Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Teixeira, P. I. C. , Sluckin, T. J. and Sullivan, D. E.(1993) 'Landau-de Gennes theory of anchoring transitions at a nematic liquid crystal-substrate interface', Liquid Crystals, 14: 4, 1243 — 1253

To link to this Article: DOI: 10.1080/02678299308027834

URL: http://dx.doi.org/10.1080/02678299308027834

LIQUID CRYSTALS, 1993, VOL. 14, NO. 4, 1243–1253

Landau–de Gennes theory of anchoring transitions at a nematic liquid crystal–substrate interface

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We have used Landau–de Gennes theory to study anchoring and anchoring transitions at the interface between a nematic liquid crystal and a smooth solid substrate. In contrast to earlier work by Sen and Sullivan, we allow for a spatially varying tilt angle and solve the Euler–Lagrange equations requiring that the order parameters be uniform far from the wall. We have found that temperature-driven anchoring transitions akin to those observed experimentally can be obtained either as a result of the change in the surface order parameter or due to competition between the ordering effects of the solid surface and the nascent isotropic–nematic interface as T_{NI} is approached, in the regime of complete wetting by the isotropic phase. Predictions have also been made for the experimentally observable values of the anchoring energy.

1. Introduction

Surface phenomena in liquid crystal systems have attracted a great deal of attention recently, on account not only of their technological importance but also of their interest as a fundamental problem in the statistical mechanics of non-uniform, ordered fluids. Anchoring phenomena in particular—the alignment of a liquid crystal by a substrate [1]—are crucial in the fabrication of display devices; furthermore, they provide invaluable insight into the nature of liquid crystal–liquid crystal and substrate interactions. In this paper we shall restrict ourselves to the anchoring of nematogenic liquid crystals, although other mesophases have been shown to exhibit similar (or related) behaviour, which opens up exciting new areas of research [2].

An anchoring transition is a transition between different types of anchoring (for a complete anchoring lexicon, see for example [2]), for instance conical to homeotropic or homeotropic to planar [3], which results from varying some parameter determining the interfacial structure. In the former example, the transition takes place continuously, i.e. it is characterized by a smooth variation of the tilt angle [3] at the surface, whereas the latter involves a discontinuous jump in the direction of preferential alignment.

Experimental observations of anchoring transitions have been reported since the mid-1970s [1]; their main driving forces seem to be temperature [4–14], addition of impurities [15–19] or, more recently, strains acting on the substrate [20]. In two previous papers, two of us [21, 22] have attempted to formulate a microscopic model of impurity-driven anchoring transitions which would explain the temperature-independence, or 'universality', of the azimuthal angle curves of E9 on gypsum when

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plotted as a function of the relative humidity of the medium, as observed by Pieranski and co-workers [17]. Although the theory enjoyed some success in predicting anchoring behaviour akin to that observed experimentally, for not entirely unrealistic values of the microscopic parameters, it contains a number of inconsistencies and oversimplifications which severely restrict its applicability.

We are now concerned with modelling the anchoring behaviour originally observed by Ryschenkow and Kléman [4, 5] and more recently by Patel [14], which can be summarized as follows: the tilt angle (measured relative to the surface normal) of MBBA spread on a glass surface treated with the products of degradation of heated paper is a decreasing function of the temperature in the low temperature region, eventually vanishing at $T=30$°C (conical to homeotropic transition); anchoring then remains homeotropic until immediately below the clearing point ($T_{\mathrm{NI}}=47$°C), whereupon the tilt angle again becomes finite and is now an increasing function of the temperature, approaching 70° as $T\to T_{\mathrm{NI}}^{-}$. The closeness of the tilt angle at $T=T_{\mathrm{NI}}$ to that which is obtained at the nematic–isotropic interface of MBBA (65°) is strongly suggestive of the operation of some mechanism related to the growth of an isotropic wetting film as $T\to T_{\mathrm{NI}}$. The observed re-entrant behaviour could then possibly be explained as the result of the competition between the aligning effects of the solid substrate and the nascent nematic–isotropic interface, with the latter becoming dominant sufficiently close to T_{NI}. In order to test this hypothesis we need a theory which is able to describe the formation of nematic/isotropic wetting films, while simultaneously allowing for the possible occurrence of biaxiality and non-uniform tilt angles close to the substrate. The simplest theory which fulfils these requirements is the Landau–de Gennes theory of nematics at surfaces, as formulated by Sen and Sullivan [23].

This paper is organized as follows: in § 2 we present the Landau–de Gennes theory of a nematic in contact with a solid substrate. The problem of the choice of boundary conditions for the Euler–Lagrange minimization equations is discussed in conjunction with that of the prediction of experimentally measured anchoring strengths and surface tilt angles. In § 3 we present results for the temperature dependence of the equilibrium tilt angle and contrast them with the predictions of the naive theory. Moreover, it is shown that re-entrant anchoring behaviour may indeed be obtained in the present theory. Some preliminary results are also presented for the experimental anchoring energy function. Finally in § 4 we summarize our conclusions and discuss the future directions of our research.

2. Theory

Following Sen and Sullivan [23], we consider a nematic fluid occupying the upper half space, in contact with a flat, structureless surface lying in the xOy plane. Neglecting fluctuations, the (tensor) order parameter $\mathbf{Q}$ can be assumed to vary only in the z direction, i.e. perpendicular to the surface. Then according to Landau–de Gennes theory, the equilibrium surface tension is the minimum of the functional

$$\sigma=\int_{0}^{+\infty} dz[f_{\mathrm{L}}(\mathbf{Q}(z))-f_{\mathrm{L}}(\mathbf{Q}_{\mathrm{b}})+f_{\mathrm{G}}(\dot{\mathbf{Q}}(z))]+f_{\mathrm{s}}(\mathbf{Q}(0)), \tag{1}$$

where $\mathbf{Q}_{\mathrm{b}}=\mathbf{Q}(z\to\infty)$ is the bulk order parameter tensor and $\dot{\mathbf{Q}}=d\mathbf{Q}(z)/dz$. f_{L} is the bulk free energy density, constructed as usual from the invariants of the (traceless) order parameter up to fourth order,

$$f_{\mathrm{L}}(\mathbf{Q})=A\,\mathrm{Tr}\,\mathbf{Q}^{2}-B\,\mathrm{Tr}\,\mathbf{Q}^{3}+C(\mathrm{Tr}\,\mathbf{Q}^{2})^{2}, \tag{2}$$

where Tr denotes the trace operation, A is a linear function of the temperature, and B and C are constants. The curvature term f_G is taken from de Gennes's [24] theory,

$$f_G(\dot{\mathbf{Q}})=\tfrac{1}{2}L_1 \operatorname{Tr}\dot{\mathbf{Q}}^2+\tfrac{1}{2}L_2\mathbf{k}\cdot\dot{\mathbf{Q}}^2\cdot\mathbf{k}, \tag{3}$$

where $\mathbf{k}$ is a unit vector along z and L_1, L_2 are temperature-independent elastic constants. L_2 favours parallel alignment at the nematic–isotropic interface if it is positive, and homeotropic if it is negative.

Finally $f_s(\mathbf{Q}(0))$ has been modelled by the most general expansion of the surface energy to order $\mathbf{Q}^2$ which is consistent with tangential isotropy

$$f_s(\mathbf{Q})=c_1\mathbf{k}\cdot\mathbf{Q}\cdot\mathbf{k}+c_2\operatorname{Tr}\mathbf{Q}^2+c_3(\mathbf{k}\cdot\mathbf{Q}\cdot\mathbf{k})^2+c_4\mathbf{k}\cdot\mathbf{Q}^2\cdot\mathbf{k}, \tag{4}$$

where c_1–c_4 are constants. This is the nematic analogue of the expression encountered in the Landau theory of an Ising model surface [25–27], and it assumes no preferred orientation in the plane of the surface.

We now write $\mathbf{Q}$ in the form

$$\mathbf{Q}(z)=\tfrac{1}{2}\eta(3\mathbf{nn}-\mathbf{I})+\frac{3^{1/2}}{2}\mu(\mathbf{ll}-\mathbf{mm}), \tag{5}$$

where the unit vectors $\mathbf{l}$, $\mathbf{m}$, $\mathbf{n}$ form a local orthonormal triad and $\mathbf{I}$ is the second rank unit tensor. The direction of maximum orientational order is by convention associated with the director axis, $\mathbf{n}$. Thus η is the usual uniaxial order parameter, while μ is a measure of the biaxiality induced by spatial non-uniformity in directions other than $\mathbf{n}$. If we neglect twist-type excitations (which is consistent with equation (4)), the director can be assumed to lie in a single plane, which we take to be the xOz plane. Hence the orientation of the triad depends on a single angle $\psi=\cos^{-1}(\mathbf{n}\cdot\mathbf{k})$—the tilt angle, and substitution of equation (5) into (4) yields for the bare surface free energy

$$f_s=w_0+w_2\cos^2\psi(0)+w_4\cos^4\psi(0), \tag{6}$$

where

$$w_0=\tfrac{1}{2}((3)^{1/2}\mu-\eta)[c_1+\tfrac{1}{2}c_4((3)^{1/2}\mu-\eta)] +\tfrac{3}{4}c_2(2\eta^2+\mu^2)+\tfrac{1}{4}c_3((3)^{1/2}\mu+\eta)^2, \tag{7a}$$

$$w_2=\frac{3^{1/2}}{2}((3)^{1/2}\eta-\mu)[c_1+c_3((3)^{1/2}\mu\mu-\eta)+\tfrac{1}{2}c_4((3)^{1/2}\mu+\eta)], \tag{7b}$$

$$w_4=\tfrac{3}{4}c_3((3)^{1/2}\eta-\mu)^2 \tag{7c}$$

Equation (6) is similar to that derived in [21] from a microscopic theory using the Fowler approximation for the density and order parameter profiles. In [21], the equilibrium tilt angle is obtained by minimizing f_s; in the present theory it is determined by the balance of surface (equations (4) or (6)) and curvature (equation (3)) terms, which may lead to quite different results. In particular, solutions which admit a spatially varying tilt become possible, if the increase in elastic free energy is outweighed by the surface contribution.

For analytical simplicity it is advantageous to re-write $\mathbf{Q}$ in a lab-fixed frame,

$$Q(z)=\tfrac{1}{2}\eta_s(3\mathbf{kk}-\mathbf{I})+\frac{3^{1/2}}{2}\mu_s(\mathbf{ii}-\mathbf{jj})+\frac{3^{1/2}}{2}v_s(\mathbf{ik}+\mathbf{ki}), \tag{8}$$

where $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ denote unit vectors along the laboratory x, y, z axes, respectively. The new variables η_s, μ_s, v_s are related to η, μ, ψ by equations (2.16) of [23] with the re-scalings given by equations (2.12) of the same reference.

In this representation, equations (2)–(4) become

$$f_{\mathrm{L}}=t(\eta_{\mathrm{s}}^2+\mu_{\mathrm{s}}^2+\nu_{\mathrm{s}}^2)-(\eta_{\mathrm{s}}+(3)^{1/2}\mu_{\mathrm{s}})[2\eta_{\mathrm{s}}(\eta_{\mathrm{s}}-(3)^{1/2}\mu_{\mathrm{s}})+3\nu_{\mathrm{s}}^2]+(\eta_{\mathrm{s}}^2+\mu_{\mathrm{s}}^2+\nu_{\mathrm{s}}^2)^2, \quad (9\,a)$$

$$f_{\mathrm{G}}=\tfrac{1}{2}\dot{\eta}_{\mathrm{s}}^2+\frac{L}{2}\dot{\mu}_{\mathrm{s}}^2+\frac{M}{2}\dot{\nu}_{\mathrm{s}}^2, \quad (9\,b)$$

$$f_{\mathrm{s}}=c_1\eta_{\mathrm{s}}+c_{2\eta}\eta_{\mathrm{s}}^2+c_{2\mu}\mu_{\mathrm{s}}^2+c_{2\nu}\nu_{\mathrm{s}}^2, \quad (9\,c)$$

where the reduced elastic constants L, M and the renamed surface constants $c_{2\eta}$, $c_{2\mu}$, $c_{2\nu}$ are given by equations (2.19) and (2.20) of [23], respectively.

The Euler–Lagrange equations to be solved are

$$\ddot{\eta}_{\mathrm{s}}=\frac{\partial f_{\mathrm{L}}}{\partial \eta_{\mathrm{s}}}=2[t+2(\eta_{\mathrm{s}}^2+\mu_{\mathrm{s}}^2+\nu_{\mathrm{s}}^2)]\eta_{\mathrm{s}}-3(2\eta_{\mathrm{s}}^2-2\mu_{\mathrm{s}}^2+\nu_{\mathrm{s}}^2), \quad (10\,a)$$

$$L\ddot{\mu}_{\mathrm{s}}=\frac{\partial f_{\mathrm{L}}}{\partial \mu_{\mathrm{s}}}=2[t+2(\eta_{\mathrm{s}}^2+\mu_{\mathrm{s}}^2+\nu_{\mathrm{s}}^2)]\mu_{\mathrm{s}}+3(4\eta_{\mathrm{s}}\mu_{\mathrm{s}}-(3)^{1/2}\nu_{\mathrm{s}}^2), \quad (10\,b)$$

$$M\ddot{\nu}_{\mathrm{s}}=\frac{\partial f_{\mathrm{L}}}{\partial \nu_{\mathrm{s}}}=2[t+2(\eta_{\mathrm{s}}^2+\mu_{\mathrm{s}}^2+\nu_{\mathrm{s}}^2)]\nu_{\mathrm{s}}-6(\eta_{\mathrm{s}}+(3)^{1/2}\mu_{\mathrm{s}})\nu_{\mathrm{s}}, \quad (10\,c)$$

where t is the reduced temperature ($t_{\mathrm{NI}}=1$), supplemented by the boundary conditions at the origin

$$\dot{\eta}_{\mathrm{s}}(0)=c_1+2c_{2\eta}\eta_{\mathrm{s}}(0), \quad (11\,a)$$

$$L\dot{\mu}_{\mathrm{s}}(0)=2c_{2\mu}\mu_{\mathrm{s}}(0), \quad (11\,b)$$

$$M\dot{\nu}_{\mathrm{s}}(0)=2c_{2\nu}\nu_{\mathrm{s}}(0). \quad (11\,c)$$

We are still free to choose the remaining three boundary conditions. One possibility is to require that the order parameters η_{s}, μ_{s}, ν_{s} be uniform sufficiently far from the substrate, i.e.

$$\dot{\eta}_{\mathrm{s}}(z\to\infty)=\dot{\mu}_{\mathrm{s}}(z\to\infty)=\dot{\nu}_{\mathrm{s}}(z\to\infty)=0, \quad (12)$$

thus enabling us to find the equilibrium tilt angle (i.e. that which minimizes the surface tension) directly as a function of temperature and thereby study temperature-driven orientational transitions. If, on the other hand, we are concerned with finding the anchoring energy, the appropriate boundary conditions are those corresponding to a fixed bulk tilt angle ψ_{b} (this is equivalent to placing a strongly anchoring wall a distance l from the substrate, which is one of the techniques used in experimental determinations of the anchoring energy [28]) which does not necessarily minimize the surface tension

$$\eta_{\mathrm{s}}(z=l)=\eta_{\mathrm{b}}P_2(\cos\psi_{\mathrm{b}}), \quad (13\,a)$$

$$\mu_{\mathrm{s}}(z=l)=\frac{3^{1/2}}{2}\eta_{\mathrm{b}}\sin^2\psi_{\mathrm{b}}, \quad (13\,b)$$

$$\nu_{\mathrm{s}}(z=l)=\frac{3^{1/2}}{2}\eta_{\mathrm{b}}\sin 2\psi_{\mathrm{b}}, \quad (13\,c)$$

where the bulk uniaxial order parameter is given by [23]

$$\eta_{\mathrm{b}}=\frac{3}{4}\left[1+\left(1-\frac{8}{9}t\right)^{1/2}\right]. \quad (14)$$

Once equations (10) have been solved for the appropriate choice of boundary conditions, the (possibly z-dependent) tilt angle can be found by inverting equations (2.16) of [23]:

$$\psi = \tfrac{1}{2}\tan^{-1}\frac{2\nu_s}{(3)^{1/2}\eta_s - \mu_s}. \tag{15}$$

If $(3)^{1/2}\eta_s - \mu_s \rightarrow 0$ and $\nu_s \neq 0$, then $\psi = \pi/4$; if $\nu_s \rightarrow 0$, we can have either $\psi = 0$, if simultaneously $\mu_s \rightarrow 0$, or $\psi = \pi/2$ otherwise.

The problem of making predictions for the experimentally observable anchoring energy and surface tilt angle requires consideration of the experimental techniques used for measuring these quantities. In the more common techniques [28], the bulk tilt angle is fixed either by an external field or by a strongly anchoring surface placed a distance l from the substrate under study. Elastic theory [24] is then used to find the surface tilt by extrapolation from the bulk, and the anchoring energy is found by balancing torques at the surface. Here we shall discuss the implications of the latter method only; the inclusion of an applied field would add terms to the equations, and will be dealt with in a future publication. We start by noting that the experimentally measured surface tilt angles and anchoring energies correspond to particular choices of the Gibbs dividing surface [28], which do not necessarily coincide with the position of the substrate in a semi-microscopic theory such as ours. We defer consideration of this non-trivial problem and write the surface tension as the sum of an elastic and a surface contribution,

$$\sigma = F_{el} + W = \tfrac{1}{2}K\frac{[\psi(l) - \psi_0]^2}{l} + \bar{w}_0 + \bar{w}_2\cos^2\psi_0 + \bar{w}_4\cos^4\psi_0, \tag{16}$$

where l is the size of the system, ψ_0, $\psi(l)$ are the surface and bulk tilt angles, respectively, $K(=3M\eta_b^2)$ is an elastic constant, and $\bar{w}_i$ are renormalized surface coefficients, not necessarily identical to the bare ones given by equations (7). (Note that this corresponds to taking the Gibbs dividing surface [28] to coincide with the solid substrate on the microscopic scale.) If ψ_0 is small ($\sin\psi_0 \simeq \psi_0$), the boundary condition at the surface reads

$$K\frac{d\psi}{dz}\bigg|_0 = K\frac{\psi(l) - \psi_0}{l} = -2\bar{w}\psi_0, \tag{17}$$

where $\bar{w} = \bar{w}_2 + 2\bar{w}_4$. Substitution into equation (16) yields, after straightforward manipulations,

$$\sigma = \frac{1}{2l/K - 1/\bar{w}}\psi^2(l) + \bar{w}_0 + \bar{w}_2 + \bar{w}_4. \tag{18}$$

Hence $\bar{w}$ can be obtained from the slope of σ versus $\psi^2(l)$. We expect this quantity to change sign at a conical to homeotropic transition [3].

3. Results

Equations (10) were solved by approximating the second derivatives of the order parameters by finite differences and then solving the resulting $3N$ coupled algebraic equations in $3N$ unknowns (N is the number of lattice points) using a generalization of the Newton–Raphson method [29]. Typically, large numbers of iterations (>1000) were needed to achieve convergence if $\psi \neq 0$ or $\pi \neq \pi/2$, all the more so as anchoring transitions were approached. All results presented pertain to the regime of complete wetting by the isotropic phase, which is thought to be experimentally relevant [4, 5, 14].

In figure 1 we contrast the numerically calculated bulk tilt angle (see equations (10) with boundary conditions of equation (12)) with that obtained via the Fowler approximation (i.e. minimization of equation (6) with equation (7) and $\eta = \eta_b$, $\mu = \mu_b = 0$). The latter completely misses the conical to homeotropic transition borne out by Landau–de Gennes theory, and further overestimates the surface tension considerably (see figure 2). Input parameters are such as to be appropriate to a substrate which

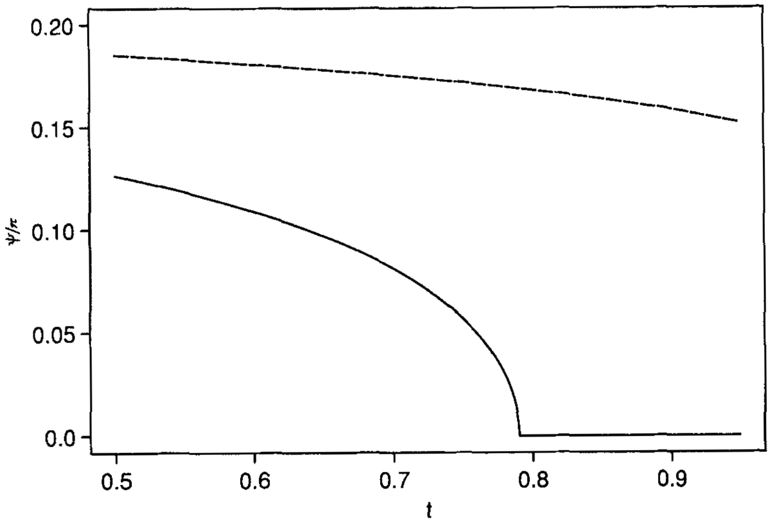

Figure 1. Bulk tilt angle versus reduced temperature in regime of complete wetting by the isotropic phase. Solid line: numerical result; dashed line: Fowler approximation.

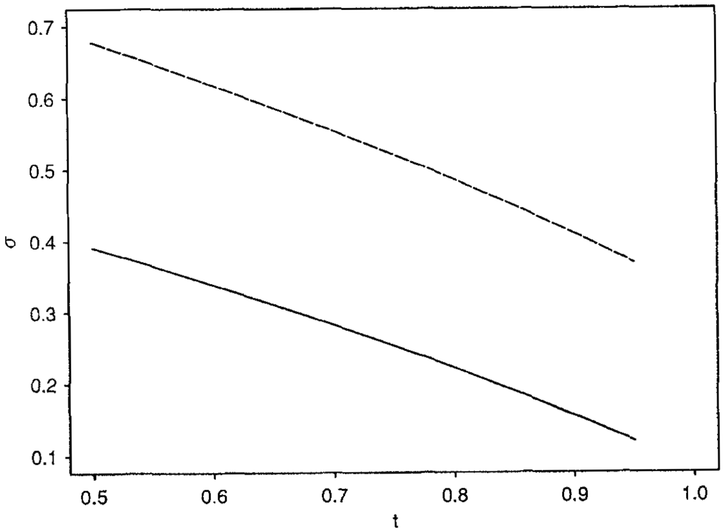

Figure 2. Numerical (solid line) and Fowler approximation (dashed line) surface tensions for the same system as in figure 1.

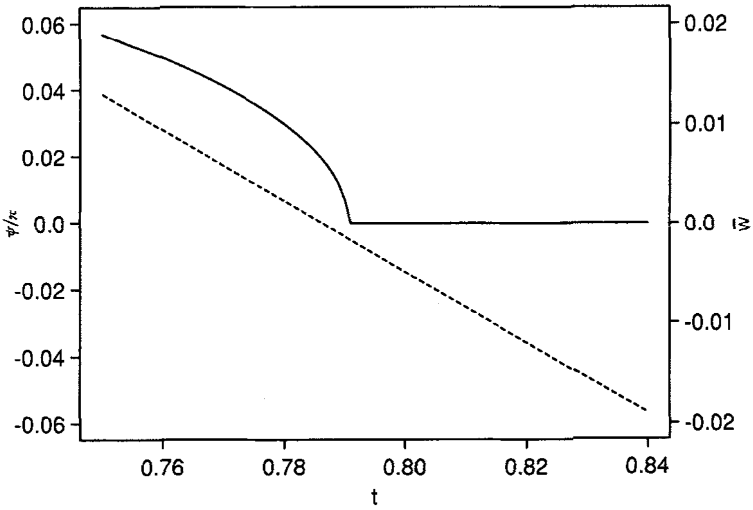

Figure 3. Bulk tilt angle (solid line) and anchoring energy function $\tilde{w}$ (dashed line) in the vicinity of the anchoring transition (small ψ regime).

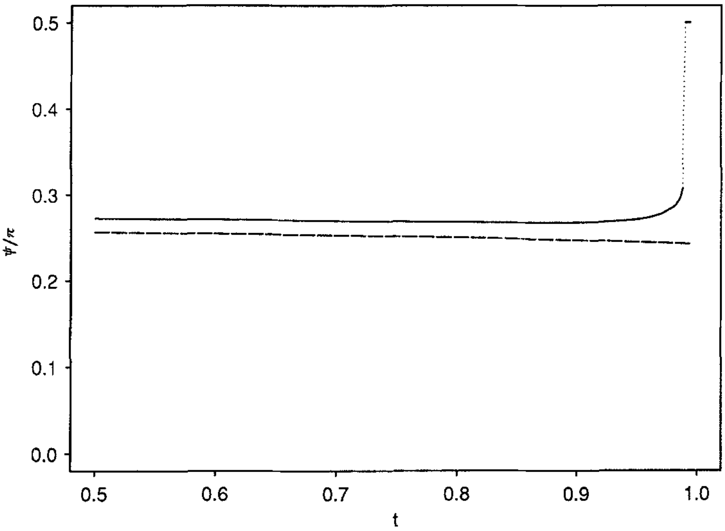

Figure 4. Bulk tilt angle versus reduced temperature in regime of complete wetting by the isotropic phase. The surface favours weaker homeotropic anchoring; the nascent N–I interface strongly favours parallel alignment, and the latter eventually wins.

favours homeotropic anchoring, viz. $L_1=L_2$, $c_1=-0{\cdot}5$, $c_{2\eta}=0{\cdot}85$, $c_{2\mu}=c_{2\nu}=0{\cdot}5$). The transition can be understood in terms of the bare surface energy, equation (6); strictly, the most stable alignment is found by minimizing the total free energy σ, but this will only (slightly) renormalize w_i. Minimization of f_s then yields a conical to homeotropic surface transition when $w=w_2+2w_4$ changes sign from positive to negative [3]. Neglecting biaxiality, it follows from equations (7 *b*) and (7 *c*) that

$$w=w_2+2w_4=\tfrac{3}{2}c_1\eta+3(c_3+\tfrac{1}{4}c_4)\eta^2; \tag{19}$$

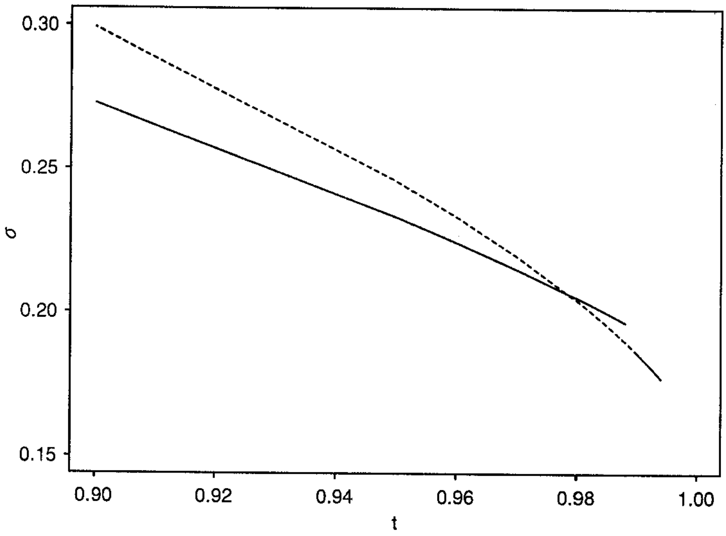

Figure 5. Surface tension versus reduced temperature as the temperature is increased (solid line) and decreased (dashed line). A pre-wetting transition occurs at $t \sim 0{\cdot}98$.

thus, if $c_1 < 0$, w will be negative provided η becomes small enough. In the regime of complete wetting by the isotropic phase, $\eta_0 \ll \eta_b$ and a transition may be obtained for $t <_{\mathrm{NI}}$. Figure 3 shows the renormalized $\bar{w}$ evaluated from equation (18) and the bulk tilt angle in the vicinity of the anchoring transition; the transition is fairly well pinpointed by the change in sign of $\bar{w}$.

In figure 4 we show the bulk tilt angle versus temperature for $L_2 = 3L_1$, $c_1 = -0{\cdot}2$, $c_{2\eta} = 0{\cdot}85$, $c_{2\mu} = c_{2\nu} = 0{\cdot}5$. As before, the surface favours homeotropic anchoring, albeit less strongly. The tilt angle is now a very weakly decreasing function of t in the low temperature regime. As $t \to t_{\mathrm{NI}}^-$, an isotropic wetting films starts to grow at the nematic–substrate interface; this gives rise to a new source of anchoring, viz. the nascent N–I interface, which favours planar anchoring since $L_2 > 0$ [23]. Hence the tilt angle bottoms out and becomes an increasing function of t at $t \sim 0{\cdot}9$, until it finally undergoes a discontinuous jump to $\psi = \pi/2$ at $t \sim 0{\cdot}9885$. We believe this transition to be associated with a pre-wetting [30] transition of the isotropic wetting film, the signature of which is a discontinuity in the slope of the surface tension (cf. figure 5) and a jump in the adsorption, defined as

$$\Gamma = -\int_0^{+\infty} [q(z) - q_b]\, dz, \tag{20}$$

(see figure 6), where q is the averaged order parameter

$$q = (\tfrac{2}{3} \operatorname{Tr} \mathbf{Q}^2)^{1/2} = (\eta_s^2 + \mu_s^2 + \nu_s^2)^{1/2} \tag{21}$$

It is clear from figure 6 that $\Gamma \sim \log(t_{\mathrm{NI}} - t)$ as $t \to t_{\mathrm{NI}}$.

Finally in figure 7 we plot the averaged order parameter profile $q = q(z)$ at three different temperatures; the profile corresponding to $t = 0{\cdot}988$ is in the metastable region of the thin film regime. At $t = 0{\cdot}99$, the profile has changed qualitatively: it is no longer monotonic, and the order parameter at the surface is now very small. As we move away from the wall, it first dips very close to zero, signalling the onset of an isotropic wetting film, before rising to the bulk value pertaining to the bulk nematic phase.

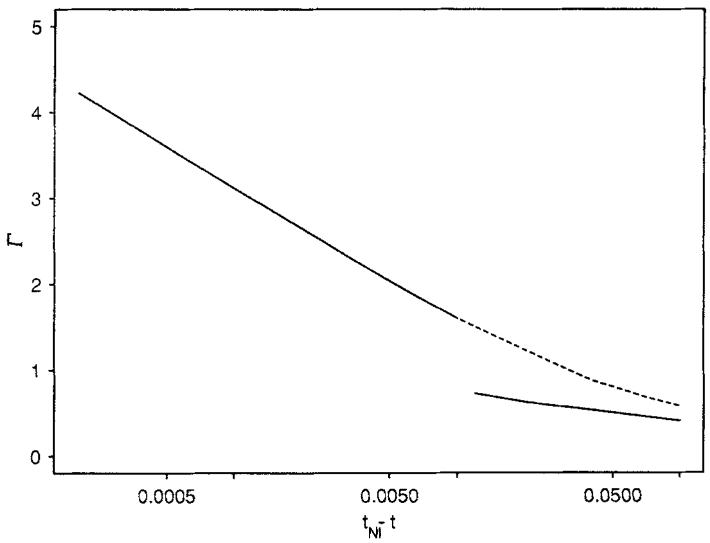

Figure 6. Adsorption versus reduced temperature as the temperature is increased (solid line) and decreased (dashed line). Note the logarithmic behaviour as $t \to t_{NI}^{-}$.

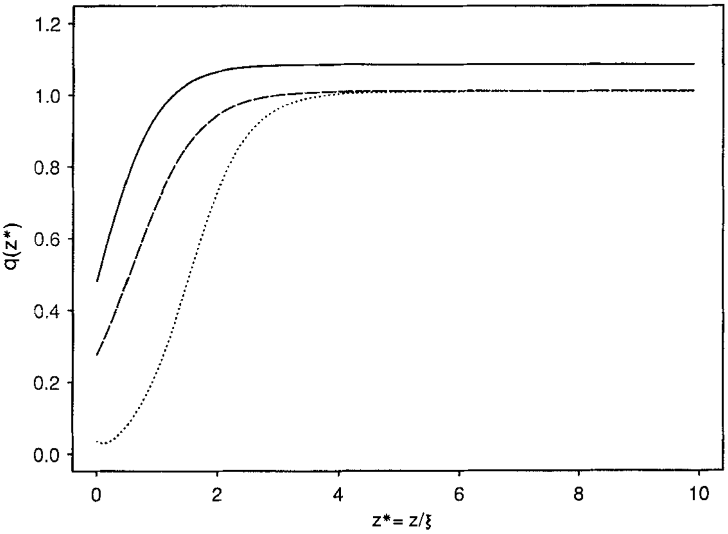

Figure 7. Averaged order parameter profiles at $t = 0{\cdot}9$ (solid line); $t = 0{\cdot}988$ (dashed line); and $t = 0{\cdot}99$ (dotted line). At the highest temperature, the surface order parameter is very low and the profile is non-monotonic, signalling the onset of growth of a thick isotropic wetting film. ξ is a length scale defined in [23].

4. Discussion and conclusions

We have formulated a Landau–de Gennes theory of temperature-driven anchoring transitions at a nematic liquid crystal–substrate interface which incorporates surface biaxiality and allows for non-uniform order parameter and director profiles. However, it neglects all substrate structure and does not allow the density to vary self-consistently.

The theory successfully anchoring transitions due to: (i) dehancement of the surface order parameter; (ii) competition between the aligning effects of the solid surface and the nascent interface between an incipient wetting film and the bulk medium, either of which is missed by the naïve Fowler approximation. Moreover, the latter effect gives rise to a non-monotonic temperature dependence of the director orientation, bearing strong resemblances to experimentally observed phenomena [4, 5, 14]. The conical to homeotropic transition which obtains for sufficiently high (low) $L_2(|c_1|)$ seems to be always discontinuous and associated with a pre-wetting transition [30] of the isotropic wetting film.

A number of points still need clarification. Firstly, we have not yet been able to reach a thermodynamically unambiguous definition of surface tilt angle (or, in other words, to pinpoint precisely the Gibbs dividing surface in the sense of Yokoyama [28]); hence all our predictions of surface tilts and anchoring energies should be taken with circumspection. Secondly, even if our procedure is sound in principle, there is no guarantee that it will allow a reliable determination of the anchoring energy function, owing to the linear approximation used for the bare surface energy. One possible solution would be to include the effect of an external field, which we are now considering. Finally, we feel that we can be confident that, for the system sizes investigated, the use of boundary conditions in equation (12) leads to essentially the same results as the use of boundary conditions of equation (13) followed by minimization of the surface tension.

The authors would like to thank Dr M. A. Osipov for many stimulating discussions and comments, and Dr J. S. Patel for communicating his results prior to publication. P. I. C. Teixeira gratefully acknowledges the financial support of JNICT/Programa Ciência of Portugal, in the form of Ph.D. studentship No. BD/8/90-RM.

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