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Shape of the nematic–isotropic interface in conditions of partial wetting†

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A nematic liquid crystal in contact with a solid substrate is studied in the partial wetting regime. Both a mesoscopic Landau–de Gennes theory and a macroscopic effective interface Hamiltonian approach are considered. A generalized Young equation for the balance of forces at the three-phase contact line is derived, which takes into account corrections due to distortions of the nematic director field. It is also shown that the asymptotic form of the separation of the nematic–isotropic interface from the substrate has a logarithmic correction to the usual linear behaviour. The characteristic length scale of this correction is given by the ratio $K/(2\sigma_{NI})$, where K and σ_{NI} are the average elastic constant and the nematic–isotropic surface tension, respectively, and is of the order of a few hundred angstroms. Then, a simple form of an effective interface Hamiltonian is proposed, and results consistent with the predictions of the Landau–de Gennes theory are obtained. It is shown, in the framework of this macroscopic approach, that the line tension associated with the contact line remains finite, when the thermodynamic limit is taken, if the anchoring at both the nematic–substrate and the nematic–isotropic interfaces is homeotropic. However, in the case of different anchoring directions, the line tension diverges logarithmically with the system size.

1. Introduction

Liquid crystals can be oriented by surfaces, and this well known phenomenon is called anchoring [1]. Although anchoring is a surface phenomenon, in the absence of bulk external fields it is responsible for the orientation of liquid crystal molecules far from the surface. A comprehensive review of anchoring in liquid crystals can be found in [2]. Wetting is another well known surface phenomenon [3–6]. It can be observed in very different systems such as simple and complex fluids, mixtures, and solids. In contrast, orientational anchoring is specific to liquid crystals. Recently there has been growing interest in the relation between anchoring and wetting in liquid crystal systems [7–10]. For instance, Vandenbrouck *et al.* [8] observed a divergence of the extrapolation length, which is related to the anchoring strength, in 5CB drops on silicon wafers close to the nematic–isotropic transition. Rodriguez-Ponce *et al.* [9] showed that an anchoring transition between states with planar and homeotropic director configurations may play the role of a prewetting transition in the regime of complete wetting of the substrate by the nematic phase. On the experimental side, Alkhairalla *et al.* [10] studied anchoring and orientational wetting of a nematic substance at the interface with a series of self-assembled monolayers using an evanescent wave ellipsometric technique.

Compared with simple fluids, wetting in nematic liquid crystals is more complex due to possible competition between different anchoring favoured by the nematic–substrate and the nematic–isotropic interfaces. This may lead to a transition between two nematic wetting phases, one of which is uniform and the other has a distorted direction configuration [11]. In the case of partial wetting, the nematic–isotropic interface is tilted with respect to the substrate, and the director field is usually distorted, even if both interfaces favour the same type of anchoring.

The excess free energy of the inhomogeneous region in the neighbourhood of the three-phase contact line is known as the line tension [12]. The line tension in simple fluid systems has been studied by several authors (see for instance [13] and references therein). An interesting question arises concerning the existence of the line tension in the thermodynamic limit, and about its behaviour when the transition from partial to complete wetting is approached. In early work, these problems were studied mainly by means of a mesoscopic

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theory, which assumes that the free energy is a functional of some order parameter field defined at each point of the system, that is, both in the interfacial regions and in the bulk [14, 15]. Later, Indekeu [16, 13] developed a macroscopic approach, the so-called interface displacement model, which is equivalent to de Gennes' approach [3]. In contrast to earlier work, the only quantity of interest in this model is the separation, l, of a two fluid-phase interface from a solid substrate, as a function of the distance from the three-phase contact line. The excess free energy due to the presence of the contact line is postulated to be a functional of l, and its minimum corresponds to the equilibrium line tension. A formal derivation of an effective interface Hamiltonian for a pinned interface has been proposed by several authors (for a recent version see, e.g., Rejmer and Napiórkowski [17]). To the best of our knowledge, an approach analogous to the interface displacement model has not yet been formulated for liquid crystal systems. We note, however, a paper by Sullivan and Lipowsky [18], who considered an effective potential for a pinned nematic–isotropic interface to study a nematic wetting layer. A similar approach was also applied by Sluckin and Poniewierski [19] to study a wetting Fréedericksz transition.

In this paper, we consider a nematic liquid crystal in contact with a solid substrate, and for the nematic–isotropic coexistence. It is assumed that partial wetting of the substrate by the nematic phase occurs. We are interested in the effect of long range elastic forces and the anisotropy on: (1) the local tilt angle of the nematic–isotropic interface, (2) the shape of the nematic–isotropic interface, and (3) the line tension. In § 2 we study the first two points, whereas the third point is discussed in § 3, where we apply a macroscopic approach.

First, we study the system by means of the Landau–de Gennes theory (mesoscopic approach) [1, 6, 20]. We follow the method of Kerins and Boiteux [21], who studied an inhomogeneous c-component fluid by means of the van der Waals theory. They derived an exact formula for the equilibrium line tension in the case of a three-phase coexistence, by applying Noether's theorem. They also used Noether's theorem to present an elegant derivation of the Neumann-triangle conditions for the balance of forces at the contact line. Here, we follow this route and derive the condition for the balance of forces at the nematic–isotropic–substrate contact line, which can be considered as a generalized Young equation. It provides a relation between the local tilt angle of the nematic–isotropic interface and the distance from the contact line. When the distance from the contact line tends to infinity, the local tilt angle approaches the contact angle, and the original Young equation is recovered. However, the presence of distortions in the nematic director field influences the condition for the local tilt angle as well as the shape of the nematic–isotropic interface.

In very recent work, Rey [22, 23] has derived the Neumann and Young equations for nematic contact lines. The first equation corresponds to a three fluid-phase coexistence, when one of the phases is nematic, whereas the second corresponds to nematic–isotropic coexistence in the presence of a solid substrate. The force balance equations are expressed in terms of the surface stress tensor. It is argued that this is a 2×3 tensor, given by the sum of the tension and the bending contributions. The bending stresses result in forces normal to the interface. Using a different approach, we derive the force balance equation, which also contains a contribution from the force normal to the nematic–isotropic interface, in agreement with Rey's result. However, our generalized Young equation contains a contribution from the bulk elastic forces too, but this contribution does not appear in the force balance equation derived by Rey. We argue that the bulk contribution is of the same order as the interfacial contribution due to the bending stress, and therefore it should not be neglected.

The paper is organized as follows. In § 2 we first recall the Landau–de Gennes theory and define the free energy functional. Then, we introduce the stress tensor and derive the force balance equation by the application of Noether's theorem. In § 2.3 we derive asymptotic formulae for the local tilt angle and for the position of the nematic–isotropic interface as functions of the distance from the contact line. In § 2.4 we define the line tension and recall the Kerins–Boiteux formula for the line tension derived in the framework of the van der Waals theory [21]. In § 3 we postulate a simple version of the effective nematic–isotropic interface Hamiltonian, in the spirit of the interface displacement model. We show that this macroscopic approach is consistent with the results derived in the framework of the Landau–de Gennes theory. We also calculate the line tension. Finally, § 4 is devoted to the discussion. Mathematical details are presented in Appendices I and II.

2. The Young equation

Let us consider a macroscopic portion of the nematic phase in coexistence with the isotropic phase, and in contact with a solid substrate; that is, we assume partial wetting of the substrate by the nematic phase. We choose the z axis of the coordinate system normal to the substrate. When the nematic drop is large (its size tends to infinity) the nematic–isotropic–substrate contact line can be considered as a straight line. Then the system

is translationally invariant in the direction parallel to the contact line, which we choose to be the y axis. The distance from the contact line is measured along the x axis, and the limit $x \to -\infty$ corresponds to a single isotropic–substrate (IS) interface, whereas the limit $x \to \infty$ corresponds to two infinitely remote interfaces: the nematic–substrate (NS) interface and the nematic–isotropic (NI) interface. Finally, the limit $z \to \infty$ corresponds to the bulk isotropic phase. Thus, we consider the geometry of a liquid wedge, rather than a drop, which is shown in figure 1.

The contact angle, α_c, is related to the three surface tensions: σ_{IS}, σ_{NS}, and σ_{NI} by the Young equation

$$\sigma_{IS} = \sigma_{NS} + \sigma_{NI} \cos \alpha_c. \tag{1}$$

In the case of partial wetting by the nematic phase $0 < \alpha_c < \pi/2$. The surface tensions in equation (1) correspond to flat interfaces considered separately, in the absence of external fields. In general, σ_{NS} and σ_{NI} are functions of the nematic director $\hat{\mathbf{n}}$ defined at the Gibbs dividing surface [2, 24, 25], which separates the interfacial region from the bulk. We do not show this dependence explicitly, however. The values of σ_{NS} and σ_{NI} that appear in equation (1) correspond to the anchoring directions at the NS interface and the NI interface, respectively. We recall that the anchoring direction induced by an interface between the nematic phase and another phase minimizes the surface tension of that interface [1, 2]. In the vicinity of the contact line, the local angle at which the NI interface is tilted with respect to the x axis differs from α_c. This local tilt angle, denoted α, is a function of the distance from the contact line, and it approaches α_c when $x \to \infty$. In general, the orientations of $\hat{\mathbf{n}}$ at the NS and at the NI interfaces can be different, even if both interfaces favour the same type of anchoring. This means that there is some elastic energy associated with distortions of $\hat{\mathbf{n}}$, which decreases in a manner inversely proportional to the distance of the NI interface from the substrate. Because of this slow decay of the elastic energy, we expect it to affect the condition for the local tilt angle. Our aim is now to derive a generalized Young equation, which can be considered as a condition for α at a finite distance from the contact line.

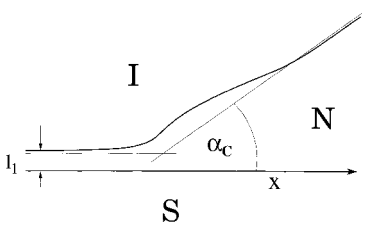

Figure 1. Schematic picture of the liquid wedge geometry considered in this paper. I, N, and S denote the isotropic phase, the nematic phase, and the substrate, respectively, and α_c denotes the contact angle. l_1 is the thickness of a nematic-like thin film adsorbed at the isotropic–substrate interface.

2.1. *The Landau–de Gennes model*

To describe the system on a mesoscopic scale we use the Landau–de Gennes theory of non-uniform nematic liquid crystals. This means that we neglect the density changes, and assume that the only relevant variable is the nematic order parameter $\mathbf{Q}$, a second rank, traceless and symmetric tensor [1]. In general, $\mathbf{Q}$ has five independent components, which can be chosen to be $q = Q_{zz}$, $p = 1/2(Q_{xx} - Q_{yy})$, Q_{xy}, Q_{xz} and Q_{yz}. The number of independent components is reduced if there are some symmetries in the system. For instance, in the case of mirror symmetry $y \mapsto -y$, $Q_{xy} = Q_{yz} = 0$, and only three independent components remain.

The free energy density, f, has two contributions: the Landau free energy of a uniform system, f_L, which must describe the nematic–isotropic coexistence, and the contribution due to spatial non-uniformities, f_G, which has a square-gradient form. Thus, we have

$$f = f_L + f_G \tag{2a}$$

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

$$f_G = \frac{1}{2}(L_1 \partial_k Q_{ij} \partial_k Q_{ij} + L_2 \partial_j Q_{ij} \partial_k Q_{ik} + L_3 \partial_k Q_{ij} \partial_j Q_{ik}) \tag{2c}$$

where the indices run over x, y, z, $\partial_k = \partial/\partial r_k$, and the summation convention is assumed. A is proportional to the temperature difference $T - T^*$, where T^* denotes the limit of stability of the isotropic phase, and B and C, together with the elastic constants L_1, L_2 and L_3, are temperature independent material constants. The last two invariants in equation (2c) differ only by a divergence term, which means that L_2 and L_3 enter the Euler–Lagrange equations as the sum $L_2 + L_3$. In the bulk nematic phase, $\mathbf{Q} = Q_b(3/2\, \hat{\mathbf{n}}\hat{\mathbf{n}} - 1/2\, \mathbf{I})$, where Q_b is the bulk value of the main nematic order parameter Q, and $\mathbf{I}$ denotes the unit tensor. When substituted in equation (2c), this uniaxial approximation for $\mathbf{Q}$ leads to the Frank elastic free energy with the elastic constants: $K_1 = K_3 = (3/2\, Q_b)^2(2L_1 + L_2 + L_3)$ and $K_2 = 2(3/2\, Q_b)^2 L_1$.

The orientation of $\hat{\mathbf{n}}$ at the NI interface depends on the sign of $L_2 + L_3$. When $L_2 + L_3 > 0$ the parallel anchoring is stable, whereas $L_2 + L_3 < 0$ favours homeotropic anchoring. These are the only stable configurations in the Landau–de Gennes theory [26]. Note that in the latter case $K_2 > K_1 = K_3$.

The interaction of the liquid crystal with the solid substrate is mimicked by a surface free energy density $f_s(\mathbf{Q}_0)$, where $\mathbf{Q}_0 = \mathbf{Q}(x, z = 0)$ [6, 20]. The simplest

choice for f_s is $f_s = -h_1(\mathbf{Q}_0)_{zz}$, where h_1 denotes the surface field. When $h_1 > 0$ the NS interface favours homeotropic anchoring, whereas $h_1 < 0$ corresponds to planar anchoring. Conical anchoring can be realized too, provided that f_s also contains quadratic terms in $\mathbf{Q}_0$ [6]. However, for our present purpose the exact form of f_s is not required.

The free energy functional per unit length of the contact line of length $\mathscr{L}$ is given by

$$F_V[\mathbf{Q}]/\mathscr{L} = \int_{\mathscr{A}} \mathrm{d}x\,\mathrm{d}z[f(\mathbf{Q}, \nabla\mathbf{Q}) + \delta(z) f_s(\mathbf{Q})] \quad (3)$$

where $\mathscr{A}$ is a large but finite domain in the xz plane, V is the volume occupied by the system, and $\delta(z)$ is the Dirac delta function. The shape of $\mathscr{A}$ will be specified later. Formally, we can minimize $F_V[\mathbf{Q}]$ as if all nine components of $\mathbf{Q}$ were independent. The constraints: $\mathrm{tr}\,\mathbf{Q} = 0$ and $Q_{ij} = Q_{ji}$ are taken into account by the Lagrange multipliers $\Lambda_{ij} = \lambda_0\delta_{ij} - \varepsilon_{ijk}\lambda_k$, where δ_{ij} is the Kronecker delta and ε_{ijk} is the fully antisymmetric tensor [27]. This leads to the Euler–Lagrange equations

$$\partial_k \frac{\partial f}{\partial \partial_k Q_{ij}} - \frac{\partial f}{\partial Q_{ij}} = \Lambda_{ij} \quad (4)$$

with the boundary condition at $z = 0$:

$$\frac{\partial f}{\partial \partial_z Q_{ij}} - \frac{\partial f_s}{\partial Q_{ij}} = \Lambda^s_{ij} \quad (5)$$

where $\Lambda^s_{ij} = \lambda^s_0\delta_{ij} - \varepsilon_{ijk}\lambda^s_k$ are the Lagrange multipliers for $\mathbf{Q}_0$. We assume that $\mathbf{Q}$ is fixed on the remaining boundaries of $\mathscr{A}$.

2.2. *Stress tensor and the force balance equation*

We assume that the substrate is homogeneous. Therefore, the system must be invariant with respect to translations of the contact line in the x direction. According to Noether's theorem [21, 28] (see Appendix I) the two-dimensional field (H_x, H_z), where

$$H_x = f - \frac{\partial f}{\partial \partial_x Q_{ij}} \partial_x Q_{ij} \quad (6\,a)$$

$$H_z = -\frac{\partial f}{\partial \partial_z Q_{ij}} \partial_x Q_{ij} \quad (6\,b)$$

has a vanishing divergence,

$$\partial_x H_x + \partial_z H_z = 0 \quad (7)$$

provided that $\mathbf{Q}$ satisfies the Euler–Lagrange equations. For our purpose, it is convenient to consider H_x and H_z as components of a second rank tensor, defined as follows

$$\Sigma^e_{kl} = f\delta_{kl} - \frac{\partial f}{\partial \partial_k Q_{ij}} \partial_l Q_{ij}. \quad (8)$$

In general, $\mathbf{\Sigma}^e$ is not symmetric. Let us consider a small deformation: $\mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r})$, and assume that the order parameter does not change, i.e. $\mathbf{Q}'(\mathbf{r}') = \mathbf{Q}(\mathbf{r})$. Keeping only linear terms in $\mathbf{u}$ we find

$$\Delta F_V[\mathbf{Q}] = F_{V'}[\mathbf{Q}'] - F_V[\mathbf{Q}] = \int_V \mathrm{d}^3 r\, \Sigma^e_{kl}(\mathbf{r}) \partial_k u_l(\mathbf{r}) \quad (9)$$

which shows that $\mathbf{\Sigma}^e$ is the stress tensor. It is easy to recognize $\mathbf{\Sigma}^e$ as a generalization of the Ericksen stress tensor [1] to the case where both the director and the order parameters can vary in space. The latter is defined as follows: $\sigma^e_{kl} = \sigma^d_{kl} - p\delta_{kl}$, where $\sigma^d_{kl} = -[\partial f_d/\partial(\partial_k \hat{n}_i)]\partial_l \hat{n}_i$ is the distortion stress tensor, f_d is the Frank distortion free energy, and $p = -f_d + const$ is the pressure (here we prefer to use the symbol $\mathbf{\Sigma}^e$ for the Ericksen stress tensor to avoid confusion with the surface tension). Far from the interfacial regions, in a distorted bulk nematic phase, $\mathbf{\Sigma}^e$ reduces to the usual Ericksen stress tensor. We note that a constant term in the definition of p, playing the role of a Lagrange multiplier [1], does not appear in our expression for $\mathbf{\Sigma}^e$ since we do not fix the volume of the nematic drop. This is justified as long as we consider the vicinity of the contact line, where we may ignore gravitational forces, as well as the macroscopic pressure difference [3].

Comparing equation (6) with (8) we find that $H_x = \Sigma^e_{xx}$ and $H_z = \Sigma^e_{zx}$, hence, equation (7) can be expressed in the usual form of the hydrostatic equilibrium condition in the x direction:

$$\partial_x \Sigma^e_{xx} + \partial_z \Sigma^e_{zx} = 0. \quad (10)$$

We note that $\partial_x \Sigma^e_{xz} + \partial_z \Sigma^e_{zz} = 0$ also holds if $\mathbf{Q}$ satisfies the Euler–Lagrange equations, although the translational symmetry in the z direction is broken by the presence of the substrate. In this case, however, it is not the full hydrostatic equilibrium condition in the z direction, as it does not take into account the liquid crystal–substrate interaction potential. In the Landau–de Gennes theory, this potential is singular since it contains the Dirac delta function $\delta(z)$; see equation (3).

It results from the definition of $\mathbf{\Sigma}^e$ that the nematic–isotropic surface tension for a single NI interface, tilted with respect to the x axis, is related to the component $\Sigma^e_{x'x'} = f$ as follows

$$\sigma_{NI} = \int_{z'_{min}}^{z'_{max}} \Sigma^e_{x'x'}(z')\,\mathrm{d}z' \quad (11)$$

where the z' axis is normal to the NI interface, and the limits of integration are in the bulk phases.

To obtain a force balance equation corresponding to the Young equation, we follow the Kerins–Boiteux

method; that is, we integrate equation (10) over $\mathscr{A}$ and transform the integral, by virtue of Gauss' theorem, to the contour integral over the boundary of $\mathscr{A}$ [21]. This gives

$$\oint_{\partial\mathscr{A}} \hat{\mathbf{k}} \cdot \boldsymbol{\Sigma}^{\mathrm{e}} \cdot \hat{\mathbf{x}}\, \mathrm{d}l = 0 \tag{12}$$

where $\hat{\mathbf{k}}$ is the outward local normal to $\partial\mathscr{A}$. Equation (12) expresses the balance of forces acting on $\mathscr{A}$ in the x direction. The force $\boldsymbol{\Psi}$ acting on a surface element of normal vector $\hat{\mathbf{k}}$ is given by $\boldsymbol{\Psi} = \hat{\mathbf{k}} \cdot \boldsymbol{\Sigma}^{\mathrm{e}}$. It can be expressed as the sum of the component along $\hat{\mathbf{k}}$ and the component along $\hat{\mathbf{N}}$, where $\hat{\mathbf{N}}$ is tangent to $\partial\mathscr{A}$. Thus, we have

$$\Psi_x = \Sigma^{\mathrm{e}}_{kk}(\hat{\mathbf{k}} \cdot \hat{\mathbf{x}}) + \Sigma^{\mathrm{e}}_{kN}(\hat{\mathbf{N}} \cdot \hat{\mathbf{x}}) \tag{13}$$

where $\Sigma^{\mathrm{e}}_{kk} = \hat{\mathbf{k}} \cdot \boldsymbol{\Sigma}^{\mathrm{e}} \cdot \hat{\mathbf{k}}$, and $\Sigma^{\mathrm{e}}_{kN} = \hat{\mathbf{k}} \cdot \boldsymbol{\Sigma}^{\mathrm{e}} \cdot \hat{\mathbf{N}}$.

In principle, the contour $\partial\mathscr{A}$ can be arbitrary. However, in order to obtain meaningful physical quantities from the integral, we have to make some assumptions concerning the form of $\mathbf{Q}$ on $\partial\mathscr{A}$. Therefore, we choose the contour locally normal to the IS, NS and NI interfaces, which is shown in figure 2. We assume that R is sufficiently large that we have well defined bulk phases between the interfaces. This means that in the interfacial regions $\mathbf{Q}$ can be well approximated by the solution of the Euler–Lagrange equations for a single IS, NS, or NI interface. Since the director field is usually distorted in the bulk nematic phase, we also have to take into account the elastic free energy of this distortion.

First, we integrate along the $z = 0$ boundary (path II in figure 2) using boundary conditions (5). Since the integration is anti-clockwise, we have

$$\begin{aligned} I_0 &= \int_{-R}^{R_1} (-\Sigma^{\mathrm{e}}_{zx})\, \mathrm{d}x = \int_{-R}^{R_1} \frac{\partial f_{\mathrm{s}}}{\partial Q_{ij}} \partial_x Q_{ij}\, \mathrm{d}x \\ &= f_{\mathrm{s}}[\mathbf{Q}(R_1, 0)] - f_{\mathrm{s}}[\mathbf{Q}(-R, 0)]. \end{aligned} \tag{14}$$

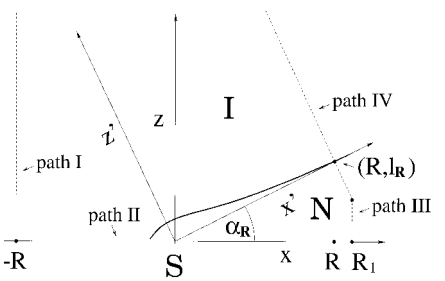

Figure 2. A fragment of the domain $\mathscr{A}$ considered in the text. The boundaries of $\mathscr{A}$ are shown as paths I–IV. The remaining boundary closing the contour $\partial\mathscr{A}$ in the bulk isotropic phase is not shown. The point (R, l_R) is on the NI interface, and α_R denotes the local tilt angle. The axis z' is normal to the NI interface at $x = R$.

Next, we perform the integral along the $x = -R$ boundary (path I), that is

$$I_{-R} = \int_0^{z_{\max}} (-\Sigma^{\mathrm{e}}_{xx})\, \mathrm{d}z = -\int_0^{z_{\max}} f\, \mathrm{d}z \tag{15}$$

where $z_{\max}$ is in the bulk isotropic phase, and we have assumed that the dependence of $\mathbf{Q}$ on x can be neglected. Integration along $x = R_1$ (path III) is similar to that along $x = -R$; it gives

$$I_{R_1} = \int_0^{z_{\mathrm{NS}}} (\Sigma^{\mathrm{e}}_{xx})\, \mathrm{d}z = \int_0^{z_{\mathrm{NS}}} f\, \mathrm{d}z \tag{16}$$

where the z_{NS} denote the position of the Gibbs dividing surface for the NS interface. In other words, we assume that in the interfacial region $0 < z < z_{\mathrm{NS}}$ the variations of $\mathbf{Q}$ with x can be neglected, and the surface tension is a function of $\hat{\mathbf{n}}$ at z_{NS}. Above z_{NS} there is a non-uniform bulk nematic phase described by the director field. The sum of integrals (14–16) gives

$$I_{-R} + I_0 + I_{R_1} = \sigma_{\mathrm{NS}} - \sigma_{\mathrm{IS}}. \tag{17}$$

To calculate the contribution from the NI interface, we express the tensor $\boldsymbol{\Sigma}^{\mathrm{e}}$ in the coordinate system $x'y'z'$ rotated in the xz plane by the angle $\alpha_R = \alpha(R)$, (see figure 2). According to equation (13) $\hat{\mathbf{k}}$ is tangent and $\hat{\mathbf{N}}$ is normal to the NI interface, and we have

$$\Psi_x = \cos\alpha_R \Sigma^{\mathrm{e}}_{x'x'} - \sin\alpha_R \Sigma^{\mathrm{e}}_{x'z'} \tag{18}$$

where $\hat{\mathbf{x}}' = \hat{\mathbf{k}}$ and $\hat{\mathbf{z}}' = \hat{\mathbf{N}}$. To express $\boldsymbol{\Sigma}^{\mathrm{e}}$ in the $x'y'z'$ frame, we simply replace, in definition (8), the derivatives with respect to x and z by the derivatives with respect to x' and z'. We assume that the derivatives parallel to the NI interface can be neglected in the interfacial region; thus, $\partial_{x'}\mathbf{Q} \approx 0$, $\Sigma^{\mathrm{e}}_{x'x'} \approx f$ and $\Sigma^{\mathrm{e}}_{z'x'} \approx 0$. In general, $\Sigma^{\mathrm{e}}_{x'z'} \neq \Sigma^{\mathrm{e}}_{z'x'}$ but we show in Appendix II that the anti-symmetric part of $\boldsymbol{\Sigma}^{\mathrm{e}}$ is related to the derivative $\partial f/\partial\theta$. The latter expresses an infinitesimal change of f when $\mathbf{Q}$ is rotated by the angle $\mathrm{d}\theta$ in the xz plane, while the coordinates remain unchanged. This relation is given by

$$\Sigma^{\mathrm{e}}_{x'z'} - \Sigma^{\mathrm{e}}_{z'x'} = \frac{\partial f}{\partial\theta} \tag{19}$$

hence, $\Sigma^{\mathrm{e}}_{x'z'} \approx \partial f/\partial\theta$ in the interfacial region. If the system has the mirror symmetry $y \mapsto -y$, and this is the case considered below, then θ defines the director orientation in the xz plane: $\hat{\mathbf{n}} = (\sin\theta, 0, \cos\theta)$. In the Landau–de Gennes theory, f does not depend on θ in the bulk nematic phase because $f_{\mathrm{G}} = 1/2\, K(\nabla\theta)^2$, where $K = K_1 = K_3$. This means that $\partial f/\partial\theta \neq 0$ only in the interfacial region. Using the Euler–Lagrange equation for θ we express $\partial f/\partial\theta$ as follows

$$\frac{\partial f}{\partial\theta} = \partial_{x'}\frac{\partial f}{\partial\partial_{x'}\theta} + \partial_{z'}\frac{\partial f}{\partial\partial_{z'}\theta} \approx \partial_{z'}\frac{\partial f}{\partial\partial_{z'}\theta} \tag{20}$$

where again we have neglected the derivative parallel to the NI interface. We can now perform the integration of Ψ_x over the interfacial region (path IV in figure 2) by combining equations (18–20). This gives

$$\int_{z'_{\mathrm{NI}}}^{z'_{\max}} \Psi_x \, \mathrm{d}z' = \int_{z'_{\mathrm{NI}}}^{z'_{\max}} \left(\cos \alpha_R f - \sin \alpha_R \frac{\partial f}{\partial \theta} \right) \mathrm{d}z'$$

$$= \cos \alpha_R \sigma_{\mathrm{NI}} + \sin \alpha_R \left(\frac{\partial f}{\partial \partial_{z'} \theta} \right)_{z'_{\mathrm{NI}}} \qquad (21)$$

where $z'_{\max}$ is in the bulk isotropic phase and z'_{NI} denotes the position of the Gibbs dividing surface for the NI interface. The last term in equation (21) is the projection of the force normal to the NI interface onto the x axis. Like the surface tension, it comes from the integration over the interfacial region. For a single, flat NI interface

$$\left(\frac{\partial f}{\partial \partial_{z'} \theta} \right)_{z'_{\mathrm{NI}}} = \frac{\partial \sigma_{\mathrm{NI}}}{\partial \theta'_{\mathrm{NI}}} \qquad (22)$$

where θ'_{NI} defines the director orientation with respect to $\hat{\mathbf{z}}'$ at z'_{NI}.

Finally, we calculate the contribution from the elastic forces. The calculation is performed in the xyz frame. In the bulk nematic phase, variations of the order parameters can be neglected, and the $\boldsymbol{\Sigma}^{\mathrm{e}}$ have the following components: $\Sigma^{\mathrm{e}}_{xx} = 1/2\, K[(\partial_z \theta)^2 - (\partial_x \theta)^2]$, $\Sigma^{\mathrm{e}}_{xz} = \Sigma^{\mathrm{e}}_{zx} = -\mathrm{K}(\partial_x \theta)(\partial_z \theta)$, and $\Sigma^{\mathrm{e}}_{zz} = -\Sigma^{\mathrm{e}}_{xx}$. The elastic contribution to the total force is given by

$$\psi^{\mathrm{el}} = \int_{\mathbf{a}}^{\mathbf{b}} (\Sigma^{\mathrm{e}}_{xx} \hat{k}_x + \Sigma^{\mathrm{e}}_{zx} \hat{k}_z) \, \mathrm{d}l = \int_{\mathbf{a}}^{\mathbf{b}} (-\Sigma^{\mathrm{e}}_{zx} \, \mathrm{d}x + \Sigma^{\mathrm{e}}_{xx} \, \mathrm{d}z) \qquad (23)$$

where **a** and **b** are points on the NS and the NI dividing surfaces, respectively. We have also used the fact that the local tangent direction to $\partial\mathcal{N}$ is given by $(-\hat{k}_z, \hat{k}_x)$. The sum of all contributions, given by equations (17), (21) and (23), leads to the following force balance equation in the limit of large R

$$\sigma_{\mathrm{NS}} - \sigma_{\mathrm{IS}} + \cos \alpha_R \sigma_{\mathrm{NI}} + \sin \alpha_R K(\hat{\mathbf{N}}_R \ \nabla \theta)_{\mathrm{NI}} + \psi^{\mathrm{el}} = 0 \qquad (24)$$

where $\hat{\mathbf{N}}_R$ is normal to the NI interface at $x = R$, and $K(\hat{\mathbf{N}}_R \ \nabla\theta)_{\mathrm{NI}} = [\partial f / \partial(\partial_{z'} \theta)]_{z'_{\mathrm{NI}}}$. Equation (24) can be considered as a generalization of the Young equation to the case of large but finite R.

2.3. *Asymptotic analysis*

We expect that the last two terms in equation (24) decay like l_R^{-1}, where $l_R = l(R)$ is the distance between the NS and the NI interfaces measured along the z direction. Since for large R, $l_R \sim R \tan \alpha_{\mathrm{c}}$, we recover the Young equation, (1), for the contact angle in the limit $R \to \infty$. At a finite R, α_R deviates from α_{c}. Assuming $\alpha_R = \alpha_{\mathrm{c}} + \delta\alpha_R$, we find from equation (24) that because of the elastic force contribution to the balance of forces $\delta\alpha_R \sim R^{-1}$, unless the last two terms in (24) exactly cancel each other. The local tilt angle is related to $l(R)$ by $\tan \alpha_R = \mathrm{d}l/\mathrm{d}R$, hence, $l(R) - R \tan \alpha_{\mathrm{c}} \sim \ln R$, for $R \to \infty$. This means that the elastic forces cause a logarithmic deviation of $l(R)$ from the asymptotic linear behaviour characteristic for simple fluids.

To make quantitative predictions we have to assume the asymptotic form of $\theta(x, z)$ far from the three-phase contact line. In the bulk nematic phase, it must satisfy the Euler–Lagrange equation

$$\nabla^2 \theta = 0. \qquad (25)$$

Here, we assume that the asymptotic solution of equation (25) does not depend on the distance from the contact line, but only on the angular variable $\phi = \arctan(z/x)$, i.e.

$$\theta(x, z) = \theta_{\mathrm{NS}} + \frac{\theta_{\mathrm{NI}} - \theta_{\mathrm{NS}}}{\alpha_{\mathrm{c}}} \arctan \frac{z}{x} \qquad (26)$$

where $\theta_{\mathrm{NI}} = \theta'_{\mathrm{NI}} - \alpha_{\mathrm{c}}$ and θ_{NS} are the anchoring directions of the NI and the NS interfaces, respectively, expressed in the xyz frame. A schematic picture of the director field is shown in figure 3. We consider the following three cases of the anchoring directions at the NS and the NI interfaces: (a) homeotropic–homeotropic, (b) homeotropic–planar, and (c) planar–homeotropic, which are compatible with $\hat{\mathbf{n}}(\mathbf{r})$ in the xz plane. It is straightforward to show that for $\theta(x, z)$ given by equation (26), $\Sigma^{\mathrm{e}}_{zx} = 1/2\, K\eta\partial_x(\partial_x \theta)$ and $\Sigma^{\mathrm{e}}_{xx} = -1/2\, K\eta\partial_z(\partial_x \theta)$, where $\eta = (\theta_{\mathrm{NI}} - \theta_{\mathrm{NS}})/\alpha_{\mathrm{c}}$. The substitution of Σ^{e}_{xx} and Σ^{e}_{zx} to (23) gives

$$\psi^{\mathrm{el}} = -\frac{1}{2} K\eta[\partial_x \theta(\mathbf{b}) - \partial_x \theta(\mathbf{a})]. \qquad (27)$$

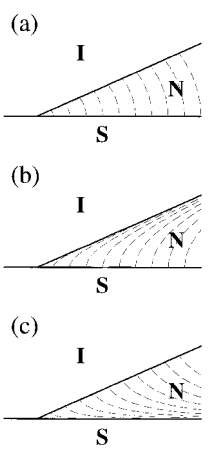

Figure 3. Schematic picture of the asymptotic director field. Anchoring at the NS and the NI interfaces is, respectively, (*a*) homeotropic and homeotropic, (*b*) homeotropic and planar, (*c*) planar and homeotropic.

If we ignore the thickness of the interfacial regions ψ^{el} assumes the following simple form

$$\psi^{el} = \frac{1}{2} K\eta^2 \frac{\sin \phi_R}{\rho_R} \tag{28}$$

where $\tan \phi_R = l_R/R$ and $\rho_R^2 = R^2 + l_R^2$. We also find that

$$K(\hat{\mathbf{N}}_R \quad \nabla\theta)_{NI} = K\eta \frac{\cos(\alpha_R - \phi_R)}{\rho_R}. \tag{29}$$

Finally, equation (24) can be expressed as follows

$$\sigma_{NS} - \sigma_{IS} + \cos \alpha_R \sigma_{NI} + \frac{1}{2} K\eta^2 \frac{\sin \phi_R}{\rho_R} + K\eta \frac{\sin \alpha_R}{\rho_R} \cos(\alpha_R - \phi_R) = 0 \tag{30}$$

where $\phi_R = \alpha_c + \delta\phi_R$ for large R. From equations (1) and (30) we find the leading term in the asymptotic expansion of $\delta\alpha_R$:

$$\delta\alpha_R \sim \frac{K}{2\sigma_{NI}\rho_R}[(\eta + 1)^2 - 1] \approx \frac{K \cos \alpha_c}{2\sigma_{NI} R}\left[\left(\frac{\Delta\theta_a}{\alpha_c}\right)^2 - 1\right] \tag{31}$$

hence,

$$l_R \sim R \tan \alpha_c + \frac{K \ln(R/R_0)}{2\sigma_{NI} \cos \alpha_c}\left[\left(\frac{\Delta\theta_a}{\alpha_c}\right)^2 - 1\right] + l_0 \tag{32}$$

where l_0 is the integration constant, and R_0 is a cut-off length. By $\Delta\theta_a = \theta'_{NI} - \theta_{NS}$ we have denoted the difference of anchoring directions measured with respect to the interface normals.

In the case of homeotropic anchoring at both the NS and the NI interfaces, $\theta'_{NI} = \theta_{NS} = 0$, and $\delta\alpha_R < 0$. For $R > R_0$, l_R deviates from linear behaviour in such a way that the NI interface is shifted towards the substrate. To make a rough estimate of this effect, we have used the data for 5CB [29] (in fact the anchoring at the NI interface is tilted for 5CB): $K = 2.1 \times 10^{-7}$ erg cm^{-1} and $\sigma_{NI} = 1.5 \times 10^{-2}$ erg cm^{-2}, which gives $K/(2\sigma_{NI}) = 700$ Å. For $\theta'_{NI} = \pm\pi/2$ (planar anchoring) and $\theta_{NS} = 0$ (homeotropic anchoring), we have $\delta\alpha_R > 0$, and the logarithmic correction to l_R is also positive when $R > R_0$. We obtain the same result also for $\theta'_{NI} = 0$ and $\theta_{NS} = \pm\pi/2$. The case of planar anchoring at both interfaces is different, as then the orientation of $\hat{\mathbf{n}}$ parallel to the contact line is energetically favourable.

2.4. *Line tension*

The line tension, τ, is defined as the excess free energy over that in the bulk phases and the interfaces, per unit length of the contact line [12]. Thus, τ is obtained from equation (3) by subtracting the surface contributions due to the three interfaces and taking the limit of infinite domain (the thermodynamic limit). We postpone the calculation of τ to the next section, where we develop a macroscopic approach. Here, we recall only the results for a c-component fluid system.

Kerins and Boiteux [21] considered a three-phase fluid system with a line of contact. Applying the van der Waals theory to the c-component system, and using Noether's theorem, they derived for τ formula analogous to that for the surface tension. In our notation, the Kerins–Boiteux free energy density is given by $f = f_G(\nabla\rho) + f_L(\rho)$, where $\rho = (\rho_1, \ldots, \rho_c)$ is a c-component density (or order parameter),

$$f_G = \frac{1}{2} \sum_{i,j=1}^{c} M_{ij}(\nabla\rho_i \quad \nabla\rho_j) \tag{33}$$

and ∇ denotes a two-dimensional gradient. The function $f_L(\rho)$ is positive, and vanishes in the bulk regions of coexisting fluid phases. The equilibrium line tension is given by the Kerins–Boiteux formula [21]

$$\tau = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dz[f_G(\nabla\rho) - f_L(\rho)] \tag{34}$$

where ρ satisfies the Euler–Lagrange equations. The integrand tends to zero both in the bulk regions and in the interfacial regions far from the contact line. Thus, it is non-zero only in the vicinity of the contact line. Perković *et al.* [30] showed that formula (34), with $\int_{-\infty}^{+\infty} dz$ replaced by $\int_{0}^{+\infty} dz$, applies also in the case of a two fluid phase–solid substrate contact line, and the proof was given for a one-component ρ. Since the Landau–de Gennes theory has a similar formal structure to the van der Waals theory considered in [30] it is natural to expect that an analogous formula to (34) holds also in the case of the nematic–isotropic–substrate contact line; however, we do not present a formal proof here.

A natural question arises concerning the convergence of τ in the thermodynamic limit. For a comprehensive review of the behaviour of τ near a wetting transition in simple fluid systems see [13]. Whether τ tends to a finite value or diverges when the thermodynamic limit is taken depends, in general, on an effective interaction potential between the substrate and the two fluid-phase interface. In liquid crystal systems, the problem is more complicated because of long range elastic forces. In principle, τ can be studied in the framework of the Landau–de Gennes theory. However, a macroscopic approach seems to be the best way of studying the problem of convergence of τ in the thermodynamic limit, in which we are mainly interested here. On the other hand, if we were interested in the contribution to τ coming

from the core region, where the description in terms of **Q** is essential, we should use the Landau–de Gennes or a microscopic theory.

3. The interface Hamiltonian

It is instructive to rederive the results of the previous Section using the interface Hamiltonian approach. We defer rigorous derivation of such a Hamiltonian for a pinned NI interface to a future work. Here, we simply postulate a form of the Hamiltonian capable of reproducing the shape of the NI interface in the asymptotic limit of large separations from the substrate. In the case of simple fluids, the interface Hamiltonian is a functional of only one variable, i.e. the separation of the interface between two fluid phases from the substrate. In the presence of orientational degrees of freedom, orientations of the director at the NS and the NI interfaces should also be included. Thus, if twist deformation is not present we deal with three field variables: the distance $l(x)$ between the NI interface and the substrate, and the two angles: $\theta_0(x)$ and $\theta_l(x)$, corresponding to the director orientations at $z = 0$ and $z = l(x)$, respectively.

First, we calculate the contribution to the free energy from the elastic forces. Let us consider a bulk nematic phase contained between two flat surfaces: $z = 0$ and $z = x \tan \alpha$. We assume that $\hat{\mathbf{n}}$ is in the xz plane, and its orientation is given by $\theta(x, z)$ satisfying the Euler–Lagrange equation $\nabla^2\theta = 0$, with the boundary conditions: $\theta(x, 0) = \theta_0$ and $\theta(x, x \tan \alpha) = \theta_l$. The solution is given by

$$\theta(x, z) = \theta_0 + \frac{\theta_l - \theta_0}{\alpha} \arctan(z/x). \tag{35}$$

The contribution to the elastic free energy from a portion of the nematic phase contained between $x - 1/2\,\mathrm{d}x$ and $x + 1/2\,\mathrm{d}x$ is $dF_{\mathrm{el}} = 1/2\,K(\theta_l - \theta_0)^2 \tan\alpha\,\mathrm{d}x/(\alpha z)$, where $z = x \tan \alpha$. To obtain the elastic free energy density we apply this formula locally replacing z and $\tan\alpha$ by $l(x)$ and $\dot{l} = \mathrm{d}l/\mathrm{d}x$, respectively, which gives

$$f_{\mathrm{el}} = \frac{1}{2} K \frac{(\theta_l - \theta_0)^2}{l} \left(\frac{\dot{l}}{\arctan \dot{l}} \right). \tag{36}$$

In the flat interface limit ($\dot{l} = 0$), we recover the usual expression for the elastic free energy in the one elastic-constant approximation.

We consider the excess free energy due to the presence of the three-phase contact line, i.e. the line tension functional

$$\tilde{\tau}[l, \theta_0, \theta_l] = \int_{-\infty}^{\infty} \{\sigma_{\mathrm{NI}}[(1 + \dot{l}^2)^{1/2} - 1] + V(l) + f_{\mathrm{el}} + f_{\mathrm{a}} + c(x)\}\,\mathrm{d}x \tag{37}$$

where

$$f_{\mathrm{a}} = \frac{1}{2} w_{\mathrm{NS}}(\theta_0 - \theta_{\mathrm{NS}})^2 + \frac{1}{2} w_{\mathrm{NI}}(\theta_l + \arctan \dot{l} - \theta'_{\mathrm{NI}})^2$$

is the sum of anchoring energies at the NS and the NI interfaces, $V(l)$ denotes the excess free energy of a uniform nematic film of thickness l, and a piecewise constant function $c(x)$ must be included to ensure that the integrand vanishes for $|x| \to \infty$. The qualitative behaviour of $V(l)$ is shown in figure 4 [13]. It has a minimum at $l_1 = \lim_{x \to -\infty} l(x)$, $V(l_1) = 0$, which corresponds to a thin, nematic-like film at the IS interface. This is the global minimum in the case of partial wetting. There is also a local minimum at $l = \infty$ corresponding to a metastable wetting layer, and $V(\infty) = \sigma_{\mathrm{NS}} + \sigma_{\mathrm{NI}} - \sigma_{\mathrm{IS}} = -S$, where S is the spreading coefficient [3]. We also assume that $V(l) - V(\infty)$ goes to zero faster than l^{-1}. In the most general form, V could also be a function of the orientational variables θ_0 and θ_l. Since we are interested only in the asymptotic form of $l(x)$, for $x \to \infty$, we do not consider such a dependence, however. In the functional $\tilde{\tau}$, we have also neglected the derivatives $\dot{\theta}_0$ and $\dot{\theta}_l$, i.e. the contributions to the free energy due to inhomogeneities of the boundary conditions, which could be included in a more refined version.

Let us assume first homeotropic anchoring at both interfaces. We minimize $\tilde{\tau}$ with respect to θ_0 and θ_l to obtain

$$\theta_0 = -\frac{b_{\mathrm{NS}}\dot{l}}{l + 2b\dot{l}/\arctan \dot{l}} \tag{38a}$$

$$\theta_l = -\frac{l \arctan \dot{l} + b_{\mathrm{NS}}\dot{l}}{l + 2b\dot{l}/\arctan \dot{l}} \tag{38b}$$

where $b = 1/2(b_{\mathrm{NS}} + b_{\mathrm{NI}})$, and $b_{\mathrm{NS}} = K/w_{\mathrm{NS}}$, $b_{\mathrm{NI}} = K/w_{\mathrm{NI}}$ denote the extrapolation lengths for the NS and the NI interfaces, respectively. Substituting equation (38) into (37) we express $\tilde{\tau}$ in terms of the field $l(x)$ alone as

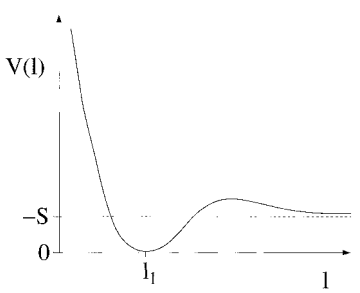

Figure 4. Qualitative behaviour of the effective interaction potential $V(l)$. S is the spreading coefficient. The global minimum of $V(l)$ at $l_1 = \lim_{x \to -\infty} l(x)$ corresponds to a thin, nematic-like film, whereas the local minimum at $l = \infty$ corresponds to a metastable wetting layer.

follows

$$\tilde{\tau}[l] = \int_{-\infty}^{\infty} \left\{ \sigma_{NI}[(1+\dot{l}^2)^{1/2} - 1] + V(l) + \frac{1}{2} K \frac{\dot{l} \arctan \dot{l}}{l + 2b\dot{l}/\arctan \dot{l}} + c(x) \right\} dx \quad (39)$$

hence $c(x) = 0$, for $x < 0$, and $c(x) = \sigma_{NI}(\cos \alpha_c - 1/\cos \alpha_c)$, for $x > 0$. Since we are interested in the asymptotic analysis for large l, we approximate the third term in (39) by $(1/2\, K/l)\dot{l} \arctan \dot{l}$. The minimum condition for $\tilde{\tau}[l]$ leads to the Euler–Lagrange equation, which has the following first integral

$$\sigma_{NI}\left[1 - \frac{1}{(1+\dot{l}^2)^{1/2}}\right] - V(l) + \frac{1}{2} K \frac{\dot{l}^2}{l(1+\dot{l}^2)} = 0. \quad (40)$$

We can also express the above condition in terms of the local tilt angle, $\alpha = \arctan \dot{l}$, as follows

$$\sigma_{NI} \cos \alpha + \sigma_{NS} - \sigma_{IS} + V(l) - V(\infty) - \frac{1}{2} K \frac{\sin^2 \alpha}{l} = 0. \quad (41)$$

Now, we consider the asymptotic limit of $x \to \infty$ and express the local tilt angle as $\alpha = \alpha_c + \delta\alpha$, where $\delta\alpha$ is small. The first term in the asymptotic expansion of $l(x)$ is $x \tan \alpha_c$, which substituted into equation (41) gives

$$\delta\alpha \approx - \frac{K \cos \alpha_c}{2\sigma_{NI} x}. \quad (42)$$

Thus, we have recovered equation (31).

To study the line tension, we return to the general case of different anchoring directions at the NI and the NS interfaces. However, to simplify calculations we assume that the contact angle is small and $\dot{l}$ is also small. Then, the functional $\tilde{\tau}[l]$ assumes the following simple form

$$\tilde{\tau}[l] = \int_{-\infty}^{\infty} \left[\frac{1}{2} \sigma_{NI} \dot{l}^2 + \frac{1}{2} K \frac{(\Delta\theta_a - \dot{l})^2}{l + 2b} + V(l) + c(x) \right] dx \quad (43)$$

where $c(x) \approx -2V(\infty)$, for $x > 0$, and $V(\infty) \approx 1/2\, \sigma_{NI} \alpha_c^2$. It is convenient to rewrite $\tilde{\tau}[l]$ as follows

$$\tilde{\tau}[l] = \int_{-\infty}^{\infty} \left[\frac{1}{2} \sigma(l) \dot{l}^2 - K \frac{\dot{l} \Delta\theta_a}{l + 2b} + V_1(l) + c(x) \right] dx \quad (44)$$

where $\sigma(l) = \sigma_{NI} + K/(l + 2b)$, and $V_1(l) = V(l) + 1/2\, K(\Delta\theta_a)^2/(l + 2b)$. The Euler–Lagrange equation has the first integral

$$\frac{1}{2} \sigma(l) \dot{l}^2 - V_1(l) = 0 \quad (45)$$

hence,

$$\dot{l} = \left[\frac{2V_1(l)}{\sigma(l)} \right]^{1/2}. \quad (46)$$

If $V(l)$ is of short range, we can solve equation (46) in the region of large l, where $V(l) \approx V(\infty)$. The solution is given in an implicit form:

$$[(l + a_1)(l + a_2)]^{1/2} + (a_1 - a_2) \ln[(l + a_1)^{1/2} + (l + a_2)^{1/2}] = \alpha_c x + \text{const} \quad (47)$$

where $a_1 = 2b + K/\sigma_{NI}$ and $a_2 = 2b + (\Delta\theta_a/\alpha_c)^2 K/\sigma_{NI}$. In the asymptotic limit of $x \to \infty$, equation (47) is consistent with asymptotic formula (32) applied to small contact angles.

To obtain the equilibrium line tension we substitute equation (46) into (44), which gives

$$\tau = \int_{l_1}^{l_0} \left\{ [2V_1(l)\sigma(l)]^{1/2} - K \frac{\Delta\theta_a}{l + 2b} \right\} dl + \int_{l_0}^{\infty} \left\{ [2\sigma(l)/V_1(l)]^{1/2} [V_1(l) - V(\infty)] - K \frac{\Delta\theta_a}{l + 2b} \right\} dl \quad (48)$$

where $l_0 = l(0)$. Note that $(2\sigma/V_1)^{1/2} \to 2/\alpha_c$ when $l \to \infty$. Thus, for large l and $\Delta\theta_a \neq 0$, the integrand in the second integral decays like $[(\Delta\theta_a/\alpha_c) - 1] K \Delta\theta_a/(l + 2b)$. When $\Delta\theta_a = 0$ it decays like $(2/\alpha_c)[V(l) - V(\infty)]$, which is faster than the l^{-1} decay. This means that τ remains finite in the thermodynamic limit in the case of homeotropic anchoring at both interfaces. However, when the anchoring directions at the NS and the NI interfaces are different, τ diverges logarithmically with the size of the system.

4. Discussion

We have presented a preliminary study of the nematic–isotropic–substrate contact line region in the case of partial wetting by the nematic phase. Using the Landau–de Gennes theory and applying Noether's theorem, we have derived the force balance equation at the contact line. The long-range elastic forces due to different orientations of the nematic director at the NS and the NI interfaces cause a logarithmic deviation of the NI interface position from the usual asymptotic form $l(x) \sim \text{const} + x \tan \alpha_c$. The characteristic length scale of this deviation, $K/(2\sigma_{NI})$, can be as large as a few hundred Å. This conclusion is based on a plausible

assumption concerning the nematic director field in the bulk nematic phase, far from the three-phase contact line.

We have also proposed a simple macroscopic model, which is similar in spirit to the interface displacement model. However, it takes into account also the long range elastic forces, which do not appear in simple fluid systems. In the framework of the macroscopic model, we have shown that the behaviour of the line tension in the thermodynamic limit depends on the type of anchoring at the NS and the NI interfaces. We note that if the asymptotic behaviour of l was simply $l \sim x\alpha_c$ (for small contact angles), i.e. without the logarithmic term, then τ would diverge logarithmically with the system size, also in the case of homeotropic anchoring at both interfaces. This is a simple conclusion from equation (43). However, when the asymptotic form $l \sim x\alpha_c - (K/2\sigma_{NI}) \ln x$, for $\Delta\theta_a = 0$, is substituted into (43) then the two terms decaying like x^{-1} in the integrand cancel each other out, and the integral is finite. In other words, an increase of the bulk free energy due to the distortion of the director field is cancelled out by a decrease of area of the NI interface, compared with the case of linear profile. No such cancellation occurs when $\Delta\theta_a \neq 0$. In that case, the interfacial area increases compared with linear $l(x)$, and this increase, together with the free energy of distortion, gives rise to the divergence of τ in the thermodynamic limit. Although we have obtained these results only for small contact angles, we believe that they are valid in general.

In two recent papers, Rey [22, 23] derived the force balance equations for nematic contact lines, which are generalizations of the Neumann and Young equations. The first concerns the situation when the nematic phase coexists with two isotropic fluid phases, which has not been considered in our study. Therefore, we concentrate on the comparison of Rey's version of the generalized Young equation with our version. The starting point in [23] is also the Landau–de Gennes theory. However, the contribution to the free energy from the nematic–isotropic interface appears explicitly (equation (3 *a*) in [23]) as a surface integral over the interfacial free energy density, $\gamma^{N\alpha}$, treated as a function of the interfacial order parameter $\mathbf{Q}$ and the surface normal. The anisotropic ($\mathbf{Q}$ dependent) part of $\gamma^{N\alpha}$ is assumed to have the same quadratic form as $f_s(\mathbf{Q})$ for the nematic phase in contact with an isotropic solid substrate [6, 20]. The force balance equation at the contact line is expressed in terms of the surface stress tensor $\mathbf{t}$. It is argued that in nematic liquid crystals $\mathbf{t}$ is generally a 2×3 tensor. The components of $\mathbf{t}$ parallel to the interface are the usual interfacial tensions. The remaining two components correspond to bending stresses, and they contribute to the balance of forces only if the interface is tilted with respect to the substrate. We note that the generalized Young equation derived by Rey (equation (27) in [23]) resembles our equation (24) if we put $\psi^{el} = 0$. Indeed, substituting (22) into (24) we obtain

$$\sigma_{NS} - \sigma_{IS} + \cos\alpha_R \sigma_{NI} + \sin\alpha_R \frac{\partial\sigma_{NI}}{\partial\theta'_{NI}} = 0 \qquad (49)$$

where $\partial\sigma_{NI}/\partial\theta'_{NI}$ is equal to the bending coefficient B^{BN} for the NI interface introduced by Rey. Equation (49) is to be compared with equation (27) in [23] or equation (11) in [22]. Since in these two equations presented by Rey the bending term appears with different signs we note that our equation (49) is consistent with the latter.

The lack of the bulk elastic term in Rey's force balance equation is not discussed by the author. As our derivation based on Noether's theorem shows, in general this term should not be neglected. It vanishes, however, when the bulk director field is not distorted. We expect it to occur when the distance l between the NI and the NS interfaces is smaller than b_{max}, the larger of the two extrapolation lengths [1]. Then, the force balance equation reduces to that derived by Rey. In our considerations, we have implicitly assumed an asymptotic limit of $l \gg b_{max}$. In principle, it is possible to imagine a sufficiently large nematic drop to satisfy this asymptotic condition. In practice, a measurement of a well defined contact angle is possible when the distance from the contact line is large compared with the size of the core region, but small compared with the droplet size [3]. Thus, in the case of weak anchoring or close to complete wetting by the nematic phase, it may be difficult to observe the asymptotic region $l \gg b_{max}$, in which the director field is distorted.

Finally, we note that the anchoring energy used in the interface Hamiltonian considered in § 3 could be replaced by the Rapini–Papoular form [31]. It is more suitable when deviations of the surface director from the anchoring direction are large, and this usually occurs when $l \lesssim b_{max}$. To study the vicinity of the contact line in more detail, in particular, a possible cross-over between the regions of distorted and uniform director fields, it might be necessary to consider the derivatives $\dot{\theta}_0$ and $\dot{\theta}_l$ in the interface Hamiltonian. At the moment, we also do not know the precise form of $V(l)$. Therefore, it would be desirable to derive an interface Hamiltonian for the nematic phase in coexistence with the isotropic phase (or vapour) from the Landau–de Gennes formalism or a microscopic theory. We defer studies of this non-trivial problem to future work.

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Appendix I

In this Appendix, we show how Noether's theorem works in a special case of one field in a two dimensional space.

Let us consider the following functional

$$F_{\mathscr{A}}[\Phi] = \int_{\mathscr{A}} \mathrm{d}x\,\mathrm{d}y f(\Phi, \nabla\Phi, x, y) \tag{A1}$$

where $\Phi = \Phi(x, y)$, and $\mathscr{A}$ is a closed, simply-connected region in the two dimensional space. The function f is usually called the Lagrangian. Then, we assume a small deformation of the variable x, that is, the point (x, y) is transformed to (x', y') as follows

$$\begin{aligned} x' &= x + u(x) \\ y' &= y \end{aligned} \tag{A2}$$

where $u(x)$ is small. The region $\mathscr{A}$ is transformed to $\mathscr{A}'$. The field variable does not change, i.e. $\Delta\Phi = \Phi'(x', y') - \Phi(x, y) = 0$. More generally one can consider a transformation of both the space points and the field variable. Now, we can calculate the change of the functional F due to transformation (A2). Keeping only the terms linear in u we find

$$\begin{aligned} \Delta F_{\mathscr{A}} &= F_{\mathscr{A}'}[\Phi'] - F_{\mathscr{A}}[\Phi] \\ &= \int_{\mathscr{A}} \mathrm{d}x\,\mathrm{d}y \left[\frac{\partial f}{\partial \partial_x \Phi} \Delta(\partial_x \Phi) + \frac{\partial f}{\partial \partial_y \Phi} \Delta(\partial_y \Phi) \right. \\ &\quad \left. + f_x u + f \frac{\mathrm{d}u}{\mathrm{d}x} \right] \end{aligned} \tag{A3}$$

where $f_x = (\partial f/\partial x)_{\Phi, \nabla\Phi}$, $\Delta(\partial_x\Phi) = \partial_{x'}\Phi' - \partial_x\Phi = -(\partial_x\Phi)(\mathrm{d}u/\mathrm{d}x)$, and $\Delta(\partial_y\Phi) = 0$. After some manipulations we obtain from (A3) the following expression

$$\begin{aligned} \Delta F = \int_{\mathscr{A}} \mathrm{d}x\,\mathrm{d}y \left\{ \partial_x \left[u \left(f - \frac{\partial f}{\partial \partial_x \Phi} \partial_x \Phi \right) \right] \right. \\ + \partial_y \left(- u \frac{\partial f}{\partial \partial_y \Phi} \partial_x \Phi \right) \\ \left. + \left(\partial_x \frac{\partial f}{\partial \partial_x \Phi} + \partial_y \frac{\partial f}{\partial \partial_y \Phi} - \frac{\partial f}{\partial \Phi} \right) u \partial_x \Phi \right\}. \end{aligned} \tag{A4}$$

Now, we assume that Φ is a solution of the Euler–Lagrange equation, so that the last term in the integrand vanishes, and that $u(x) = const$. Then, the invariance of F with respect to translations along x implies that the divergence term in the integrand must vanish, since the region $\mathscr{A}$ is arbitrary. It is easy to show by direct calculation that the divergence term vanishes, provided that Φ satisfies the Euler–Lagrange equation, and f does not explicitly depend on x. Thus, we have found that

$$\partial_x \left(f - \frac{\partial f}{\partial \partial_x \Phi} \partial_x \Phi \right) + \partial_y \left(- \frac{\partial f}{\partial \partial_y \Phi} \partial_x \Phi \right) = 0. \tag{A5}$$

In the one dimensional case, the function $\mathscr{H} = (\partial f/\partial \dot{\Phi})\dot{\Phi} - f$, where $\dot{\Phi} = \mathrm{d}\Phi/\mathrm{d}x$, is the Hamiltonian, and we have $\mathrm{d}\mathscr{H}/\mathrm{d}x = 0$ or $\mathscr{H} = const$, which is simply the energy conservation law.

If f depends neither on x nor y, we have in addition to (A5)

$$\partial_x \left(- \frac{\partial f}{\partial \partial_x \Phi} \partial_y \Phi \right) + \partial_y \left(f - \frac{\partial f}{\partial \partial_y \Phi} \partial_y \Phi \right) = 0. \tag{A6}$$

Generalization to the case of n field variables, Φ^β, $(\beta = 1, \ldots, n)$, satisfying the Euler–Lagrange equations is straightforward. One simply replaces in equations (A5) and (A6) the terms $(\partial f/\partial \partial_i \Phi)\partial_j \Phi$, where $i, j = x, y$, by the terms $\Sigma_{\beta=1}^{n} (\partial f/\partial \partial_i \Phi^\beta)\partial_j \Phi^\beta$.

Appendix II

In this Appendix, we derive identity (19). Let us first define the following two auxiliary second rank tensors:

$$U_{ij} = \frac{\partial f}{\partial \partial_k Q_{il}} \partial_k Q_{jl} \tag{A7}$$

and

$$V_{ij} = \frac{\partial f}{\partial \partial_k Q_{li}} \partial_k Q_{lj}. \tag{A8}$$

Differentiation of f with respect to $\partial_k Q_{ij}$ gives—see equation (2 *c*)

$$\frac{\partial f}{\partial \partial_k Q_{ij}} = L_1 \partial_k Q_{ij} + L_2 \partial_l Q_{il} \delta_{jk} + L_3 \partial_j Q_{ik}. \tag{A9}$$

It results from equations (A7–A9) that the tensor $\mathbf{U}$ is symmetric, whereas $\mathbf{V}$ is not symmetric. Now, we consider an infinitesimal rotation in the xz plane

$$\mathbf{R}_\varepsilon = \mathbf{I} + \varepsilon(\hat{\mathbf{x}}\hat{\mathbf{z}} - \hat{\mathbf{z}}\hat{\mathbf{x}}) \tag{A10}$$

where ε is the infinitesimal rotation angle. Of course, f must be invariant with respect to arbitrary rotations of both the coordinates and $\mathbf{Q}$. Applying $\mathbf{R}_\varepsilon$ to f we find the coefficient of ε in the expansion of f, which must vanish, i.e.

$$(U_{xz} - U_{zx}) + (V_{xz} - V_{zx}) - (\Sigma^{\mathrm{e}}_{xz} - \Sigma^{\mathrm{e}}_{zx}) = 0 \tag{A11}$$

where the first term vanishes because $\mathbf{U}$ is symmetric. We can also consider the situation when only $\mathbf{Q}$ is rotated in the xz plane, while the coordinates remain unchanged. An infinitesimal rotation by the angle $\mathrm{d}\theta$

results in an infinitesimal change of **Q**

$$d\mathbf{Q} = [\,\hat{\mathbf{x}}(\hat{\mathbf{z}}\ \ \mathbf{Q}) - \hat{\mathbf{z}}(\hat{\mathbf{x}}\ \ \mathbf{Q}) + \hat{\mathbf{x}}(\mathbf{Q}\ \ \hat{\mathbf{z}}) - \hat{\mathbf{z}}(\mathbf{Q}\ \ \hat{\mathbf{x}})\,]\,d\theta \tag{A12}$$

hence

$$\frac{\partial f}{\partial \theta} = \frac{\partial f}{\partial \partial_k Q_{ij}} \frac{\partial \partial_k Q_{ij}}{\partial \theta} = (U_{xz} - U_{zx}) + (V_{xz} - V_{zx}). \tag{A13}$$

From equations (A11) and (A13) we find that

$$\frac{\partial f}{\partial \theta} = \Sigma^{e}_{xz} - \Sigma^{e}_{zx}. \tag{A14}$$

Identity (A14) can be expressed in any coordinate frame rotated with respect to the *xyz* frame about the *y* axis, hence identity (19) follows.

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