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A thermodynamic approach to the anchoring phenomenon in the nematic liquid crystal–substrate system

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The phenomenon of anchoring in the nematic liquid crystal–amorphous substrate system is considered and model independent definitions of the surface nematic director, the surface tension and the anchoring energy coefficient are proposed. Then the Landau–de Gennes model of the system is studied for a specific choice of the surface parameters, which leads to a continuous homeotropic–conical anchoring transition. The free energy as a function of the director at a distance l from the surface is found. It is shown that its form is different in two regions of the temperature–distance plane separated by the line of a Fréedericksz transition. The asymptotic behaviour of the free energy for large l and for infinitesimal deviations of the director from the anchoring direction is studied. It is found that the asymptotic formula holds also in the vicinity of the anchoring transition. Finally, the results of numerical studies of the Landau–de Gennes model are compared with the predictions of a simple phenomenological model.

1. Introduction

It is well known that nematic liquid crystals (NLCs) can be oriented by various limiting surfaces, for instance the surface of a solid substrate. This phenomenon is called the anchoring of the NLC at interfaces [1–7]. Due to the interaction of the NLC with the substrate, there exists a set of preferred orientations of the bulk nematic director $\hat{\mathbf{n}}$, called the anchoring directions, which correspond to the equilibrium states of the system. In the case of an amorphous substrate the set of anchoring directions is continuously degenerate. If θ denotes the angle between $\hat{\mathbf{n}}$ and the surface normal $\hat{\mathbf{k}}$ then the homeotropic (H), planar (P), and conical (C) anchorings correspond to $\theta = 0$, $\theta = \pi/2$, and $0 < \theta < \pi/2$, respectively. The phenomenon of anchoring and phase transitions between different types of anchoring attract a good deal of attention, and they have been studied both experimentally [8–13] and theoretically [14–23].

The anchoring of the NLC is usually characterized by two quantities: the anchoring direction and the anchoring strength. While the anchoring direction is a well defined concept, there have been some problems with the definition of the anchoring strength [3]. The latter usually appears as a parameter in phenomenological expressions for the surface tension γ between the NLC and the substrate, and it is called the anchoring energy coefficient [2]. An example of such a phenomenological approach is the Rapini–Papoular [24] formalism, in which the form of the orientation dependent part of γ, referred to as the anchoring energy function, is merely postulated. The problem can be formulated more generally as follows: how can we define γ as a function of the director at the interface $\hat{\mathbf{n}}_0$ and what is really meant by $\hat{\mathbf{n}}_0$? To consider γ as a function of $\hat{\mathbf{n}}_0$, it is necessary to deform the equilibrium configuration of the director by means of an external field or by a strongly anchoring wall placed a distance l from the substrate. Then γ is defined as the surface part of the grand-canonical potential Ω per unit area. In the absence of bulk external fields, the bulk contribution to Ω consists of two parts: Ω_0, which is independent of any deformation, and the Frank elastic energy of deformation. To define the surface contribution to Ω, Yokoyama [3] has introduced a Gibbs dividing surface placed at some distance z_d from the surface of the substrate. The NLC above the dividing surface is considered as having a bulk-like behaviour. Then $\gamma(z_d, \hat{\mathbf{n}}_d)$ is defined with respect to that arbitrarily chosen dividing surface. Hence, the anchoring energy coefficient, which is defined as the second derivative of γ with respect to the director orientation taken at the anchoring direction [2], is meaningful only in relation to the dividing surface.

In this paper we reconsider the problem of the thermodynamic definition of the anchoring strength. First, we define Ω as a function of the 'bulk' director $\hat{\mathbf{n}}_l$ at a distance l from the substrate surface. This is the only

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physical surface in the problem and as long as it is smooth, l is a well defined thermodynamic parameter. Therefore, there is no reason to introduce an extra dividing surface that separates the interfacial region of the NLC from the bulk, as there is no good criterion for locating such a surface. In general, Ω depends also on l and its minimum at l fixed defines the equilibrium orientation of the director at $z=l$, denoted $\hat{\mathbf{n}}_{\min}$. To determine the bulk contribution to Ω, we define a 'surface direction' $\bar{\hat{\mathbf{n}}}_0$; it is usually different from the actual director at $z=0$. It follows from our definition of $\bar{\hat{\mathbf{n}}}_0$ that if $\hat{\mathbf{n}}_l=\hat{\mathbf{n}}_{\min}$ then also $\bar{\hat{\mathbf{n}}}_0=\hat{\mathbf{n}}_{\min}$ and the Frank elastic energy vanishes. Then the surface tension is defined as a function of l and $\hat{\mathbf{n}}_l$ rather than $\bar{\hat{\mathbf{n}}}_0$. However, close to $\hat{\mathbf{n}}_{\min}$ the relation between $\hat{\mathbf{n}}_l$ and $\bar{\hat{\mathbf{n}}}_0$ can be inverted and γ can also be considered as a function of $\bar{\hat{\mathbf{n}}}_0$, which allows us to define the anchoring energy coefficient. For a finite system, this coefficient formally depends on l; however, we are mainly interested in its limiting value when $l\to\infty$. We show that in this limit the anchoring energy coefficient is related to the extrapolation length [1].

The rest of the paper is devoted to numerical studies of the Landau–de Gennes model. This model can be considered as a semi-microscopic one to distinguish it from the phenomenological models in which the director field is the only variable. It also takes into account variations of the order parameters. Recently we have used a second order approximation of the Landau–de Gennes free-energy functional to study anchoring transitions and the asymptotic behaviour of the free energy for $l\to\infty$ and for infinitesimal deviations of $\hat{\mathbf{n}}_l$ from the anchoring direction [25, 26]. In this paper we concentrate on the dependence of the free energy on $\hat{\mathbf{n}}_l$, which is studied for various temperatures t and for various l. For simplicity, we choose only one set of the surface parameters that has already been studied by Teixeira *et al.* [17] in the context of the homeotropic–conical anchoring transition. We show that below the anchoring transition the dependence of the free energy on $\hat{\mathbf{n}}_l$ is qualitatively different in two regions of the (t, l) plane, and the border line is the line of a Fréedericksz transition. We also study the asymptotic behaviour of the free energy for large l and $\hat{\mathbf{n}}_l$ close to the anchoring direction, and we find that the asymptotic formula holds even very close to the continuous anchoring transition. It is also found that the anchoring energy coefficient vanishes at the continuous anchoring transition.

Our paper is arranged as follows. In § 2 we provide thermodynamic definitions of the surface director, the surface tension, and the anchoring energy coefficient. We also generalize the concept of the extrapolation length. In § 3 we define the model and study the stability of the homeotropic alignment by means of the bifurcation analysis. The results obtained from the numerical solutions of the Euler–Lagrange equations are presented in § 4, and § 5 is devoted to a discussion.

2. Thermodynamics of anchoring

We consider a NLC in contact with an isotropic solid substrate. The nematic direction $\hat{\mathbf{n}}$, the density and the order parameters depend only on z, i.e. the distance from the surface of the substrate located at $z=0$. We consider an idealized situation where it is possible to control the orientation of the director at $z=l$ by some external factor without changing the structure of the fluid. In other words, if l is large compared with the thickness of the interfacial region, then the density and the order parameters at $z=l$ are very close to the bulk values. When the temperature, chemical potential and volume are fixed, the grand-canonical potential Ω is a functional of the one-particle distribution function $\rho^{(1)}$, and the global minimum of Ω corresponds to the equilibrium state of the system. Formally we can also consider a minimization of Ω over a set of $\rho^{(1)}$ satisfying the constraint $\theta(z=l)=\theta_l$. Then the minimum of Ω over the constrained distributions, denoted Ω, is a function of l and θ_l, and the equilibrium state results from the minimization of Ω with respect to θ_l.

The anchoring direction θ_a is a property of a single NLC–substrate interface, i.e. it is the equilibrium orientation assumed by the director infinitely far from the interface if there are no bulk external fields or other surfaces. Thus, if $\theta_{\min}(l)$ denotes the minimum of $\Omega(l, \theta_l)$ at l fixed, then $\theta_a=\lim_{l\to\infty}\theta_{\min}(l)$. Before we provide thermodynamic definitions of interfacial quantities, we recall briefly the phenomenological approaches, e.g. the Rapini–Papoular formalism, in which $\hat{\mathbf{n}}$ is the only relevant variable and the free energy (per unit area) of the NLC is postulated to be the following functional of $\theta(z)$:

$$\mathcal{F}[\theta]=F_0+\frac{1}{2}\int_0^l K(\theta)\left(\frac{\mathrm{d}\theta}{\mathrm{d}z}\right)^2\mathrm{d}z+f_s(\theta_0). \qquad (1)$$

In equation (1) F_0 is the orientation independent bulk contribution, $K(\theta)=K_1\sin^2\theta+K_3\cos^2\theta$, where K_1, K_3 are the splay and bend Frank elastic constants, respectively. The surface contribution to the free energy f_s is assumed to depend only on $\theta_0=\theta(z=0)$. Usually the explicit dependence on the anchoring direction is also included in the functional form of f_s. However, since we do not assume at this stage any particular form of f_s, we do not show this dependence explicity. It suffices to say that θ_a minimizes $f_s(\theta_0)$. In the absence of constraints and external fields, $\theta(z)=\theta_a$ also minimizes the functional $\mathcal{F}[\theta]$. If the constraint $\theta(z=l)=\theta_l$ is introduced, then one has to solve the Euler–Lagrange

equation with the appropriate boundary conditions. We denote the free energy calculated for $\theta(z)$ satisfying the Euler–Lagrange equation by F, to distinguish it from the functional $\mathcal{F}$. F as a function of θ_0, θ_l, and l has the following form

$$F(\theta_0, \theta_l, l) = F_0 + F_{el}(\theta_0, \theta_l, l) + f_s(\theta_0), \tag{2}$$

where the elastic contribution is given by

$$F_{el}(\theta_0, \theta_l, l) = \frac{1}{2l}\left\{ \int_{\theta_0}^{\theta_l} [K(\theta)]^{1/2} \mathrm{d}\theta \right\}^2 \tag{3}$$

and $\theta_0 = \theta_0(\theta_l, l)$ is found from the condition $\partial F/\partial\theta_0 = 0$. Hence, F can also be considered as a function of θ_l and l alone, and we have

$$\left(\frac{\partial F}{\partial \theta_l}\right)_l = \left(\frac{\partial F}{\partial \theta_l}\right)_{\theta_0, l} = \left(\frac{\partial F_{el}}{\partial \theta_l}\right)_{\theta_0, l}. \tag{4}$$

It follows from equation (4) that $F(\theta_l, l)$ is minimized by $\theta_l = \theta_a$ independently of l. We note that if $F(\theta_l, l)$ was given *a priori*, then relation (4) could serve as the definition of θ_0. We shall use this fact later to define thermodynamically the 'surface orientation' $\bar{\theta}_0$ of the director. This $\bar{\theta}_0$ can be understood as a result of extrapolation of the director field from the region well described by the Frank theory into the interfacial region. Therefore, it usually differs from the actual orientation of $\hat{\mathbf{n}}$ at $z = 0$.

It is instructive to find the explicit form of $F(\theta_l, l)$ in the case of small deviations from the anchoring direction. Then we have

$$F(\theta_0, \theta_l, l) = F_0 + \frac{1}{2l} K_a (\theta_l - \theta_0)^2 + \frac{1}{2} w (\theta_0 - \theta_a)^2, \tag{5}$$

where $K_a = K(\theta_a)$ and w is the anchoring energy coefficient. Minimization of F with respect to θ_0 leads to the following expression

$$F(\theta_l, l) = \frac{1}{2} K_a \frac{(\theta_l - \theta_a)^2}{l + K_a/w}, \tag{6}$$

where the ratio K_a/w has the dimension of length.

In general, the strength of anchoring can be characterized by the extrapolation length b [1], which appears in the asymptotic form of $\theta(z)$ for large z. It results from the minimization of the Frank elastic energy that far from the surface

$$\theta(z) \sim \theta_a + \text{const} \times (z + b), \tag{7}$$

provided that the deviation of $\theta(z)$ from θ_a is infinitesimally small. We shall consider the case of arbitrary deviations later in this section. Dubois-Violette and de Gennes [15] studied the effect of van der Waals forces on the anchoring and showed that b can be positive or negative. In the model considered above the extrapolation length is given by $b = K_a/w$ [1] and it is positive, because both K_a and w must be positive to ensure the stability of the free energy functional.

We now proceed to the general case and define the function

$$\omega(\theta_l, l) = \frac{1}{A}[\Omega(\theta_l, l) - \Omega_0], \tag{8}$$

where Ω_0 is the orientation independent bulk contribution to Ω and A is the area. The surface orientation $\bar{\theta}_0$ is defined as follows

$$\left(\frac{\partial \omega}{\partial \theta_l}\right)_l = \left(\frac{\partial F_{el}}{\partial \theta_l}\right)_{\bar{\theta}_0, l} = \frac{1}{l}[K(\theta_l)]^{1/2} \int_{\bar{\theta}_0}^{\theta_l} [K(\theta)]^{1/2} \mathrm{d}\theta. \tag{9}$$

The above definition is a natural generalization of relation (4); $\bar{\theta}_0$ as a function of θ_l and l can be determined provided that $\omega(\theta_l, l)$ is known. If $K_1 = K_3 = K$ we have $\bar{\theta}_0 = \theta_l - (l/K)\partial\omega/\partial l$. Strictly speaking, if $|(\partial\omega/\partial\theta_l)_l|$ was sufficiently large, equation (9) might have no solutions. Nevertheless, it is always possible to find $\bar{\theta}_0$ satisfying (9) when θ_l is close to $\theta_{min}(l)$, and this is the case of our main interest. We note that for $\theta_l = \theta_{min}(l)$ also $\bar{\theta}_0 = \theta_{min}(l)$. This means that in the absence of external constraints there are no macroscopic deformations of $\hat{\mathbf{n}}$, i.e. on a scale large compared with the thickness of the interfacial region, and $F_{el} = 0$. However, even in the absence of macroscopic deformations there can be some variations of $\hat{\mathbf{n}}$ in the interface, but they contribute only to the surface part of Ω together with variations of the order parameters and density. Equation (9) can also be written in a more familiar form, i.e.

$$\left(\frac{\partial \omega}{\partial \theta_l}\right)_l = K(\theta_l) \frac{\mathrm{d}\bar{\theta}}{\mathrm{d}z}(z = l), \tag{10}$$

where the profile $\bar{\theta}(z)$ minimizes the Frank elastic energy alone and it is given by

$$\int_{\bar{\theta}_0}^{\bar{\theta}(z)} [K(\theta)]^{1/2} \mathrm{d}\theta = \frac{z}{l} \int_{\bar{\theta}_0}^{\theta_l} [K(\theta)]^{1/2} \mathrm{d}\theta. \tag{11}$$

Let us suppose that $z = l$ is a mathematical surface dividing a larger system into two sub-systems and ω corresponds to the sub-system containing the interface. On the general grounds of variational principle, equation (10) is expected to hold also for the real profile $\theta(z)$, provided that l is well inside the bulk region. Thus, for large z the profiles $\theta(z)$ and $\bar{\theta}(z)$ approach each other. This means that $\bar{\theta}(z)$ can be considered as an extrapolation of the real profile into the interfacial region in the spirit of the Frank theory. We note that the mathematical surface $z = l$ has the same meaning as the

dividing surface introduced in ref. [3], whereas $\omega(\theta_l, l)$ can be identified with what Yokoyama calls the interfacial tension with respect to the dividing surface. We take a different point of view, however, and define the surface part of Ω with respect to the physical surface at $z=0$ as follows

$$\gamma(\theta_l, l) = \omega(\theta_l, l) - F_{\mathrm{el}}(\bar{\theta}_0, \theta_l, l), \tag{12}$$

where $\bar{\theta}_0$ is given by expression (9). This means that we have included in γ only this part of the elastic energy due to the director distortions which results from the difference between the real profile and the extrapolated one. Such a difference may result from the fact that the Frank theory does not properly describe the inhomogeneous interfacial region or from the presence of long range forces between the solid and the NLC [15].

In the case of the phenomenological model considered above we simply have $\gamma(\theta_l, l) = f_s[\theta_0(\theta_l, l)]$. When $l \to \infty$ the torque transmitted to the surface of the substrate by the elastic forces becomes vanishingly small and the interfacial region is unaffected by changes of θ_l. This means that $\gamma(\theta_l, l)$ tends to the equilibrium surface tension for $l \to \infty$ independently of θ_l. Using definitions (3), (9), and (12) we can express γ explicitly as a function of θ_l and l, i.e.

$$\gamma(\theta_l, l) = \omega(\theta_l, l) - \frac{l}{2K(\theta_l)}\left(\frac{\partial \omega}{\partial \theta_l}\right)^2. \tag{13}$$

To make some contact with the phenomenological approach, we invert the relation between $\bar{\theta}_0$ and θ_l at l fixed. It follows from the definitions of γ and $\bar{\theta}_0$ that

$$\left(\frac{\partial \gamma}{\partial \theta_l}\right)_l = -\left(\frac{\partial F_{\mathrm{el}}}{\partial \bar{\theta}_0}\right)_{\theta^{\prime}, l}\left(\frac{\partial \bar{\theta}_0}{\partial \theta_l}\right)_l, \tag{14}$$

hence

$$\left(\frac{\partial \gamma}{\partial \bar{\theta}_0}\right)_l = -\left(\frac{\partial F_{\mathrm{el}}}{\partial \bar{\theta}_0}\right)_{\theta^{\prime}, l} = K(\bar{\theta}_0)\frac{\mathrm{d}\bar{\theta}}{\mathrm{d}z}(z=0) = \left[\frac{K(\bar{\theta}_0)}{K(\theta_l)}\right]^{1/2}\left(\frac{\partial \omega}{\partial \theta_l}\right)_l, \tag{15}$$

from which we conclude that $\bar{\theta}_0 = \theta_{\min}(l)$ is an extremum of $\gamma(\bar{\theta}_0, l)$. Note that relation (15) is satisfied only for $\bar{\theta}(z)$ and, in general, it does not hold for the real profile.

Differentiating (15) with respect to $\bar{\theta}_0$ we find

$$\frac{\partial^2 \gamma}{\partial \bar{\theta}_0^2} = \left[\frac{K(\bar{\theta}_0)}{K(\theta_l)}\right]^{1/2}\left\{\frac{K'(\bar{\theta}_0)}{2K(\bar{\theta}_0)}\frac{\partial \omega}{\partial \theta_l} + \left[\frac{\partial^2 \omega}{\partial \theta_l^2} - \frac{K'(\theta_l)}{2K(\theta_l)}\frac{\partial \omega}{\partial \theta_l}\right]\left(\frac{\partial \bar{\theta}_0}{\partial \theta_l}\right)^{-1}\right\}, \tag{16}$$

where

$$\frac{\partial \bar{\theta}_0}{\partial \theta_l} = \left[\frac{K(\theta_l)}{K(\bar{\theta}_0)}\right]^{1/2}\left[1 + \frac{lK'(\theta_l)}{2K^2(\theta_l)}\frac{\partial \omega}{\partial \theta_l} - \frac{l}{K(\theta_l)}\frac{\partial^2 \omega}{\partial \theta_l^2}\right], \tag{17}$$

and all derivatives have been calculated at l fixed. Analogously with the phenomenological definition of the anchoring energy coefficient [2] we define

$$\bar{w} = \left(\frac{\partial^2 \gamma}{\partial \bar{\theta}_0^2}\right)_{\min} = \left(\frac{\partial^2 \omega}{\partial \theta_l^2}\right)_{\min}\left[1 - \frac{l}{K(\theta_{\min})}\left(\frac{\partial^2 \omega}{\partial \theta_l^2}\right)_{\min}\right]^{-1}, \tag{18}$$

where the subscript min corresponds to $\theta_{\min}(l)$; we also define $\bar{b} = K(\theta_{\min})/\bar{w}$. Formally both $\bar{w}$ and $\bar{b}$ depend on l, but we expect them to have finite limits for $l \to \infty$, which we denote by w and b, respectively, and hence $w = K_a/b$. We note that this assumption is compatible with the asymptotic formula for $l \to \infty$

$$\left(\frac{\partial^2 \omega}{\partial \theta_l^2}\right)_{\min} \sim \frac{K_a}{l+b}. \tag{19}$$

To show that expression (19) holds and b is the extrapolation length, let us consider ω as a function of l and p_l, where p_l is the gradient $\mathrm{d}\theta/\mathrm{d}z$ at $z=l$. Then θ_l is not an independent variable, but is also a function of l and p_l, and we have

$$\left(\frac{\partial \omega}{\partial l}\right)_{p_l} = \left(\frac{\partial \omega}{\partial l}\right)_{\theta^{\prime}} + \left(\frac{\partial \omega}{\partial \theta_l}\right)_l\left(\frac{\partial \theta_l}{\partial l}\right)_{p_l}. \tag{20}$$

It follows from the definition of the extrapolation length that for large l and infinitesimally small gradients

$$\theta_l \approx \theta_a + p_l(l+b). \tag{21}$$

If p_l is fixed and l is large an infinitesimal change of l cannot affect the structure of the interfacial region. Then the change of ω is simply equal to the change of the elastic energy and it is given by

$$\left(\frac{\partial \omega}{\partial l}\right)_{p_l} = \frac{1}{2}K_a p_l^2. \tag{22}$$

In the neighbourhood of $\theta_{\min}(l)$, $\omega(\theta_l, l)$ has the following form

$$\omega(\theta_l, l) \approx \frac{1}{2}\omega_2(l)[\theta_l - \theta_{\min}(l)]^2 \approx \omega_2(l)\frac{1}{2}(\theta_l - \theta_a)^2, \tag{23}$$

where we have included only the leading term in the asymptotic expansion for large l. Substituting equations (22) and (23) into (20) and using (21) we find that the

coefficient $\omega_2(l)$ satisfies

$$\frac{\mathrm{d}\omega_2}{\mathrm{d}l}+\frac{2\omega_2}{l+b}=\frac{K_a}{(l+b)^2}, \tag{24}$$

hence $\omega_2(l)=K_a/(l+b)$. Thus, we have shown that for large l and small deivations from the anchoring direction the asymptotic formula

$$\omega(\theta_l, l)\approx\frac{1}{2}K_a\frac{(\theta_l-\theta_a)^2}{l+b}, \tag{25}$$

where b is the extrapolation length, is valid.

It does not follow from the definition of γ that it is independent of l when $\bar{\theta}_0$ is fixed. Therefore, we have to consider a possible change of γ with l, which is given by

$$\left(\frac{\partial\gamma}{\partial l}\right)_{\bar{\theta}_0}=\left(\frac{\partial\gamma}{\partial l}\right)_{\theta'}-\left(\frac{\partial\gamma}{\partial\bar{\theta}_0}\right)_l\left(\frac{\partial\bar{\theta}_0}{\partial l}\right)_{\theta'}. \tag{26}$$

Differentiating equations (9) and (13) with respect to l and using (15) we find, after the substitution into (26), that

$$\left(\frac{\partial\gamma}{\partial l}\right)_{\bar{\theta}_0}=\left(\frac{\partial\omega}{\partial l}\right)_{\theta'}+\frac{1}{2K(\theta_l)}\left(\frac{\partial\omega}{\partial\theta_l}\right)_l^2. \tag{27}$$

If we keep in equation (27) only the terms of order $(\theta_l-\theta_a)^2$ we can approximate $K(\theta_l)$ by $K(\theta_a)$, and substituting the asymptotic form (25) into (27) we find that $(\partial\gamma/\partial l)_{\bar{\theta}_0}=0$. In this asymptotic sense $\gamma-\gamma_a$, where γ_a corresponds to the anchoring direction, is a function of $\bar{\theta}_0$ alone and it can be identified with the anchoring energy function. There are, however, important differences betweeen γ defined by equation (12) and $f_s(\theta_0)$ postulated phenomenologically. First of all, f_s appears in the free energy functional (1), where θ_0, θ_l, and l are considered as independent variables. Usually, it is tacitly assumed that $f_s(\theta_0)$ is well defined not only in the neighbourhood of the anchoring direction but in the whole range between 0 and π. In our approach, we consider only the states of the system that mimimize the grand-canonical potential. Therefore, the range of $\bar{\theta}_0$ in which γ is defined depends on l, and it decreases when $l\to\infty$. This means that γ is defined only in some neighbourhood of $\theta_{\min}(l)$, and when l is large γ becomes a function of $\bar{\theta}_0$ alone. Although the leading term of the asymptotic expansion of $\gamma(\bar{\theta}_0, l)$ is independent of l, in general, some l dependent corrections are expected. However, the form of these corrections will depend on the range of the NLC-substrate interactions.

We have identified w with the anchoring energy coefficient (see equation (18)), which is related to the extrapolation length via $w=K(\theta_a)/b$. However, the phenomenological model of the form given by equation (1) is self-consistent only if the anchoring energy coefficient is positive. Since there is no reason to assume that b is always positive [15], $w<0$ is also possible. To maintain a simple phenomenological description of the NLC–substrate interface in the case of $w<0$, it is necessary to add other tems to the free energy functional, as was done for instance by Dubois-Violette and de Gennes [15]. Then $f_s(\theta_0)$ takes into account only the short range forces. Therefore, its minimum can be different from the macroscopic anchoring direction, because of the presence of other interactions. On the other hand, $\bar{w}$ obtained from equation (18) is always meaningful, even though $\bar{w}<0$ means that $\gamma(\bar{\theta}_0, l)$ has a maximum at $\bar{\theta}_0=\theta_{\min}(l)$. However, this does not violate the stability condition, since $\bar{\theta}_0$ and θ_l cannot be varied independently of each other.

So far we have concentrated on the case of infinitesimal deviations of θ_l from the anchoring direction. However, it is possible to generalize the definition of the extrapolation length to the case of arbitrary θ_l and l. To do this, we consider the profile $\bar{\theta}(z)$ and define the function $b_e(\theta_l, l)$ that satisfies the condition $\bar{\theta}(z=-b_e)=\theta_{\min}(l)$, i.e.

$$b_e(\theta_l, l)=l\int_{\theta_{\min}}^{\bar{\theta}_0}[K(\theta)]^{1/2}\mathrm{d}\theta\Big/\int_{\bar{\theta}_0}^{\theta'}[K(\theta)]^{1/2}\mathrm{d}\theta. \tag{28}$$

Using definition (9) we find the explicit relation between ω and b_e

$$\left(\frac{\partial\omega}{\partial\theta_l}\right)_l=\frac{1}{l+b_e(\theta_l, l)}\left(\frac{\partial g}{\partial\theta_l}\right)_l, \tag{29}$$

where

$$g(\theta_l, l)=\frac{1}{2}\left\{\int_{\theta_{\min}}^{\theta'}[K(\theta)]^{1/2}\mathrm{d}\theta\right\}^2.$$

Using (29) and the definition of $\bar{b}$ one verifies that $\bar{b}=b_e(\theta_{\min}, l)$.

Then we integrate equation (29) to express $\omega(\theta_l, l)$ in terms of b_e as follows

$$\omega(\theta_l, l)=\omega_{\min}(l)+\frac{g(\theta_l, l)}{l+b_e(\theta_l, l)}+\Delta\omega(\theta_l, l), \tag{30}$$

where $\omega_{\min}(l)=\omega[\theta_{\min}(l), l]$ and

$$\Delta\omega(\theta_l, l)=\int_{\theta_{\min}}^{\theta'}\left(\frac{\partial b_e}{\partial\theta}\right)_l\frac{g(\theta, l)\mathrm{d}\theta}{[l+b_e(\theta, l)]^2}.$$

Hence, for large l and θ_l close to θ_a, $b_e\approx b$ and we recover formula (25). Using equation (13) we can also express γ in terms of b_e as follows

$$\gamma(\theta_l, l)=\omega_{\min}(l)+\frac{g(\theta_l, l)b_e(\theta_l, l)}{[l+b_e(\theta_l, l)]^2}+\Delta\omega(\theta_l, l). \tag{31}$$

Because of the relation between $g(\bar{\theta}_0, l)$ and $g(\theta_l, l)$,

which follows from the definition of b_e, we find that

$$\gamma = \omega_{\min}(l) + \frac{g(\theta_0, l)}{b_e(\theta_l, l)} + \Delta\omega(\theta_l, l), \tag{32}$$

where $\bar{\theta}_0$ and θ_l are treated as dependent variables. If we neglect variations of $\omega_{\min}$ and $\theta_{\min}$ with l and assume that $b_e(\theta_l, l) \approx b$ then

$$\gamma \approx \omega_{\min}(\infty) + \frac{g(\bar{\theta}_0, \infty)}{2b}, \tag{33}$$

i.e. γ can be treated as a function of $\bar{\theta}_0$ alone. Although in some practical cases this may be a good approximation, in general it is justified only if $l \to \infty$ and $\theta_l \to \theta_a$.

As we have argued above, to study the phenomenon of anchoring from the thermodynamic point of view it is not really necessary to introduce a concept of the surface tension as a function of the surface director. In some sense, in our considerations it has been only an auxiliary quantity, introduced to show the correspondence between the thermodynamic and the phenomenological approaches. The whole information about the system is contained in the function $\omega(\theta_l, l)$, which is uniquely defined. The asymptotic behaviour of ω for $l \to \infty$ simply reflects the presence of elastic forces, but it also provides information about the strength of anchoring, expressed in terms of the extrapolation length.

3. The Landau–de Gennes model

In the Landau–de Gennes model, the NLC is described in terms of the nematic order parameter $\mathbf{Q}$, which is a traceless, symmetric tensor. The director $\hat{\mathbf{n}}$ is the eigenvector corresponding to the largest eigenvector of $\mathbf{Q}$, called the scalar order parameter Q. We neglect fluctuations and assume that $\mathbf{Q}$ depends only on z, and the free energy density is given by $f = f_L(\mathbf{Q}) + f_G(\mathbf{Q})$, where $\mathbf{Q} = d\mathbf{Q}/dz$. The first term describes a homogeneous system and the second term takes into account spacial inhomogeneities. The following forms of f_L and f_G are assumed:

$$f_L(\mathbf{Q}) = A \operatorname{Tr}\mathbf{Q}^2 - B \operatorname{Tr}\mathbf{Q}^3 + C(\operatorname{Tr}\mathbf{Q}^2)^2 \tag{34}$$

$$f_G(\mathbf{Q}) = \frac{1}{2}L_1 \operatorname{Tr}\mathbf{Q}^2 + \frac{1}{2}L_2 \hat{\mathbf{k}}\ \mathbf{Q}^2\ \hat{\mathbf{k}}. \tag{35}$$

The parameter A is assumed to depend linearly on the temperature, whereas B, C and the elastic constants L_1, L_2 are considered as temperature independent.

We consider a NLC sample of finite thickness l and assume the free energy functional in the following form [16, 27]:

$$F = \int_0^l dz\{ f_L[\mathbf{Q}(z)] - f_L(\mathbf{Q}_l) + f_G[\mathbf{Q}(z)]\} + f_s(\mathbf{Q}_0), \tag{36}$$

where $\mathbf{Q}_0 = \mathbf{Q}(z=0)$ and $\mathbf{Q}_l = \mathbf{Q}(z=l)$. The surface contribution to the free energy f_s is expanded up to the second order terms in $\mathbf{Q}_0$, which for isotropic substrates gives

$$f_s(\mathbf{Q}_0) = c_1 \hat{\mathbf{k}}\ \mathbf{Q}_0\ \hat{\mathbf{k}} + c_2 \operatorname{Tr}\mathbf{Q}_0^2 + c_3(\hat{\mathbf{k}}\ \mathbf{Q}_0\ \hat{\mathbf{k}})^2 + c_4 \hat{\mathbf{k}}\ \mathbf{Q}_0^2\ \hat{\mathbf{k}}, \tag{37}$$

where $c_1, \ldots, c_4$ are constants. F is minimized subject to fixed boundary conditions at $z = l$, specified by θ_l, Q_l, and the biaxiality P_l. If l is large compared with the thickness of the interfacial region, one can use the approximation $Q_l \approx Q_b$, $P_l \approx P_b = 0$, where Q_b and P_b denote the bulk values. However, to solve numerically the set of Euler–Lagrange equations, we assume different boundary conditions at $z = l$, i.e. $\dot{Q}(l) = \dot{P}(l) = 0$. We return to this point in the next section.

To reduce the number of parameters in the free energy and to deal with dimensionless quantities, we perform the following scaling: $\mathbf{Q} \mapsto (B/4C)\mathbf{Q}$, $z \mapsto [6(L_1C)^{1/2}/B]z$, $F \mapsto [(L_1C)^{1/2}B^3/96C^3]F$, $c_1 \mapsto [(L_1C)^{1/2}B^2/24C^2]c_1$, and $c_i \mapsto [(L_1C)^{1/2}B/6C]c_i$, $i = 2, 3, 4$. Then $\mathbf{Q}$ is expressed in a laboratory fixed frame as follows:

$$\mathbf{Q} = \begin{pmatrix} -\frac{1}{3}q + p & 0 & v \\ 0 & -\frac{1}{3}q - p & 0 \\ v & 0 & \frac{2}{3}q \end{pmatrix}. \tag{38}$$

Hence, the dimensionless f_G, f_L, and f_s are given by

$$f_G = \frac{1}{2}(M_1\dot{q}^2 + M_2\dot{p}^2 + M_3\dot{v}^2), \tag{39}$$

where $M_1 = 2/3 + (4/9)L_2/L_1$, $M_2 = 2$, $M_3 = 2 + L_2/L_1$,

$$f_L = tq^2 - 2q^3 + q^4 + 3(t + 6q + 2q^2)p^2 + 3(t - 3q + 2q^2)v^2 - 27pv^2 + 9(p^2 + v^2)^2, \tag{40}$$

where $t = 24AC/B^2$ measures the temperature, and

$$f_s = -hq_0 + \frac{1}{2}(g_1 q_0^2 + g_2 p_0^2 + g_3 v_0^2), \tag{41}$$

where $h = -(2/3)c_1$, $g_1 = (4/9)(3c_2 + 2c_3 + 2c_4)$, $g_2 = 4c_2$, $g_3 = 2(2c_2 + c_4)$. For simplicity, we have used the same symbols (c_i) in the dimensionless f_s. The minimization of F results in the following set of non-linear differential equations:

$$M_1\ddot{q} = 2tq - 6q^2 + 4q^3 + 3(6 + 4q)p^2 + 3(-3 + 4q)v^2 \tag{42}$$

$$M_2\ddot{p} = 6(t + 6q + 2q^2)p - 27v^2 + 36p(p^2 + v^2) \tag{43}$$

$$M_3\ddot{v} = 6(t - 3q + 2q^2)v - 54pv + 36v(p^2 + v^2) \tag{44}$$

with the boundary conditions at $z=0$:

$$M_1\dot{q}(0) = -h + g_1 q(0) \tag{45}$$

$$M_2\dot{p}(0) = g_2 p(0) \tag{46}$$

$$M_3\dot{v}(0) = g_3 v(0). \tag{47}$$

If at $z=l$ the boundary conditions $Q_l = Q_b$ and $P_l = 0$ are chosen then

$$q_l = Q_b\left(1 - \frac{3}{2}\sin^2\theta_l\right) \tag{48}$$

$$p_l = \frac{1}{2}Q_b \sin^2\theta_l \tag{49}$$

$$v_l = \frac{1}{2}Q_b \sin 2\theta_l. \tag{50}$$

We focus our attention on the problem of the homeotropic–conical anchoring transition. First, we seek the limit of stability of the homeotropic anchoring. To do this, we assume that $q(z)$, $p(z)$, and $v(z)$ can be expanded in θ_l around $\theta_l = 0$ up to the second order as follows

$$q(z) \approx q^{(0)}(z) + q^{(2)}(z)\theta_l^2 \tag{51}$$

$$p(z) \approx p^{(2)}(z)\theta_l^2 \tag{52}$$

$$v(z) \approx v^{(1)}(z)\theta_l \tag{53}$$

with the boundary conditions at $z=l$: $q_l \approx Q_b(1-3\theta_l^2/2)$, $p_l \approx Q_b\theta_l^2/2$, and $v_l \approx Q_b\theta_l$. It can be shown that the contribution to the equilibrium free energy up to the second order in θ_l comes only from $q^{(0)}$ and $v^{(1)}$. The uniaxial solution $q^{(0)}(z)$ satisfies

$$M_1\ddot{q}^{(0)} = 2tq^{(0)} - 6[q^{(0)}]^2 + 4[q^{(0)}]^3 \tag{54}$$

with the boundary conditions: $M_1\dot{q}^{(0)}(0) = -h + g_1 q^{(0)}(0)$, $q^{(0)}(l) = Q_b$, and $v^{(1)}$ satisfies the linearized equation

$$M_3\ddot{v}^{(1)} = 6\{t - 3q^{(0)} + 2[q^{(0)}]^2\}v^{(1)} \tag{55}$$

with the boundary conditions: $M_3\dot{v}^{(1)}(0) = g_3 v^{(1)}(0)$, $v^{(1)}(l) = Q_b$. The expansion of the free energy in θ_l has the following simple form:

$$F \approx F^{(0)} + \frac{1}{2}M_3 Q_b \dot{v}^{(1)}(l)\theta_l^2 \tag{56}$$

and the loss of stability of the homeotropic anchoring occurs when $\dot{v}^{(1)}(l) = 0$. We have solved equation (55) numerically to find the bifurcation temperature t_{HC} as a function of l (see figure 1).

It is also of interest to find when the homeotropic alignment becomes unstable if the boundary condition $\theta_l = 0$ is assumed. This instability can be classified as a Fréedericksz transition [1], although in this particular case it is driven by changes of the temperature or the sample thickness, and not by a bulk external field.

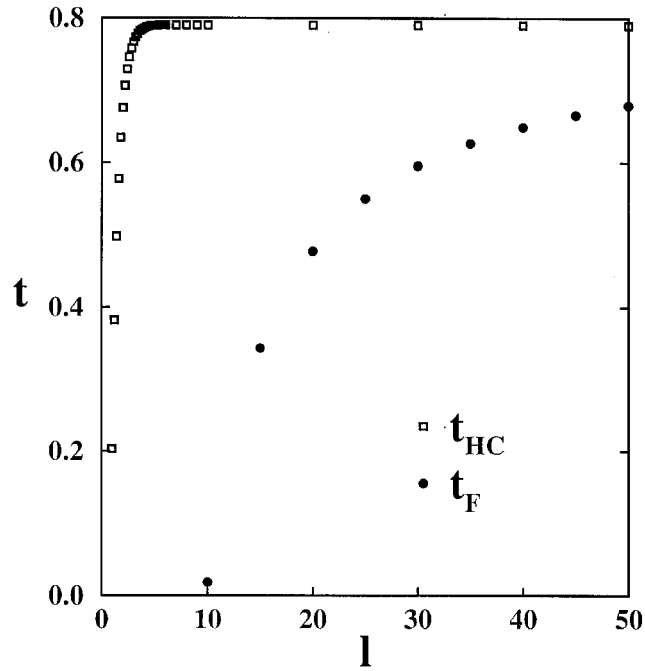

Figure 1. Temperatures of the homeotropic–conical transition t_{HC} (squares) and the Fréedericksz transition t_F (circles) as functions of the sample thickness l; results obtained from the birfurcation analysis.

Because of the elastic energy contribution, the nematic sample can remain homeotropic even though close to the substrate a tilted alignment is already favoured by the NLC–substrate interaction. The instability occurs when a non-zero solution of the linearized version of equation (44), which satisfies the boundary condition $v(l) = 0$, appears. In figure 1 we plot both t_{HC} and the temperature of the Fréedericksz transition t_F as functions of l. We have chosen the following surface parameters: $h \approx -0{\cdot}527$, $g_1 \approx 1{\cdot}792$, $g_2 = g_3 \approx 3{\cdot}162$, obtained from the surface parameters of ref. [17]: $c_1 = -0{\cdot}5$, $c_{2\eta} = 0{\cdot}85$, $c_{2\mu} = c_{2\nu} = 0{\cdot}5$, for which the homeotropic–conical transition is continuous. The two sets of surface parameters are related to each other as follows: $h = -c_1\xi_0$, $g_1 = 2c_{2\eta}\xi_0$, $g_2 = 6c_{2\mu}\xi_0$, $g_3 = 6c_{2\nu}\xi_0$, where $\xi_0 = [2/3 + (4/9)L_2/L_1]^{1/2}$ and $L_1 = L_2$ have been assumed. For large l, $t_{HC}(l)$ tends to the limiting value $t_{HC}(\infty) \approx 0{\cdot}7908$, which differs only slightly from the transition temperature found in ref. [17] for a particular value of l, not given by the authors, however. The bulk correlation length parallel to the director $\xi_\parallel \approx 0{\cdot}51$ at $t = t_{HC}(\infty)$. Larger deviations of $t_{HC}(l)$ from $t_{HC}(\infty)$ occur only when $l < 5$. In figure 2 we have plotted t_{HC} against $\exp[-l/\xi_\parallel(t_{HC})]$ to show an asymptotically linear relation between them. When $l \to \infty$ the temperature of the Fréedericksz transition tends to the same limit as $t_{HC}(l)$, albeit much more slowly. We have found

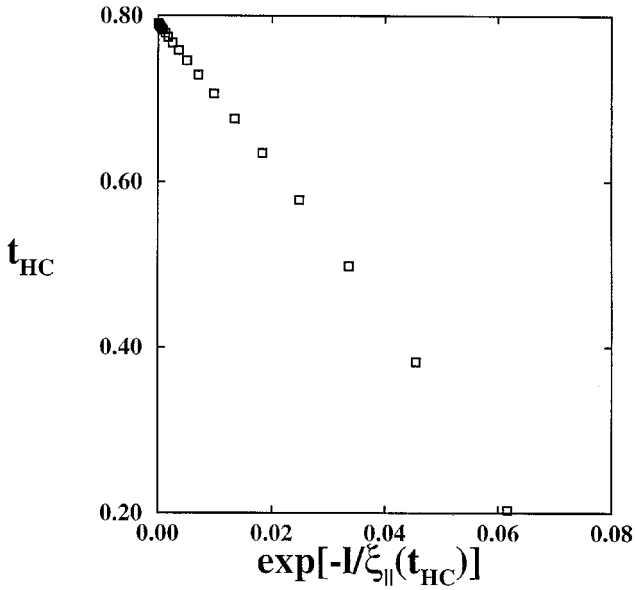

Figure 2. Temperature of the homeotropic–conical transition versus $\exp[-l/\xi_{\|}(t_{HC})]$; $\xi_{\|}$ denotes the bulk correlation length in the direction parallel to $\hat{\mathbf{n}}$.

that for large l the asymptotic relation $t_F(l) \sim 1/l$ holds, which is shown in figure 3.

4. Results

In the case of the conical anchoring, differential equations (42–44) for the components of $\mathbf{Q}$ can only be solved numerically. To do this, we have used a relaxation method for solving two point boundary value problems [28]. The boundary conditions at $z=0$ are given by

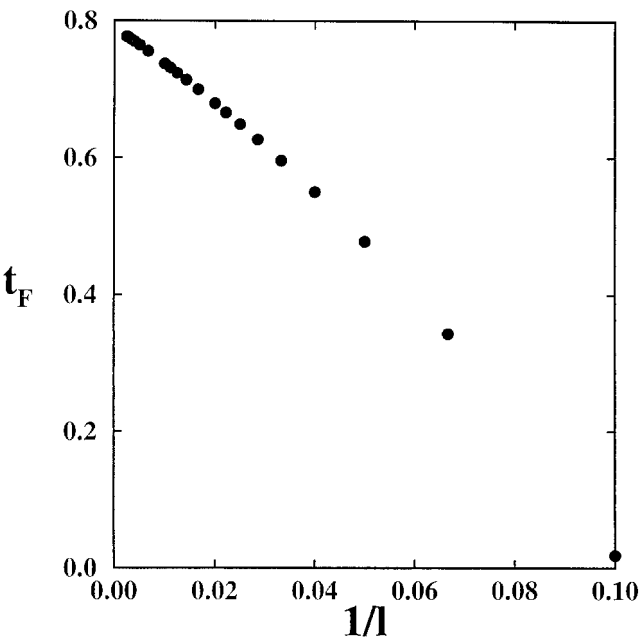

Figure 3. Temperature of the Fréedericksz transition versus $1/l$.

equations (45–47), and at $z=l$ we have assumed $Q(l)=P(l)=0$, $\theta(l)=\theta_l$, which for smaller values of l is more realistic than the bulk boundary conditions: $Q(l)=Q_b$, $P(l)=0$. To transform the boundary conditions at $z=l$ to the laboratory fixed frame, we use the relation between q, p, v and Q, P, θ:

$$q=\frac{1}{2}Q(3\cos^2\theta-1)+\frac{3}{2}P\sin^2\theta \tag{57}$$

$$p=P+\frac{1}{2}(Q-P)\sin^2\theta \tag{58}$$

$$v=\frac{1}{2}(Q-P)\sin 2\theta, \tag{59}$$

and hence we find the relation between $\dot{q}, \dot{p}, \dot{v}$ and $\dot{Q}, \dot{P}, \dot{\theta}$. Eliminating $\theta(l)$, $Q(l)$, and $P(l)$ we obtain the three boundary conditions at $z=l$:

$$\dot{q}(l)\cos 2\theta_l+\frac{3}{2}\dot{v}(l)\sin 2\theta_l=0 \tag{60}$$

$$\dot{p}(l)\cos 2\theta_l-\frac{1}{2}\dot{v}(l)\sin 2\theta_l=0 \tag{61}$$

$$[q(l)-p(l)]\sin 2\theta_l-2v(l)\cos 2\theta_l=0. \tag{62}$$

In all cases, as an input for the relaxation method, we have used constant profiles: $q(z)=(Q_b/2)(3\cos^2\theta_l-1)$, $p(z)=(Q_b/2)\sin^2\theta_l$, and $v(z)=(Q_b/2)\sin 2\theta_l$. The convergence of the method is very good as the number of iterations required to obtain the solution with an acccuracy $\sim 10^{-7}$ has been smaller than 20. We have been solving the Euler–Lagrange equations for various values of t and l assuming the same surface parameters as in ref. [17] and $L_1=L_2$.

In figure 4 we plot the equilibrium free energy $F(\theta_l)$ (for simplicity the dependence on l and t has been suppressed), for $l=50$ and $t=0{\cdot}6$. This is well below the Fréedericksz transition at $t_F(50)\approx 0{\cdot}68$ obtained from the bifurcation analysis. Since $F(-\theta_l)=F(\theta_l)$, only the branch with $\theta_l \geqslant 0$ is shown. The minimum of $F(\theta_l)$ corresponds to the equilibrium tilt angle, and at $\theta_l=0$ there is a local maximum in the form of a cusp. At $\theta_l=0$ there are three solutions of the Euler–Lagrange equations: the uniaxial solution $p(z)=v(z)=0$, with the free energy $F^*(0)$, and two solutions with a distorted director field, corresponding to the equilibrium free energy $F(0)$. The equilibrium solutions differ only in the sign of $v(z)$. The uniaxial solution belongs to the unstable branch of the free energy (not shown in figure 4); hence $F^*(0)>F(0)$. Occasionally, our numerical procedure has converged to a solution belonging to the metastable branch of F, which is the analytic continuation of $F(\theta_l)$ into the region of $\theta_l<0$. For $t_F<t<t_{HC}$, the metastable and unstable branches of $F(\theta_l)$ disappear and the free

energy of the uniaxial solution is equal to $F(0)$. An example of such a behaviour is shown in figure 5 for a temperature slightly above t_F. In figures 4 and 5 we have restricted the range of θ_l to 30° to show the shape of $F(\theta_l)$ in the vicinity of $\theta_l = 0$ in more detail; otherwise $F(\theta_l)$ would appear very flat for $0 < \theta_l < \theta_{min}$. We note that $F^*(\theta_l = 90°)$ obtained from the solution of the Euler–Lagrange equations with $v(z) = 0$ also differs from the equilibrium value $F(90°)$, and the difference is much larger than in the previous case. By analogy, we can expect that for a suitable choice of parameters a Fréedericksz transition at $\theta_l = 90°$ could be observed. We have not studied this problem, however.

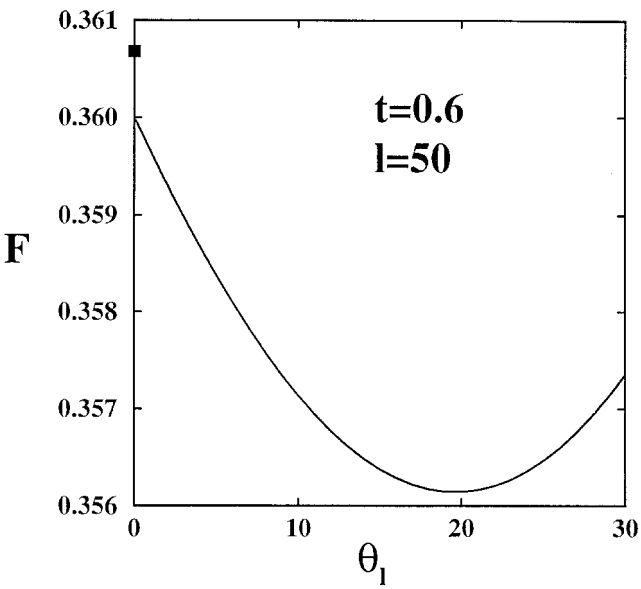

Figure 4. Free energy as a function of θ_l for $l = 50$; $t = 0{\cdot}6$ is below the Fréedericksz transition. The square corresponds to the unstable uniaxial solution of the Euler–Lagrange equations.

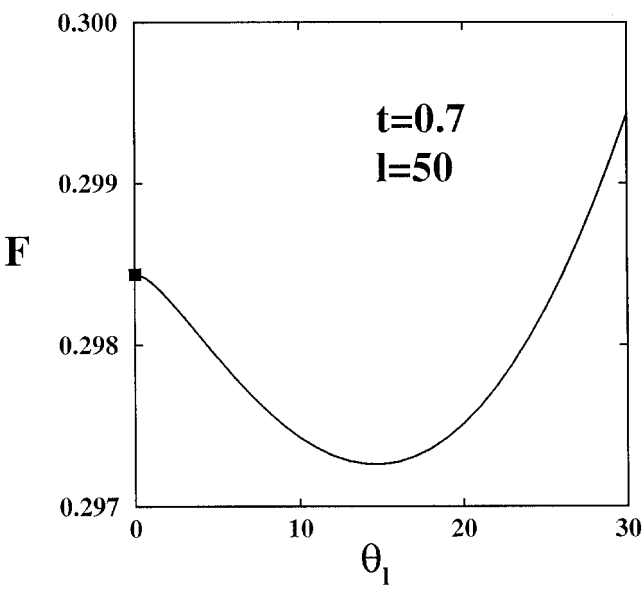

Figure 5. Free energy as a function of θ_l for $l = 50$; $t = 0{\cdot}7$ is slightly above the Fréedericksz transition. The uniaxial solution (square) belongs to the stable branch of $F(\theta_l)$.

In figure 6 we plot $\theta_0 = \theta(z = 0)$ against θ_l for two temperatures: below and above t_F. For $t < t_F$, the function $\theta_0(\theta_l)$ is discontinuous at $\theta_l = 0$, which is an indication of a first order transition between the states $\theta_0(0^+)$ and $\theta_0(0^-)$. At $t = t_F$ the discontinuity disappears, and for $t > t_F$, θ_0 goes smoothly through zero. Here θ_l plays a similar role to an external field, and $t = t_F$, $\theta_l = 0$ is the critical point in the (t, θ_l) plane.

We have also calculated the second derivative of F with respect to θ_l using the cubic spline interpolation. In figure 7 (*a*) to 7 (*c*) we plot $\alpha_{min}(l)$ and $\alpha_0(l)$, defined as $K(\partial^2 F/\partial\theta_l^2)^{-1}$ at the minimum and at $\theta_l = 0$, respectively, for $t = 0{\cdot}6$, $0{\cdot}785$, $0{\cdot}789$, and $5 \leqslant l \leqslant 50$. In all cases the function $\alpha_{min}(l) = l + \bar{b}(l)$ is linear with the unit slope, in accord with equation (19), even for temperatures very close to t_{HC}. In the case of α_0 we have also found a linear dependence on l, but very close to t_{HC} the slope slightly deviates from unity. For $t = 0{\cdot}6$ (see figure 7 (*a*)), $\alpha_0(l) = 0$ at $l \approx 30$. This corresponds to the Fréedericksz transition, at which $(\partial^2 F/\partial\theta_l^2)(0)$ diverges. We have not shown $\alpha_0(l)$ on the other side of the Fréedericksz transition, as the calculation of $(\partial^2 F/\partial\theta_l^2)(0)$ with the help of the spline interpolation is less reliable in this case because of the cusp (see figure 4).

To find the behaviour of the anchoring energy in the

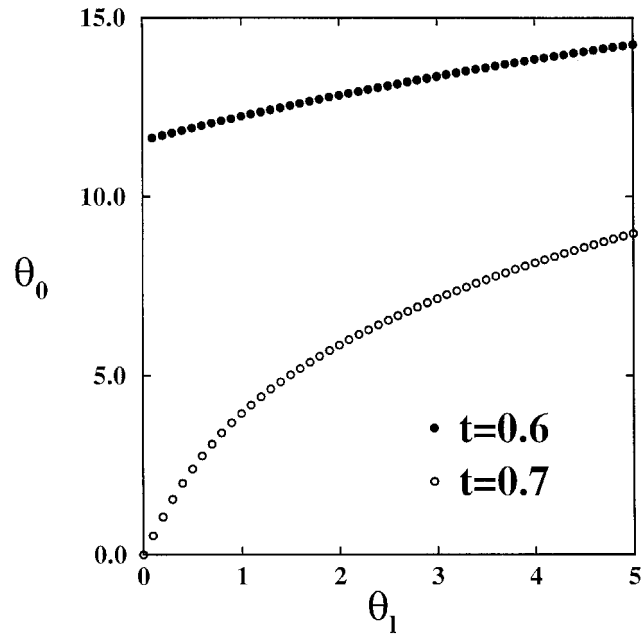

Figure 6. Orientation of the director at the substrate θ_0 versus θ_l below ($t = 0{\cdot}6$) and above ($t = 0{\cdot}7$) the Fréedericksz transition, for $l = 50$.

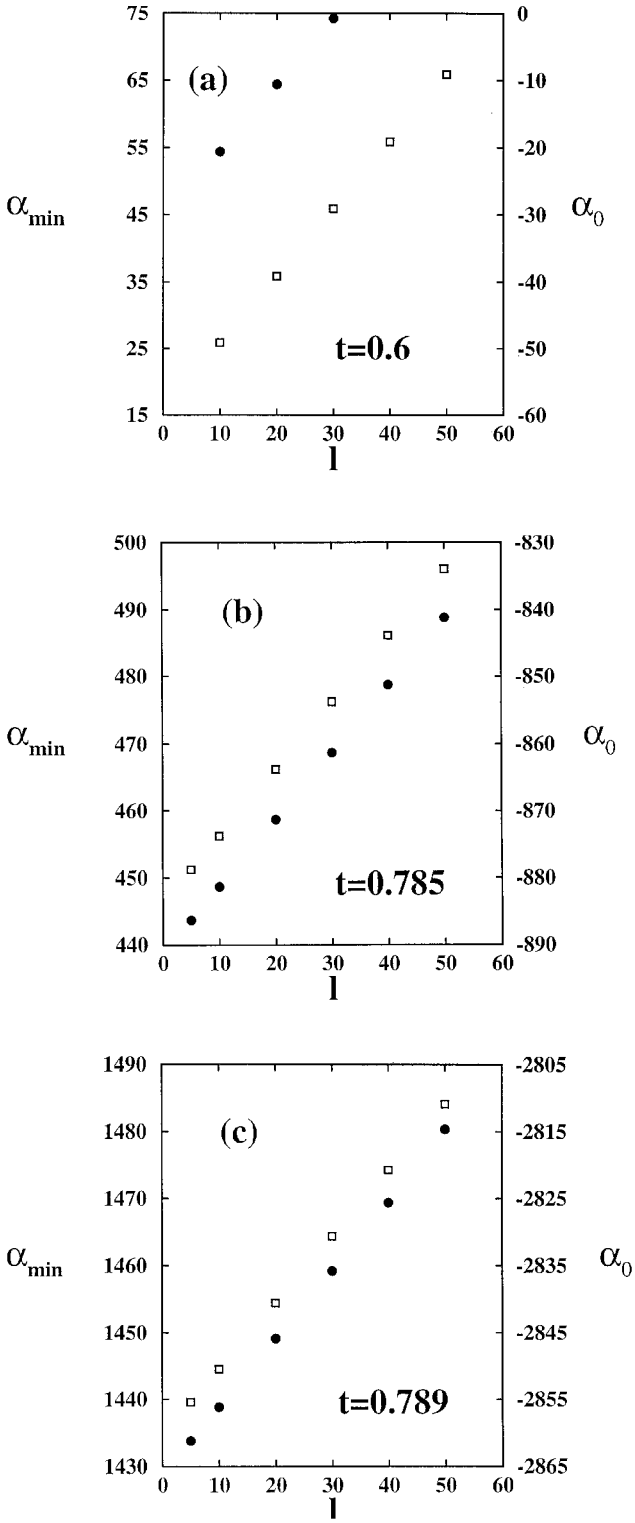

Figure 7. $K(\partial^2 F/\partial\theta_l^2)^{-1}$ as a function of l; $\alpha_{\min}=l+\bar{b}$ (squares) and α_0 (circles) correspond to $\theta_l=\theta_{\min}$ and $\theta_l=0$, respectively: (*a*) $t=0{\cdot}6$, (*b*) $t=0{\cdot}785$, (*c*) $t=0{\cdot}789$.

vicinity of the homeotropic–conical anchoring transition, we first define

$$u=\frac{\partial^2 F}{\partial\theta_l^2}\left(1-\frac{l}{K}\frac{\partial^2 F}{\partial\theta_l^2}\right)^{-1}, \tag{63}$$

hence $u_{\min}=u(\theta_{\min})=\bar{w}$ (see equation (19)) and $u_0=u(0)$. Both $u_{\min}$ and u_0 as functions of t are plotted in figure 8, for $l=10$. In the range of temperatures shown in figure 8 the dependence on t is approximately linear. At $t=t_{\mathrm{HC}}$ both $u_{\min}$ and u_0 are equal to zero, but u_0 changes sign at the transition, whereas $u_{\min}\geqslant 0$. The ratio of the slopes of $u_{\min}$ and u_0 is approximately -2.

The results presented above can be qualitatively explained by means of the phenomenological model considered in § 2. In the case of $K_1=K_3=K$ we have

$$F(\theta_0,\theta_l,l)=\frac{K}{2l}(\theta_l-\theta_0)^2+w_2\theta_0^2+w_4\theta_0^4, \tag{64}$$

where we have assumed a specific form of $f_s(\theta_0)$ with $w_4>0$ and w_2 changing sign at the homeotropic–conical transition. The minimization of F with respect to θ_0 at constant θ_l gives

$$\left(2w_2+\frac{K}{l}\right)\theta_0+4w_4\theta_0^3=\frac{K}{l}\theta_l. \tag{65}$$

The global minimum of F occurs at $\theta_0=\theta_l=\theta_a$, where θ_a is the minimum of f_s independently of l. Also in the Landau–de Gennes model $\theta_{\min}$ is approximately constant provided that $l\gg\xi_{\parallel}$. For $\theta_l=0$, the Fréedericksz

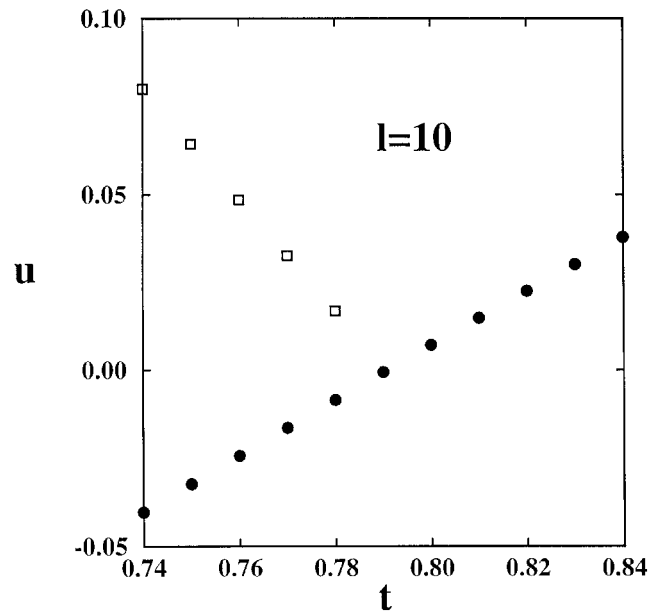

Figure 8. $u=(\partial^2 F/\partial\theta_l^2)[1-(l/K)(\partial^2 F/\partial\theta_l^2)]^{-1}$ versus temperature in the vicinity of the homeotropic–conical transition, for $\theta_l=\theta_{\min}$ (squares) and $\theta_l=0$ (circles); $\theta_{\min}=0$ above t_{HC}.

transition occurs when $2w_2 + K/l = 0$. Then we calculate the second derivative of the function $F[\theta_0(\theta_l, l), \theta_l, l]$ with respect to θ_l at the minimum and $\theta_l = 0$, respectively. This gives

$$\frac{\partial^2 F}{\partial \theta_l^2}(\theta_a) = \begin{cases} K(l + K/2w_2)^{-1} & \text{if } w_2 > 0 \\ K(l - K/4w_2)^{-1} & \text{if } w_2 < 0 \end{cases} \tag{66}$$

and

$$\frac{\partial^2 F}{\partial \theta_l^2}(0) = \begin{cases} K(l + K/2w_2)^{-1} & \text{if } l + K/2w_2 < 0 \\ K(1 + 3K/4w_2 l)(l + K/2w_2)^{-1} & \\ & \text{if } l + K/2w_2 > 0 \end{cases}, \tag{67}$$

which means that at the Fréedericksz transition $(\partial^2 F/\partial\theta_l^2)(0)$ diverges. Since at the Fréedericksz transition $1 + 3K/4w_2 l = -1/2$, $(\partial^2 F/\partial\theta_l^2)(0) < 0$ above and directly below the Fréedericksz transition, and it changes sign at $w_2 = -3K/4l$. Using the definition of u we find that

$$u_{\min} = \begin{cases} 2w_2 & \text{if } w_2 > 0 \\ -4w_2 & \text{if } w_2 < 0 \end{cases} \tag{68}$$

and

$$u_0 = \begin{cases} 2w_2 & \text{if } l + K/2w_2 < 0 \\ -(4w_2 + 3K/l) & \text{if } l + K/2w_2 > 0 \end{cases}, \tag{69}$$

which explains the behaviour of u in the vicinity of the homeotropic–conical transition shown in figure 8. It follows from equations (66) and (67) that the slopes of $\alpha_{\min}$ and α_0 are the same in the limit of $l \to \infty$. Equation (67) also predicts that above the Fréedericksz transition α_0 is a linear function of l with unit slope. The difference between the two slopes shown in figure 7(*c*) is too small to draw any definite conclusions. However, it suggests that for l above the Fréedericksz transition the dependence of α_0 on l may differ from that predicted by equation (67). This point requires further investigation.

Finally, we find that at the Fréedericksz transition:

$$F = K\frac{\theta_l^2}{2l} - 3w_4^{-1/3}\left(\frac{K\theta_l}{4l}\right)^{4/3}, \tag{70}$$

which is non-analytic at $\theta_l = 0$.

5. Discussion

We have studied the polar anchoring in the NCL–amorphous substrate system and proposed thermodynamic definitions of the surface director, the surface tension and the anchoring strength. It follows from these definitions that γ as a function of the surface director $\tilde{\mathbf{n}}_0$ can be defined only locally in some neighbourhood of the anchoring direction. The range of accessible orientations of $\tilde{\mathbf{n}}_0$ depends on l and it reduces to the anchoring direction when $l \to \infty$. The anchoring strength can be defined by means of the anchoring energy coefficient or the extrapolation length. The latter appears most naturally in the asymptotic expansion of the excess grand-canonical potential for $l \to \infty$, and we have argued that it must be the same as the extrapolation length introduced by de Gennes [1] by means of the asymptotic behaviour of the director field. Since the surface excess part of Ω is uniquely defined, the definition of the extrapolation length is also unique. This is in some contrast with the approach used by Yokoyama [3], who defines various surface quantities with respect to an arbitrary dividing surface; thus, the surface tension and the anchoring strength are meaningful only in relation to that surface. From the experimental point of view this approach turns out to be convenient. Indeed, in experiment one measures some response of the system, e.g. the optical phase retardation, to the given stimulus. Then the result of measurement is interpreted in terms of the theoretical response calculated for the ideal system, i.e. for the NLC which is bulk-like between the dividing surfaces. However, there always exists some ambiguity in the location of the dividing surface, because of the unknown interfacial structure. On the other hand, the problem of ambiguity of the extrapolation length does not appear on the conceptual level, at least as long as the surface is flat and smooth. Then the distance from the solid substrate is a well defined thermodynamic variable, and a thermodynamically consistent definition of the extrapolation length should refer to the physical surface of the substrate.

In our studies we have considered explicitly only a single NLC–substrate interface. The surface $z = l$, where the orientation of the director can be controlled, has a sense of a mathematical surface which does not modify the NLC structure. If there is another substrate at $z = l$ we can easily extend our analysis by introducing a mathematical surface at $z = l/2$. The total ω is a sum of the two contributions from both interfaces and in the equilibrium it has to be minimal. We find that for large l it is given by the asymptotic expression

$$\omega = \frac{1}{2[l + b^{(1)} + b^{(2)}]}\left\{\int_{\theta_a^{(1)}}^{\theta_a^{(2)}} [K(\theta)]^{1/2} \mathrm{d}\theta\right\}^2, \tag{71}$$

where $\theta_a^{(1)}$, $b^{(1)}$ and $\theta_a^{(2)}$, $b^{(2)}$ correspond to $z = 0$ and $z = l$, respectively. $\partial\omega/\partial l$ is related to the disjoining pressure, which has been measured in the case of simple fluids [29].

We have applied the general formalism to study the Landau–de Gennes model of the NLC–substrate interface. Even very close to a continuous homeotropic–

conical transition the asymptotic formula for the free energy holds. However, the function $b_e(\theta_l, l)$ can be approximated by its limiting value for $l \to \infty$ only if l is sufficiently above the value at which the Fréedericksz transition at the given temperature occurs. The phenomenological model considered in § 4 (see equation (64)) predicts the Fréedericksz transition at $l = 2b$, where $b = -K/(4w_2)$ and $w_2 < 0$. For l below the Fréedericksz transition the dependence of b_e on θ_l becomes important, especially when $\theta_l \to 0$. Thus, for temperatures close to t_{HC}, the asymptotic relation $b_e(\theta_l, l) \approx b$ is satisfied only if l is very large, and eventually $l \to \infty$ when $t \to t_{HC}^-$. On the other hand, the convergence of $\bar{b}(l)$ to b is rather fast, and for l fixed and $t \to t_{HC}(l)$, $\bar{b} \to \infty$. This means that the anchoring energy coefficient vanishes at a continuous homeotropic–conical transition.

In our studies of the Landau–de Gennes model we have considered only the case of a positive extrapolation length. Certainly it must be positive and large in the vicinity of a continuous anchoring transition. However, far from the transition, negative values are also possible. We think that the case of a negative extrapolation length might be interesting, since it cannot be studied by means of the phenomenological model introduced in § 2, and requires a different approach. We defer studies of this problem to a future work.

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