

In this paper we are concerned with the isotropic-nematic phase transition in systems with a restricted geometry. In the more general context of the theory of phase transitions such systems can be further subdivided into wetting problems, in which one studies semi-infinite systems and the growth or otherwise of surface order, and capillary condensation problems, in which one studies the effect of a finite geometry on a bulk first order phase transition. The general phenomenology of both these subclasses has been much studied recently [1,2], and a variety of interesting

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effects are predicted. Liquid crystal systems may be expected to show even more interesting effects because of the possibility of competing surface textures. We explore these effects in this paper.

2.1 WETTING

We first present a brief review of what we shall need of the phenomenon of wetting. We consider two phases 1 and 2 of a system. The system undergoes a first order transition at a temperature T_c such that for $T > T_c$ phase 1 is in equilibrium. The system is placed in a semi-infinite geometry close to a flat wall. We suppose that the wall favours phase 2, sufficiently so that close to the wall, at a temperature $T_c + \Delta T$, a layer of thickness ℓ of phase 2 is adsorbed at the wall. Phase 2 is said to wet the wall completely, if, as $\Delta T \rightarrow 0$, $\ell \rightarrow \infty$. Precise calculations of this phenomenon depend both on an understanding of the interparticle interactions in phases 1 and 2, and on the interactions between these particles and the wall. However the phenomenology of a completely wetting system can be understood using the following simple free energy argument [1,2].

The free energy of a layer of thickness ℓ is (per unit area)

$$\Delta A = \Delta S\ \Delta T \ell + V(\ell) \tag{1}$$

where $\Delta S = S_2 - S_1$ is the entropy difference between the two phases per unit volume, and $V(\ell)$ is a term which takes into account the advantage of having phase 2 at the boundary and the interaction between a wall-2 and a 1-2 surface separated by a distance ℓ. In the complete wetting case we are interested in

$$V(\ell) = - V_0 + V_1(\ell) \ . \qquad (2)$$

The form of $V_1(\ell)$ depends on (a) the wall-particle interactions and (b) how close the first order 1 - 2 transition is to criticality. If the wall-particle interactions are of the form $u(z) \sim z^{-\delta}$ then $V_1(\ell) = A\ell^{1-\delta}$. Minimising (1) then yields

$$\ell \sim \Delta T^{-1/\delta} \ . \qquad (3)$$

In the case of the van der Waals interaction $\delta = 3$. If interactions are short-ranged, this is equivalent to an exponential form for $V_1(\ell) \sim \exp-(\ell/\xi)$, where ξ is a correlation length. In this case

$$\ell \sim \ln|\Delta T| \ , \qquad (4)$$

a much slower divergence. If the phase transition is near critical, then $V_1(\ell)$ also has an effective, fluctuation-induced exponential form, and thus the film thickness ℓ diverges logarithmically for $\ell < \xi$ the correlation length.

2.2 MODELLING LIQUID CRYSTAL SURFACES

We first formulate the problem of a nematic close to a wall in its full generality. The liquid crystal is defined by a density profile $\rho(z,\Omega)$, where Ω is a solid angle and z is distance from the wall. In a uniform system - far from the wall, for instance

$$\rho(z,\Omega) = \rho f(\Omega) \qquad (5)$$

where $f(\Omega)$ is the angular distribution, calculated for example in the Maier-Saupe theory, and for the isotropic phase $f(\Omega) = (4\pi)^{-1}$. A knowledge of $f(\Omega)$ implies a knowledge of the liquid crystal ordering tensors, which in turn yields knowledge of the magnitude and direction of the liquid crystal order parameter. To find $\rho(z,\Omega)$ we must minimize a free energy of the form

$$\Omega = \mathcal{F}[\{\rho(z,\Omega)\}] + \int_0^\infty [V(z,\Omega)-\mu]\rho(z,\Omega)\,dz\,d\Omega \;, \tag{6}$$

where $V(z,\Omega)$ is the potential on a particle oriented in direction Ω at position z , $\mathcal{F}$ is the Helmholtz free energy functional, and μ is the chemical potential [3]. The situation is further complicated by a lack of knowledge of $\mathcal{F}$, and a difficulty in specifying $V(z,\Omega)$ in many useful circumstances. Another factor to be borne in mind is that most surfaces used in technological applications are *rough*, not as an inconvenient complication, but deliberately made so in the preparation process in order to possess some desired orientation properties. Thus some averaging of Ω over a set of potentials $V(z,\Omega)$ is required to take account of the randomness.

Faced with a problem of this degree of complication some simplification is clearly necessary. As far as the *physics* of the phenomenon is concerned, a useful idealization is the *Landau-de Gennes* approach in which a model continuum-like free energy is minimised. We write the total free energy of a nematogen as

$$F = \int_0^\infty [f_b(\underline{\underline{Q}}) + K(\nabla\underline{\underline{Q}})^2]dz + f_s(\underline{\underline{Q}}_0) \;, \tag{7}$$

where the free energy has now been divided into a *bulk* and a surface contribution. Here $\underline{\underline{Q}}(z)$ is the ordering tensor, $f_b(\underline{\underline{Q}})$ the bulk Landau-de Gennes free energy functional the $K(\nabla\underline{\underline{Q}})^2$ represents three terms which indicate the cost of changing the free energy [4]. The effect of the surface potential - and, hopefully, of the randomness in the surface itself - have been subsumed in the surface free energy f_s , which is a functional of $\underline{\underline{Q}}_0 = \underline{\underline{Q}}(z=0)$, a quantity which is not strictly defined in eqs. (5) or (6) because the "wall" position is not uniquely defined on a microscopic scale. It is, however, defined on this mesoscopic scale. For an isotropic, structureless wall [5]

$$f_s(\underline{\underline{Q}}) = -gQ_{zz} + \tfrac{1}{2}[u_1\, Q_{zz}^2 + u_2(Q^2)_{zz} + u_3\mathrm{tr}(\underline{\underline{Q}}^2)] \ , \qquad (8)$$

We are interested in growth of nematic layers close to a wall just above the isotropic-nematic onset temperature T_{NI} . Thus with respect to the general background discussion in the previous section, phase 1 is the isotropic phase and phase 2 is the nematic phase, and T_c is T_{NI} .

However, even the problem as defined in eqs. (7) (8) provides a large parameter space and some formidable mathematical difficulties. Some progress has been made, initially by ourselves [6], and latterly by Sen and Sullivan [7]. Unfortunately it seems that some of the most interesting behaviour occurs when the director varies within the sample, and this is the case which provides most of the numerical problems. We can, however, discuss these cases from the phenomenological point of view adopted in section 2.1, although this theoretical level is yet one more degree removed from the real problem. Clearly solutions of the Landau-de Gennes model would be of major interest.

2.3 WETTING AND THE LIQUID CRYSTAL SURFACE

The crucial new piece of physics which distinguishes liquid crystal interfaces from other liquid interfaces is the association of a director orientation with a surface. Let us consider the growth of a nematic phase from a wall above T_{NI} , as indicated above. For definiteness, let us suppose that the surface induces in the nematic a director orientation *perpendicular* to itself. There is then a region of "nematic" fluid, an incipient nematic-isotropic interface, and far from the wall isotropic fluid. The crucial question is - what is the director orientation at a free nematic - isotropic interface? We dispose of the less interesting case first. If the director orientation at the free nematic-isotropic interface is parallel to that at the wall (in this case perpendicular to the wall) then the only relevant order parameter is a scalar, for

$$\underline{\underline{Q}}(z) = \tfrac{1}{2}Q(z)[2\underline{\hat{z}}\underline{\hat{z}} - \underline{\hat{x}}\underline{\hat{x}} - \underline{\hat{y}}\underline{\hat{y}}]$$

$$\text{or} \quad Q_{ij}(z) = \tfrac{1}{2}Q(z)[3\hat{z}_i\hat{z}_j - \delta_{ij}] \ . \tag{9}$$

This case, which has been examined in detail within the Landau-de Gennes theory by a number of authors [5] is broadly analogous to other wetting scenarios summarised in section 2.1 with, in particular, the same power law behaviour for the nematic film thickness ℓ .

We now pass to the more interesting case where the free nematic-isotropic surface has a different director orientation from that at the wall. The initial studies of such systems within the Landau-de Gennes framework [6,7] reveal a rich phase diagram with a variety of wetting transitions, and transitions between wetting phases at different orientations. We concentrate here on some aspects of the wetting behaviour which is presumably implicit in the Landau-de Gennes theory, which has not yet been specifically demonstrated, but which is accessible to phenomenological arguments of the type used in section 2.1.

Let us make the specific further assumption that the free nematic-isotropic interface orients the director parallel to itself. The surface free energy of the nematic-isotropic interface is then of the form

$$\gamma(\theta) = \gamma_0 + \gamma_1(\theta) \tag{10}$$

where θ is the angle between the director at the interface and the normal to the interface. Within our model we may suppose

$$\gamma_1(\theta) = \gamma_1 \cos 2\theta \ . \tag{11}$$

The free energy associated with a change in director from $\underline{\hat{n}} = \hat{z}$ at $z = 0$ to $\underline{\hat{n}} = [\sin\theta, 0, \cos\theta]$ at $z = \ell$ is

$$\Delta A_c = \tfrac{1}{2} K \frac{\theta^2}{\ell} \tag{12}$$

where K is a combination of the nematic elastic constants.

From eqs. (1), (11) and (12) we can construct an effective free energy per unit area for a nematic film of thickness ℓ with orientation θ at the nematic edge:

$$\Delta A(\ell,\theta) = \Delta S_{NI}\, \Delta T \ell + \gamma_1 \cos 2\theta + A_1 \exp(-\ell/\xi_{NI}) + A_2 \left(\frac{r_0}{\ell}\right)^2 + \tfrac{1}{2} K \frac{\theta^2}{\ell} \tag{13}$$

where ξ_{NI} is the correlation length associated with critical fluctuations at the nematic-isotropic transition, r_0 is a characteristic molecular length of the problem, and A_1 and A_2 are amplitudes.

For ΔT large, ℓ will be relatively small, the director will be uniform $(=\underline{\hat{z}})$ within the film, and

$$\ell \sim \xi_{NI} \ln|\Delta T| \quad \text{or} \quad \ell \sim \Delta T^{-1/3} \tag{14}$$

depending on whether the fluctuation-induced logarithmic term dominates over the van-der Waals term. There will be a cross-over between the logarithmic and the power law behaviour.

Before this cross-over intervenes, however, it may be more favourable for the director to turn in order to take advantage of the easy direction at the nematic-isotropic interface. We can examine the stability of the free energy (13) against such an eventuality. For small θ :

$$\Delta A(\ell,\theta) \sim \tfrac{1}{2}\theta^2[K/\ell - 4\gamma_1] \ . \tag{15}$$

Thus we expect a transition for film thickness

$$\ell_{WF} \sim \left[\frac{K}{\gamma_1}\right] , \tag{16}$$

at temperature

$$\Delta T_{WF} \sim \frac{A_1}{\xi_{NI}} \Delta S \ \exp - \frac{K}{\gamma_1 \xi_{NI}} \ . \tag{17}$$

We can call this a *wetting Frederiks transition*, by analogy with the usual Frederiks transition, in which surface anchoring forces are pitted against the effect of a bulk field. This wetting Frederiks transition is a continuous transition, immediately beyond which

$$\begin{aligned} \theta &= \left[1 - \frac{\ell_{WF}}{\ell}\right]^{\frac{1}{2}} \\ &\sim (\Delta T_{WF} - \Delta T)^{\frac{1}{2}} \ . \end{aligned} \tag{18}$$

Eventually, however, θ saturates at $\pi/2$, in order that the nematic-isotropic surface free energy be minimised. In this regime the film growth is governed by a balance of the first and last terms in eq. (13), and

$$\ell \sim \Delta T^{-\frac{1}{2}} \ . \tag{19}$$

The director change causes an effective repulsion between the wall and the incipient nematic-isotropic interface.

We thus have *three* possible power law régimes for nematic film growth. A number of workers have observed the logarithmic film growth, including, recently, Shen and coworkers [8]. This last experiment concerned the growth of a layer of 5CB against a wall which has normal boundary conditions, and for which the nematic-isotropic interface has an equilibrium tilt angle of $\sim \pi/3$. This is just a set of circumstances in which one might expect to observe a cross-over between logarithmic and $\Delta T^{-\frac{1}{2}}$ behaviours, and we encourage further experiments.

2.4 EFFECT OF A BULK FIELD

Adding a bulk field which couples to the director adds another dimension yet to wetting film growth. We recall that a magnetic field $\underline{H}$ provides a term in the nematic free energy density [4]

$$F_H = -\tfrac{1}{2}\chi_A(\hat{\underline{n}}.\underline{H})^2 \ . \tag{20}$$

The director lines up (if $\chi_A > 0$) parallel to $\underline{H}$, and this alignment relaxes on the length scale of the <u>magnetic extrapolation length</u> ξ_H

$$\xi_H = \left[\frac{K}{\chi_A}\right]^{\frac{1}{2}} H^{-1} \ . \tag{21}$$

The bulk field also increases the bulk phase transition temperature by a quantity $\sim H^2$ [9], although this is rather small and hard to observe. Electric fields have qualitatively larger effects, though the effect is more difficult to calculate as a result of dielectric effects.

In general ξ_H is rather a large quantity $\sim$ microns. Nevertheless we can ask the question about what happens in a large field, so that ξ_H is minimised, and ΔT is sufficiently small that $\ell \gtrsim \xi_H$. The energy cost of turning the director so as to satisfy the boundary conditions at the isotropic-nematic and nematic-wall interfaces is now no longer given by the last term in eq. (13), but rather by $\sim K\theta^2/\xi_H$. The contribution to the free energy as a function of ℓ comes from the correction to this term as a result of the decay profile of the director being cut off by the limit of the nematic film. This contribution is exponentially small $\sim \chi_A H^2 \exp-(\ell/\xi_H)$, leading to film growth in this regime

$$\ell \sim \xi_H \ln|\Delta T| \quad . \tag{22}$$

We thus have a <u>fourth</u> power law regime at very thick film thicknesses. The onset of this regime will be sharp if a symmetry change is involved, such as, for instance, if the field is perpendicular to both boundary conditions. In this case the transition is, of course, the familiar Frederiks transition in a slightly unfamiliar context. If no symmetry change is involved we merely expect a cross-over regime between $\Delta T^{-\frac{1}{2}}$ and $\ln|\Delta T|$ behaviour.

Although this régime is only observable for high fields in which the wetting film is not too thick, this régime itself is cut-off at fields that are too high. This cut-off is marked by the condition (see eq. (15))

$$K/\xi_H \gtrsim \gamma_1 \quad \text{or} \quad H \gtrsim H_{sat} \tag{23}$$

where γ_1 is interpreted now as the maximum of the anchoring energies at the limits of the nematic wetting film, and H_{sat} is the <u>saturation</u> field [5] at which the boundary conditions can no longer compete against the bulk field. Once in this régime, the order parameter is once again effectively a scalar, and the normal behaviour described in section 2.1 resumes.

3.1 CAPILLARY CONDENSATION

Again we give a brief review of this phenomenon [10]. We consider two phases 1 and 2, separated by a first order phase transition at T_c in the bulk. Capillary condensation concerns the shift in the phase transition, to $T_c + \Delta T$, when the material is placed in a restricted geometry, as a result of one of the phases having a lower surface free energy with respect to the container. Consider first material placed between two parallel surfaces a distance ℓ apart.

The phase transition occurs when the grand thermodynamic potentials Ω and the chemical potentials μ are equal. If we measure Ω per unit volume we obtain

$$\Omega_1(T_c + \Delta T) + \frac{2\gamma_1}{\ell} = \Omega_2(T_c + \Delta T) + \frac{2\gamma_2}{\ell} , \tag{24}$$

where the subscripts refer to each of the phases, and γ are the surface free energies. Using

$$\frac{\partial\Omega}{\partial T} = -S , \tag{25}$$

where S is the entropy density. Expanding in ΔT, we obtain

$$\Delta T = \frac{2T_c(\gamma_2-\gamma_1)}{L\ell} \tag{26}$$

where $L = T_c(S_1-S_2)$, is the latent heat of the first order 1 - 2 phase transition.

For a cylinder of radius ℓ analogous considerations lead to the result

$$\Delta T = \frac{2T_c(\gamma_2-\gamma_1)}{L\ell} \tag{27}$$

and similarly for a sphere of radius ℓ

$$\Delta T = \frac{3T_c(\gamma_2-\gamma_1)}{L\ell} . \tag{28}$$

Equations (26) to (28) are examples of Kelvin equation which governs the asymptotic behaviour of the phase transition temperature as a function of system size ℓ. In fact in the last two cases there is also some finite-size broadening of the phase transition as a result of the dimensionality of the system, but this is not important at this stage.

3.2 PLANAR GEOMETRY

The case of a liquid crystal between absolutely identical walls has been dealt at length by us elsewhere and presents qualitatively the same picture as described in eq. (26). Let us consider a slightly different case, in which each surface is identical, with an easy axis parallel to the surface, such that the surface free energy of the nematic obeys the rule

$$\gamma_N(\phi) = \gamma_N + \gamma_{N1}\sin^2\phi \qquad (29)$$

where the surface director orientation is supposed in the plane of the surface, and at an angle ϕ to the easy axis. Let us suppose that the two walls are set up so that their easy axes are oriented perpendicular to each other. We investigate the shift of T_{NI} as a function of surface separation ℓ .

We can write down the analogue of the Kelvin equation by observing that the thermodynamic potential of a layer filled with nematic (per unit length) is

$$A = \ell\left[\Omega_N + \frac{2\gamma_N}{\ell} + \frac{2\gamma_{N1}}{\ell}\sin^2\phi + \tfrac{1}{2}\frac{K}{\ell^2}\left(\frac{\pi}{2} - 2\phi_s\right)^2\right] . \qquad (30)$$

Hence following the reasoning of equations (25) and (26) the free energy cost of a nematic layer at temperature $T_{NI} + \Delta T$ is

$$\Delta A = \frac{\ell L}{T_{NI}}\Delta T + 2(\gamma_N - \gamma_I) + 2\gamma_{N1}\sin^2\phi_s + \tfrac{1}{2}\frac{K}{\ell}\left(\frac{\pi}{2} - 2\phi_s\right)^2 . \qquad (31)$$

The length $\ell_{WF} \cong (K/\gamma_{N1})$ defined in eq. (16) is again important. For $\ell \gtrsim\!\!> \ell_{WF}$ each surface minimises its surface free energy with respect to ϕ independently, so that the phase transition takes place at a temperature $T_{NI} + \Delta T$, where

$$\Delta T = \frac{T_{NI}}{L}\left[\frac{2(\gamma_I-\gamma_N)}{\ell} - \frac{\pi^2}{8}\frac{K}{\ell^2}\right] \tag{32}$$

In particular if $\gamma_N < \gamma_I$ the transition temperature first increases and then subsequently decreases to account for the price paid in twisting the nematic. Finally at $\ell \sim \ell_{WF}$ the cost of twisting the director is higher than that of changing the boundary condition, and in this régime

$$\Delta T \cong \frac{T_{NI}}{L}\left[\frac{2(\gamma_N'-\gamma_I)}{\ell}\right] \tag{33}$$

where

$$\gamma_N' = \gamma_N + \gamma_{N1}\sin^2\phi = \gamma_N + \tfrac{1}{2}\gamma_{N1} \tag{34}$$

is the effective nematic surface free energy corresponding to $\phi = \frac{\pi}{4}$, and the nematic texture is uniform through the sample.

Changing the boundary conditions changes the details but not the important qualitative considerations. These details govern whether the cross-over between behaviours (32), (33) is gradual or in the form of a phase transition.

3.3 CURVED GEOMETRY

As an example we choose a spherical geometry, with sphere radius ℓ. We recall that in a nematic, director changes cost an elastic free energy

$$\begin{aligned} el = {} & K_{11}(\nabla\cdot\underline{\hat{n}})^2 + K_{22}(\underline{\hat{n}}\cdot(\nabla\times\underline{\hat{n}}))^2 + K_{33}(\underline{\hat{n}}\times(\nabla\times\underline{\hat{n}}))^2 \\ & + K_{13}\,\nabla\cdot(\underline{\hat{n}}\nabla\cdot\underline{\hat{n}})\ . \end{aligned} \tag{35}$$

The Euler-Lagrange equations which govern the bulk director configuration depend only on K_{11}, K_{22}, K_{33} (respectively the splay, twist and bend elastic constants). The quantity K_{13} only enters the energy as a surface term. It has been pointed out [11] that under certain circumstances the quantity K_{13} - which depends on *bulk* molecular properties - can be comparable in magnitude to the other elastic constants.

Let us suppose boundary conditions on the inside of a spherical surface which favour a normal alignment at that surface (*homeotropic* boundary conditions). The geometry then demands that the nematic inside the sphere possess a *topological* defect, in this case the so-called *hedgehog* defect. The precise energy of this defect depends on the ratio of K_{11}, K_{22}, K_{33}. Far from the centre of the sphere the director $\underline{\hat{n}} = \underline{\hat{r}}$, with origin at the centre of the sphere. Recent calculations [12] have elucidated the structure of the hedgehog defect. If $\frac{1}{2}K_{33} + K_{22} - 2K_{11} > 0$ the hedgehog has a point defect at $\underline{r} = 0$, with $\underline{\hat{n}} = \underline{\hat{r}}$, $\nabla \cdot \underline{\hat{n}} = 2/r$ everywhere outside the defect core. On the other hand, if $\frac{1}{2}K_{33} + K_{22} - 2K_{11} < 0$, the point defect is replaced by a line defect in the form of a ring of radius ρ, where $\rho/\ell \propto [2K_{11} - K_{22} - \frac{1}{2}K_{33}]^{\frac{1}{2}}$. In this case the pure splay geometry of the point defect is somewhat distorted. The elastic free energy of the defected structure is

$$A_{el} = 8\pi\ell K_{13} + 16\pi\ell[K_{11} + \Delta_K] , \tag{36}$$

where $\Delta_K(K_{11}, K_{22}, K_{33})$ takes account of the distortion of the hedgehog defect into a ring-like structure.

Hence, at temperature $T_{NI} + \Delta T$, the free energy cost of replacing isotropic fluid by a nematic is

$$\Delta A = \frac{4}{3}\pi \ell^3 \frac{L}{T_{NI}} \Delta T + 4\pi\ell^2(\gamma_N-\gamma_I) + 16\pi\ell[K_{11}+\tfrac{1}{2}K_{13}+\Delta_K] \, , \tag{37}$$

where we assume that the homeotropic anchoring energy is sufficiently strong to effectively pin the director at the surface. The phase transition then takes place at $T_{NI} + \Delta T$, where

$$\Delta T = \frac{T_{NI}}{L}\left[\frac{3(\gamma_I-\gamma_N)}{\ell} - \frac{12}{\ell^2}(K_{11}+\tfrac{1}{2}K_{13}+\Delta_K)\right] \tag{38}$$

The extra interesting feature here is that the quantity K_{13}, which seems to be accessible from conventional experiments only with difficulty, may be accessible by observing the behaviour of $T_{NI}(\ell)$ in a finite curved geometry. We note here that we expect similar effects in a cylindrical geometry. In addition, for both geometries, for sufficiently small systems a further phase transition will shift the system to a more uniform texture by analogy with eq. (33).

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