Liquid Crystals

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

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To cite this Article Alexe-Ionescu, A. L. and Barber, G.(1998) 'Non-local description of nematic liquid crystals', Liquid Crystals, 25: 2, 189 — 197

To link to this Article: DOI: 10.1080/026782998206335

URL: http://dx.doi.org/10.1080/026782998206335

LIQUID CRYSTALS, 1998, VOL. 25, NO. 2, 189–197

Non-local description of nematic liquid crystals

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(*Received 3 February 1998; accepted 4 March 1998*)

A non-local description of nematic liquid crystals is presented. By considering a generic two body interaction, the total energy of a nematic sample is formally evaluated. It is given by a generalized non-local functional. The minimization of the total energy shows that the actual nematic tilt angle profile, characterizing the nematic director, is a solution of an integral equation that in the simplest case is of the Freedholm type. This new equation takes the place of the well known Euler–Lagrange equation used in the elastic theory of nematic liquid crystals. The existence of sub-surface deformations localized close to the limiting surfaces is studied by means of this integral equation. The analysis has been performed for cases of strong and weak anchoring, with and without external fields. The sources of the subsurface deformations are discussed in the framework of the usual Frank elastic theory.

1. Introduction

The elastic theory for nematic liquid crystals was written down long ago by Oseen [1] and Zocher [2]. According to these authors, the bulk elastic behaviour of these media is described by three elastic constants, usually indicated by k_{11}, k_{22} and k_{33}. They are connected with three bulk fundamental deformations called, after Frank [3], splay, twist and bend, respectively. In the elastic formulation proposed in [1, 2] there are also two surface elastic constants, known as splay–bend and saddle–splay elastic constants, indicated by K_{13} and K_{24} and associated with the surface elastic contributions to the total elastic energy.

A long time ago it was shown that the K_{13} term in the elastic expansion is unbounded from below [4–6]. In order to solve this intrinsic contradiction in the elastic theory, different recipes have been proposed. A few groups resolved the K_{13}-problem by selectively introducing higher order gradient terms [7–13]. This often leads to very rapid orientation changes close to the interface, known as sub-surface deformations. Other groups have proposed looking for the solution to the elastic problem among solutions of the Euler–Lagrange equations valid for the bulk [14–18], or by assuming K_{13} is identically zero [19].

The problem is very hard, and the only way of distinguishing between rival theories is to examine molecular models in the hope that they will throw light on what is happening in the continuum theory. For this reason the investigations of the sub-surface deformation have recently been performed employing semi-molecular models, without any use of elastic theory [20–23]. In these investigations the analyses were done by assuming an intermolecular interaction g between two molecules of a nematic located in $\mathbf{R}$ and $\mathbf{R}'=\mathbf{R}+\mathbf{r}$. It usually depends on the nematic orientation at $\mathbf{R}$ and $\mathbf{R}'$, that will be indicated by $\mathbf{n}=\mathbf{n}(\mathbf{R})$ and $\mathbf{n}'=\mathbf{n}(\mathbf{R}')$. Hence $g=g(\mathbf{n},\mathbf{n}';\mathbf{r})$. Then the total energy of the sample, which is given by

$$\mathscr{F}=\frac{1}{2}\iint g(\mathbf{n},\mathbf{n}';\mathbf{r})\,\mathrm{d}\tau\,\mathrm{d}\tau' \tag{1}$$

was evaluated in the lattice [20, 23] or continuum [21, 22] approximation. The actual profile $\mathbf{n}=\mathbf{n}(\mathbf{R})$ was obtained by minimizing $\mathscr{F}$ directly. The details of the calculations and the simplifying hypotheses are discussed in [20–23]. The results of this kind of analysis are that: (i) if g depends not only on $\mathbf{n}\ \mathbf{n}'$ and $r=|\mathbf{r}|$, but also on $\mathbf{n}\ \mathbf{u}$ and $\mathbf{n}'\ \mathbf{u}$, where $\mathbf{u}=\mathbf{r}/r$, a sub-surface deformation exists close to the interface, except in the special cases of planar or homeotropic surface alignments; (ii) the sources of this sub-surface deformation are the K_{13}-elastic constant and the uniform part of the elastic

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energy density, (iii) the K_{13}-elastic constant is not well defined, and it does not depend only on the nematic liquid crystal, but also on the existence of surface fields [24].

In this paper we shall present a non-local description of nematic liquid crystals in order to describe the nematic orientation close to a substrate. This kind of analysis is not new. It goes back to Nehring and Saupe [25] and it has been extensively used by density-functional theoretists [26–32]. It has also been applied intensively in [20–23, 33]. Our aim is to find, in the framework of constant density and scalar order parameter, the integral equation whose solutions extremize the total energy in the non-local approach. In this way, the result that a uniform nematic orientation does not correspond to a stable state is evident, without any calculations. In particular we will be able to re-obtain the result reported in [34], deduced by means of a direct calculation of the first variation of the total free energy. An analysis similar to the one developed in our paper, when the interparticle interaction is a generalized Maier–Saupe interaction [35], has been recently published by Texeira [36].

We shall also show that in the elastic expansion of the total free energy in terms of the deformation tensor characterizing the nematic distortion, the linear term is absent. From this result we can infer that the main elastic term connected with the spontaneous splay and with the splay–bend deformations [37] balance each other, and the remaining parts renormalize the Frank elastic constants. Hence, the K_{13} elastic constant disappears from the free energy. This result agrees with that obtained by Faetti and Riccardi [38] in one particular case. These authors in [38] reached this result by means of a Taylor expansion of the intermolecular interaction energy in terms of the invariants characterizing the interaction. We show, on the contrary, that this result is very general and depends only on the symmetry of the nematic phase. Our result coincides also with the one obtained recently by Yokoyama [39] in a completely different and extremely complicated way. Finally we shall show that the uniform part of the free energy density reduces to an anchoring term plus a term similar to the one connected with the K_{13}-elastic term. The connection between this term, which in the past was interpreted as the source of the sub-surface deformation, and the uniform part of the free energy density is discussed. Our conclusion about this term is that, even if it can be interpreted as an effective splay–bend elastic constant, it is not useful for an elastic description of nematic liquid crystals. According to our view, an elastic description of a nematic liquid crystal close to a surface has to be made in terms of the Frank elastic constants k_{11}, k_{22}, k_{33} and of a delocalized surface field which describes the distorting effects of the incomplete interaction.

The paper is organized as follows. In §2 the integral equation satisfied by the director field minimizing $\mathscr{F}$ given by equation (1) is deduced. This integral equation is the fundamental equation for a non-local description of nematic liquid crystals. It takes the place of the well known Euler–Lagrange equation used in the theory of elasticity of these media. Particular types of intermolecular interaction laws are considered in §3 and §4. In §5 a superposition of two simple intermolecular interactions is analysed. There we show that the existence of the sub-surface deformation in tilted nematic samples follows immediately, without any calculations, from the integral equation obtained before. The interaction of the nematic liquid crystal with an external field, in our non-local approach, is discussed in §6. The elastic description of a nematic liquid crystal, with special emphasis on the homogeneous part of the elastic energy density, and on the linear terms in the first and second derivatives is presented in §7. In §8 the sources of the sub-surface deformation in tilted nematic samples are analysed. There, we show that the sub-surface deformation exists whenever the homogeneous part of the elastic energy density in the surface layer depends on the nematic director. In this case it is possible to introduce an effective splay–bend elastic constant connected to this functional dependence. In §9 the main results of our paper are critically discussed.

2. Non-local description

We shall assume that the nematic liquid crystal occupies the $z \geqslant 0$ half space. When we do the slab approximation, the surfaces of the slab will be assumed to be at $z = \pm d/2$. The nematic director $\mathbf{n}$ is assumed to be everywhere parallel to the (y, z)-plane and given by $\mathbf{n}(z) = (0, \sin\phi(z), \cos\phi(z))$, where $\phi(z)$ is the tilt angle. In this framework the total energy per unit surface of the sample due to the nematic–nematic interaction is given by

$$\mathscr{F}_{\mathrm{b}} = \int_0^\infty \int_0^\infty f[\phi(z), \phi(z'); z, z']\,\mathrm{d}z\,\mathrm{d}z' \qquad (2)$$

where $f[\phi(z), \phi(z'); z, z']$ is obtained by integrating $g[\phi(z), \phi(z'); x, y, z, x', y', z']$ over x, y, x' and y'. A simple analysis shows that

$$f[\phi(z), \phi(z'); z, z'] = f[\phi(z'), \phi(z); z', z]. \qquad (3)$$

Let us consider first the case of strong anchoring, for which $\phi_0 = \phi(0)$ is fixed by the short range nematic–substrate interactions. In this case the function $\phi(z)$ minimizing $\mathscr{F}_{\mathrm{b}}$ given by equation (2) can be deduced by operating in the usual manner [40]. Let $\bar{\phi}(z)$ be the function minimizing $\mathscr{F}_b$, and

$$\phi(z)=\bar{\phi}(z)+\varepsilon\eta(z) \tag{4}$$

a function close to $\bar{\phi}(z)$ in the variational sense [41]. ε is a small parameter and $\eta(z)$ an arbitrary function of C_1-class. Due to the strong anchoring hypothesis at $z=0$, $\phi(0)=\bar{\phi}(0)=\phi_0$. Consequently $\eta(0)=0$. However this condition does not play any important role here. By substituting equation (4) into (2) we obtain at the first order in ε

$$\mathscr{F}_b(\varepsilon)=\mathscr{F}_b(0)+\varepsilon\int_0^\infty\int_0^\infty\left\{\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z)}\eta(z)+\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z')}\eta(z')\right\}\mathrm{d}z\,\mathrm{d}z'. \tag{5}$$

From equation (3) it follows that

$$\int_0^\infty\int_0^\infty\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z')}\eta(z')\,\mathrm{d}z\,\mathrm{d}z'=\int_0^\infty\int_0^\infty\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z)}\eta(z)\,\mathrm{d}z\,\mathrm{d}z'. \tag{6}$$

Consequently expansion (5) becomes

$$\mathscr{F}_b(\varepsilon)=\mathscr{F}_b(0)+2\varepsilon\int_0^\infty\int_0^\infty\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z)}\eta(z)\,\mathrm{d}z\,\mathrm{d}z'. \tag{7}$$

Since $\bar{\phi}(z)$ for the hypothesis minimizes $\mathscr{F}_b$, it follows that

$$\left(\frac{\mathrm{d}\mathscr{F}_b}{\mathrm{d}\varepsilon}\right)_{\varepsilon=0}=0. \tag{8}$$

Hence from equation (7) one deduces

$$\int_0^\infty\int_0^\infty\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z)}\eta(z)\,\mathrm{d}z\,\mathrm{d}z'=0 \tag{9}$$

$\forall\eta(z)\in C_1$-class. As well known from equation (9) it follows that [41]

$$\int_0^\infty\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z)}\mathrm{d}z'=0 \tag{10}$$

which is an integral equation. Hence the continuous functions extremizing the functional (2) are solutions of integral equation (10).

As an example, let us consider the case in which

$$f[\phi(z),\phi(z');z,z']=K(z,z')[\phi(z')-\phi(z)]^2 \tag{11}$$

where the kernel $K(z,z')$ is of the kind

$$K(z,z')=A\exp\left[-\left(\frac{z'-z}{\lambda}\right)^2\right]. \tag{12}$$

In equation (12), λ is a molecular dimension and A a positive constant. As is evident from equation (11), $f=0$ for $\phi(z')=\phi(z)$, otherwise $f\geqslant 0$. Hence f tends to induce homogeneous orientation. Substituting equation (11) into (10) one obtains

$$\phi(z)\int_0^\infty K(z,z')\,\mathrm{d}z'=\int_0^\infty K(z,z')\phi(z')\,\mathrm{d}z' \tag{13}$$

which is a homogeneous Freedholm integral equation [42]. Hence in this non-local description, the actual tilt angle distribution is the solution of equation (13). A simple inspection shows that $\phi(z)=\phi_0$ is a solution of equation (13) which minimizes the total energy per unit surface $\mathscr{F}$ given by (2). In fact for $\phi(z)=\phi_0$, $\mathscr{F}(\phi_0)=0$, whereas for all other $\phi(z)$, $\mathscr{F}(\phi(z))\geqslant 0$. It follows that in this case no sub-surface deformation exists. If the sample is a slab of thickness d, whose surfaces at $z=-d/2$ and $z=d/2$ are characterized by the surface tilt angles $\phi_1=\phi(-d/2)$ and $\phi_2=\phi(d/2)$, equation (13) writes

$$\phi(z)\int_{-d/2}^{d/2}K(z,z')\,\mathrm{d}z'=\int_{-d/2}^{d/2}K(z,z')\phi(z')\,\mathrm{d}z'. \tag{14}$$

From equation (14) we derive again that if $\phi_1=\phi_2=\phi_0$, then $\phi(z)=\phi_0$, $\forall z\in[-d/2,d/2]$. Other situations in which $\phi_1\neq\phi_2$ can be analysed by solving directly equation (14). However, this aspect of the problem is not very important in this context. It has been discussed in [43].

3. Maier–Saupe interaction

The Maier–Saupe interaction [44] is of the kind

$$g_{\mathrm{MS}}=-C_{\mathrm{MS}}\exp(r/r_e)^2(\mathbf{n}\ \mathbf{n}')^2 \tag{15}$$

where C_{MS} is a positive constant and r_e a molecular dimension [21]. Using g_{MS}, $f[\phi(z),\phi(z');z,z']$ appearing in equation (2) is found to be, besides a $\phi(z)$-independent contribution

$$f[\phi(z),\phi(z');z,z']=\mu(z,z')\sin^2[\phi(z')-\phi(z)] \tag{16}$$

where the kernel $\mu(z,z')$ is given by [21]

$$\mu(z,z')=D_{\mathrm{MS}}\exp\left[-\left(\frac{z'-z}{r_e}\right)^2\right] \tag{17}$$

and D_{MS} is a new positive constant. Substituting equation (16) into (10) one finds

$$\int_0^\infty\mu(z,z')\sin\{2[\phi(z')-\phi(z)]\}\,\mathrm{d}z'=0 \tag{18}$$

which has the solution $\phi(z)=\phi_0$, $\forall z\in(0,\infty)$. Hence, in this case also the sub-surface deformation is absent. In the slab approximation, discussed at the end of the previous section, equation (18) writes

$$\int_{-d/2}^{d/2} \mu(z, z') \sin\{2[\phi(z') - \phi(z)]\}\, \mathrm{d}z' = 0 \qquad (19)$$

whose boundary conditions are $\phi_1 = \phi(-d/2)$ and $\phi_2 = \phi(d/2)$, as discussed above. Again if $\phi_1 = \phi_2 = \phi_0$, $\phi(z) = \phi_0$, $\forall z \in [-d/2, d/2]$ is a solution of equation (19), which minimizes the total energy per unit surface $\mathscr{F}$, because $\mathscr{F}(\phi_0) = 0$, whereas for any other $\phi(z)$, $\mathscr{F}(\phi(z)) \geqslant 0$. If $\phi_1 \neq \phi_2$, $\phi(z)$ is not constant across the sample. In this situation one obtains from equation (19)

$$\cos[2\phi(z)] \int_{-d/2}^{d/2} \mu(z, z') \sin[2\phi(z')]\, \mathrm{d}z' = \sin[2\phi(z)] \int_{-d/2}^{d/2} \mu(z, z') \cos[2\phi(z')]\, \mathrm{d}z' \qquad (20)$$

which is a kind of non-linear integral equation of the Freedholm type.

4. Nehring-Saupe interaction

The Nehring-Saupe interaction [25] is of the kind

$$g_{\mathrm{NS}} = -\frac{C_{\mathrm{NS}}}{r^6}[\mathbf{n}\ \mathbf{n}' - 3(\mathbf{n}\ \mathbf{u})(\mathbf{n}'\ \mathbf{u})]^2 \qquad (21)$$

where C_{NS} is a positive constant and $\mathbf{u} = \mathbf{r}/r$. By using equation (21), $f[\phi(z), \phi(z'); z, z']$ appearing in equation (2) is found to be [33, 21]

$$\begin{aligned} f[\phi(z), \phi(z'); z, z'] = C_{\mathrm{NS}}\{&\alpha(z, z')[\cos^2\phi(z) + \cos^2\phi(z')] \\ &+ \beta(z, z')\cos^2\phi(z)\cos^2\phi(z') \\ &+ \gamma(z, z')\sin[2\phi(z)]\sin[2\phi(z')]\} \end{aligned} \qquad (22)$$

where, besides a multiplicative constant,

$$\alpha(z, z') = \begin{cases} -3(z'-z)^{-4}, & \text{for } |z'-z| \geqslant r_{\mathrm{e}}, \\ 63(z'-z)^4 - 88(z'-z)^2 + 22, & \text{for } |z'-z| \leqslant r_{\mathrm{e}} \end{cases} \qquad (23)$$

$$\beta(z, z') = \begin{cases} -9(z'-z)^{-4}, & \text{for } |z'-z| \geqslant r_{\mathrm{e}}, \\ -171(z'-z)^4 + 200(z'-z)^2 - 38, & \text{for } |z'-z| \leqslant r_{\mathrm{e}} \end{cases} \qquad (24)$$

and

$$\gamma(z, z') = \begin{cases} 0, & \text{for } |z'-z| \geqslant r_{\mathrm{e}}, \\ 36(z'-z)^4 - 40(z'-z)^2 + 4, & \text{for } |z'-z| \leqslant r_{\mathrm{e}}. \end{cases} \qquad (25)$$

By substituting equation (22) into (10), one has

$$\sin[2\phi(z)]\left\{\int_0^\infty \alpha(z, z')\, \mathrm{d}z' + \int_0^\infty \beta(z, z')\cos^2\phi(z')\, \mathrm{d}z'\right\} = \cos[2\phi(z)]\int_0^\infty 2\gamma(z, z')\sin[2\phi(z')]\, \mathrm{d}z'. \qquad (26)$$

If $\phi_0 = 0$ or $\phi_0 = \pi/2$, $\phi(z) = 0$ or $\phi(z) = \pi/2$, $\forall z \in (0, \infty)$ is a solution of equation (26). In this case no sub-surface deformation exists. However, if ϕ_0 is different from 0 or $\pi/2$, $\phi(z) = \phi_0$ is no longer a solution of the integral equation (26). In this case a sub-surface deformation localized close to the surface exists and occurs over a few molecular lengths. In the slab approximation equation (26) writes

$$\sin[2\phi(z)]\left\{\int_{-d/2}^{d/2} \alpha(z, z')\, \mathrm{d}z' + \int_{-d/2}^{d/2} \beta(z, z')\cos^2\phi(z')\, \mathrm{d}z'\right\} = \cos[2\phi(z)]\int_{-d/2}^{d/2} 2\gamma(z, z')\sin[2\phi(z')]\, \mathrm{d}z' \qquad (27)$$

where, in the strong anchoring case, $\phi_1 = \phi(-d/2)$ and $\phi_2 = \phi(d/2)$.

5. Superposition of the Maier–Saupe and Nehring–Saupe interactions

Let us consider now the more general case in which f appearing in equation (2) is a superposition of the Maier–Saupe and Nehring–Saupe interactions of the kind

$$f = (1-e)f_{\mathrm{MS}} + e f_{\mathrm{NS}} \qquad (28)$$

where f_{MS} and f_{NS} are given by equations (16) and (22) reported above, and $0 \leqslant e \leqslant 1$. In this case equation (10) gives

$$\begin{aligned} \cos[2\phi(z)]&\int_0^\infty [(1-e)\mu(z, z') + 2e\gamma(z, z')]\sin[2\phi(z')]\, \mathrm{d}z' \\ &= \sin[2\phi(z)]\left\{e\int_0^\infty \left[\alpha(z, z') + \frac{1}{2}\beta(z, z')\right]\mathrm{d}z'\right. \\ &\quad \left.+ \int_0^\infty \left[(1-e)\mu(z, z') + \frac{e}{2}\beta(z, z')\right]\cos[2\phi(z')]\, \mathrm{d}z'\right\}. \end{aligned} \qquad (29)$$

This equation shows that the homogeneous orientation $\phi(z) = \phi_0$, $\forall z \in (0, \infty)$ extremizes the total energy only if $\phi_0 = 0$ or $\phi_0 = \pi/2$. For ϕ_0 different from these values, a sub-surface deformation exists. If $e \ll 1$, i.e. the Nehring–Saupe contribution to f is very small, equation (29) may be solved in a perturbative way. In fact, for $e = 0$,

$\phi(z)=\phi_0$ is a solution of equation (29). In the limit of small e we put

$$\phi(z)=\phi_0+e\varphi(z). \qquad (30)$$

By substituting equation (30) into (29), at the first order in e one finds that $\varphi(z)$ is a solution of the integral equation

$$\int_0^\infty \mu(z,z')\varphi(z')\,\mathrm{d}z'-\varphi(z)\int_0^\infty \mu(z,z')\,\mathrm{d}z'=h(\phi_0;z) \qquad (31)$$

where $h(\phi_0;z)$ is given by

$$h(\phi_0;z)=\frac{1}{2}\sin(2\phi_0)\left[\int_0^\infty \alpha(z,z')\,\mathrm{d}z' + \cos^2\phi_0\int_0^\infty \beta(z,z')\,\mathrm{d}z' - 2\cos(2\phi_0)\int_0^\infty \gamma(z,z')\,\mathrm{d}z'\right]. \qquad (32)$$

Equation (31) is of the kind

$$\varphi(z)=\int_0^\infty H(z,z')\varphi(z')\,\mathrm{d}z'-L(\phi_0;z) \qquad (33)$$

where

$$H(z,z')=\frac{\mu(z,z')}{\int_0^\infty \mu(z,z')\,\mathrm{d}z'}$$

and

$$L(\phi_0;z)=\frac{h(\phi_0;z)}{\int_0^\infty \mu(z,z')\,\mathrm{d}z'}. \qquad (34)$$

As is well known from the theory of integral equations, the solutions of equation (33) can be obtained by means of iterated kernels [42]. The final result is that $\varphi(z)$ is given by

$$\varphi(z)=-L(\phi_0;z)+\int_0^\infty \mathscr{H}(z,z')L(\phi_0;z')\,\mathrm{d}z' \qquad (35)$$

where $\mathscr{H}(z,z')$ is the iterated kernel [42]. From equations (35) and (32) it follows that the amplitude of the sub-surface deformation vanishes for $\phi_0=0$ and $\phi_0=\pi/2$, due to the presence of the factor $\sin(2\phi_0)$. This result agrees with that obtained in another way [21, 22].

6. Interaction of a nematic liquid crystal with an external field

In the previous sections we have considered the total energy per unit surface due to the intermolecular interaction. In our non-local description it is given by equation (2) in which $f[\phi(z),\phi(z');z,z']$ depends on the intermolecular interaction. Let us assume now that the nematic liquid crystal is submitted to an external field, whose interaction with the nematic molecules is described by $f_e[\phi(z);z]$. This field could be the one describing the interaction among the molecules of the nematic liquid crystal and those of the solid substrate limiting the sample. Alternatively, it could be an external magnetic or electric field. If an external field is taken into account the total energy per unit surface, in the slab approximation, is given by

$$\mathscr{F}=\mathscr{F}_b+\mathscr{F}_e=\int_{-d/2}^{d/2}\int_{-d/2}^{d/2} f[\phi(z),\phi(z');z,z']\,\mathrm{d}z\,\mathrm{d}z' + \int_{-d/2}^{d/2} f_e[\phi(z);z]\,\mathrm{d}z. \qquad (36)$$

An analysis similar to the one reported in §2 shows that the continuous function extremizing $\mathscr{F}$ given by equation (36) is a solution of the integral equation

$$2\int_{-d/2}^{d/2}\frac{\partial f[\phi(z),\phi(z');z,z']}{\partial\phi(z)}\,\mathrm{d}z'+\frac{\partial f_e[\phi(z);z]}{\partial\phi(z)}=0. \qquad (37)$$

As underlined above, the external field interaction has to take into account the interaction with the substrate, $f_s[\phi(z);z]$, and with the magnetic or electric field acting on the nematic, $f_f[\phi(z);z]$. Usually $f_s[\phi(z);z]$ is different from zero only in two thin surface layers close to the bounding walls. On the contrary $f_f[\phi(z);z]$ depends on z only through $\phi(z)$, because the external fields can often be considered position independent. Simple expressions for these energy densities are

$$f_s[\phi(z);z]=w_1(z)\sin^2[\phi_1-\phi(z)]+w_2(z)\sin^2[\phi_2-\phi(z)] \qquad (38)$$

and

$$f_f[\phi(z);z]=-\frac{1}{2}\varepsilon_a E^2\cos^2[\phi_E-\phi(z)]. \qquad (39)$$

In equation (38) $\phi_{1,2}$ are the easy directions and $w_{1,2}$ the anchoring energy strengths [45]. In the strong anchoring case considered above $w_i(z)=W_i\delta(z\pm d/2)$, where $\delta(z)$ is the Dirac's function, and $W_i\to\infty$. In equation (39) ε_a is the macroscopic anisotropy of the nematic liquid crystal with respect to the external field $\mathbf{E}$ at an angle ϕ_E with the z-axis [46].

An analysis of the same kind as presented above shows that if $\phi_1=\phi_2=\phi_0$, different from 0 and $\pi/2$, and $E=0$, the homogeneous orientation $\phi(z)=\phi_0$, $\forall z\in[-d/2,d/2]$ is a solution of equation (37) if $f=f_{MS}$, whereas if $f=f_{NS}$ it is not. The influence of the penetration range of the surface forces on the sub-surface deformation, taking into account the spatial variation of the scalar order parameter, when the interaction energy g is a special kind of modified Maier–Saupe interaction, has been discussed recently by Texeira [36]. If $\phi_1 \neq \phi_2$ and $E \neq 0$, there is a sharp variation of the nematic orientation localized close to the surfaces, and a smooth spatial variation localized over a length which is proportional to $1/E$.

7. Elastic description of a nematic liquid crystal

In the previous sections we have presented a non-local description of a nematic liquid crystal. It is based on the total energy per unit surface given by equation (2), where $f[\phi(z), \phi(z'); z, z']$ is evaluated directly from the intermolecular interaction energy. In the analysis we have assumed the problem to be planar and one dimensional. However the generalization to three dimensional problems does not present any conceptual difficulty. In this section we now show that it is possible to derive from equation (2) an elastic energy density. This analysis is not new; it was discussed several years ago by Nehring and Saupe [25]. Some years ago the analysis by Nehring and Saupe was critically discussed by Somoza and Tarazona [47] and by Texeira *et al.* [48], mainly in connection with the meaning of the surface-like elastic constants. Recently Yokoyama [39] has shown that linear terms in the derivatives of any order give no contribution to the total energy per unit surface given by equation (2). This conclusion implies that the contribution to the elastic energy of terms like k_1 and K_{13} balance each other. In this framework, the source of the sub-surface deformation is not the K_{13}-elastic constant. This result has already been partially discussed by Faetti and Riccardi [34, 38]. In this section we shall show that the homogeneous part of f could be considered to be the source of the sub-surface deformation.

To obtain the elastic approximation of equation (2), let us rewrite $\mathscr{F}_b$ as follows

$$\mathscr{F}_b = \frac{1}{2}\left\{\int_{-d/2}^{d/2}\int_{-d/2}^{d/2} f[\phi(z), \phi(z'); z, z']\,dz\,dz' + \int_{-d/2}^{d/2}\int_{-d/2}^{d/2} f[\phi(z'), \phi(z); z', z]\,dz\,dz'\right\}. \quad (40)$$

In the first addendum the reference state is the one described by $\phi(z)$, and in the second addendum it is the one described by $\phi(z')$. For small deviations from the reference state we have

$$\phi(z') = \phi(z) + \delta\phi(z, z') \quad (41)$$

for the first contribution, and

$$\phi(z) = \phi(z') + \delta\phi(z', z) \quad (42)$$

for the second contribution. As is evident from equations (41) and (42)

$$\delta\phi(z', z) = -\,\delta\phi(z, z'). \quad (43)$$

In the limit of small deviations from the reference state, simple calculations give

$$f[\phi(z), \phi(z'); z, z'] = F[\phi(z); z, z'] + A[\phi(z); z, z']\delta\phi(z, z') + \frac{1}{2}C[\phi(z); z, z'][\delta\phi(z, z')]^2 \quad (44)$$

and

$$f[\phi(z'), \phi(z); z', z] = F[\phi(z'); z', z] + A[\phi(z'); z', z]\delta\phi(z', z) + \frac{1}{2}C[\phi(z'); z', z][\delta\phi(z', z)]^2 \quad (45)$$

where

$$F[\phi(z); z, z'] = f[\phi(z), \phi(z); z, z'] \quad (46)$$

$$A[\phi(z); z, z'] = \left\{\frac{\partial f[\phi(z), \phi(z'); z, z']}{\partial\phi(z')}\right\}_{\phi(z')=\phi(z)} \quad (47)$$

and

$$C[\phi(z); z, z'] = \left\{\frac{\partial^2 f[\phi(z), \phi(z'); z, z']}{\partial\phi(z')^2}\right\}_{\phi(z')=\phi(z)}. \quad (48)$$

In a similar manner are defined $F[\phi(z'); z', z]$, $A[\phi(z'); z', z]$ and $C[\phi(z'); z', z]$. By substituting the expansions (44) and (45) into equation (40), we obtain

$$\mathscr{F}_b = \mathscr{F}_{bu} + \mathscr{F}_{b1} + \mathscr{F}_{b2}$$

where

$$\mathscr{F}_{bu} = \int_{-d/2}^{d/2}\int_{-d/2}^{d/2} F[\phi(z); z, z']\,dz\,dz' \quad (49)$$

is the total energy per unit surface at the reference state

$$\mathscr{F}_{b1} = \frac{1}{2}\int_{-d/2}^{d/2}\int_{-d/2}^{d/2} \{A[\phi(z); z, z']\delta\phi(z, z') + A[\phi(z'); z', z]\delta\phi(z', z)\}\,dz\,dz' \quad (50)$$

is the term of the first order in $\delta\phi$, and

$$\mathscr{F}_{b2} = \frac{1}{4}\int_{-d/2}^{d/2}\int_{-d/2}^{d/2} \{C[\phi(z); z, z'][\delta\phi(z, z')]^2 + C[\phi(z'); z', z][\delta\phi(z', z)]^2\}\,dz\,dz' \quad (51)$$

is the term of second order in the variation with respect to the reference state. Since

$$f[\phi(z), \phi(z'); z, z'] = f[\phi(z), \phi(z'); z', z] \quad (52)$$

because the interaction energy depends only on $|z'-z|$, we deduce that

$$A[\phi(z'); z', z] = A[\phi(z'); z, z']$$

and

$$C[\phi(z'); z', z] = C[\phi(z'); z, z']. \tag{53}$$

Hence, by taking into account equation (43), $\mathscr{F}_{\mathrm{b1}}$ and $\mathscr{F}_{\mathrm{b2}}$ can be rewritten in the form

$$\mathscr{F}_{\mathrm{b1}} = \frac{1}{2}\int_{-d/2}^{d/2}\int_{-d/2}^{d/2}\{A[\phi(z); z, z'] - A[\phi(z'); z, z']\}\,\delta\phi(z, z')\,\mathrm{d}z\,\mathrm{d}z' \tag{54}$$

and

$$\mathscr{F}_{\mathrm{b2}} = \frac{1}{4}\int_{-d/2}^{d/2}\int_{-d/2}^{d/2}\{C[\phi(z); z, z'] + C[\phi(z'); z, z']\}\,[\delta\phi(z, z')]^2\,\mathrm{d}z\,\mathrm{d}z'. \tag{55}$$

As is evident from equation (54), $\mathscr{F}_{\mathrm{b1}}$ is actually of second order in $\delta\phi(z, z')$, because

$$A[\phi(z); z, z'] - A[\phi(z'); z, z'] = B[\phi(z); z, z']\,\delta\phi(z, z') \tag{56}$$

where

$$B[\phi(z); z, z'] = -\left\{\frac{\partial A[\phi(z'); z, z']}{\partial\phi(z')}\right\}_{\phi(z')=\phi(z)}. \tag{57}$$

Consequently at the second order in $\delta\phi(z, z')$, the total energy per unit surface is given by

$$\mathscr{F}_{\mathrm{b}} = \mathscr{F}_{\mathrm{bu}} + \frac{1}{2}\int_{-d/2}^{d/2}\int_{-d/2}^{d/2} D[\phi(z); z, z'][\delta\phi(z, z')]^2\,\mathrm{d}z\,\mathrm{d}z' \tag{58}$$

where we have put

$$D[\phi(z); z, z'] = B[\phi(z); z, z'] + C[\phi(z); z, z']. \tag{59}$$

Expression (58) can be used to build an elastic theory for nematic liquid crystals (for planar deformations) in the slab approximation. It shows clearly that linear terms in $\delta\phi(z, z')$ are absent, when the reference state used for the elastic description is the stable one.

8. The sources of the sub-surface deformation

In the non-local analysis of the nematic liquid crystal profile we have shown that the Nehring–Saupe intermolecular interaction g_{NS} gives rise to a sub-surface deformation, except in the special cases of planar or homeotropic surface alignments. As discussed elsewhere, a sharp variation of the nematic orientation close to the substrate exists whenever g depends not only on $\mathbf{n}\ \mathbf{n}'$, but also on $\mathbf{n}\ \mathbf{u}$ and $\mathbf{n}'\ \mathbf{u}$. The origin of the sub-surface deformation is then the functional dependence of g on $\mathbf{n}\ \mathbf{u}$ and $\mathbf{n}'\ \mathbf{u}$. Since in the Nehring–Saupe model the k_1 (spontaneous splay) and the K_{13} (splay–bend)-elastic constants depend also on this functional dependence, the sub-surface deformation was considered to be due to elastic contributions, linear in the first and second order derivatives, to the elastic energy density [49]. More recently it has been suggested that the homogeneous part of the energy density $F[\phi(z); z, z']$ could also contribute to the sub-surface deformation [20–23]. Now we wish to show that:

(i) the linear elastic contributions connected to k_1 and K_{13}, renormalize the usual Frank's elastic constants and hence they do not induce any sub-surface deformation;
(ii) the homogeneous part of the energy density is the only one responsible for the deformation localized close to surface;
(iii) by means of $F[\phi(z); z, z']$ it is possible to define an effective K_{13}-elastic constant, connected to an elastic term similar to the one introduced by Nehring and Saupe.

To obtain an expression for the elastic density from equation (58), $\delta\phi(z, z')$ has to be expanded in power series of $(z'-z)$. As is well known, an elastic description works well only if the intermolecular interactions are short range. In this case $f[\phi(z), \phi(z'); z, z']$ is different from zero only for $|z'-z|$ of the order of a few molecular dimensions. The same conclusion holds true for $A[\phi(z); z, z']$, $B[\phi(z); z, z']$, $C[\phi(z); z, z']$ and $D[\phi(z); z, z']$, which are obtained from $f[\phi(z), \phi(z'); z, z']$. In this framework we have

$$\delta\phi(z, z') = \left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)_z (z'-z) + \frac{1}{2}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2}\right)_z (z'-z)^2 + \ldots \tag{60}$$

By substituting equation (60) into (58) simple calculations give

$$\mathscr{F}_{\mathrm{b}} = \mathscr{F}_{\mathrm{bu}} + \frac{1}{2}\int_{-d/2}^{d/2} k[\phi(z); z]\left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)^2 \mathrm{d}z \tag{61}$$

at the lowest order. In equation (61), $k[\phi(z); z]$ plays the role of elastic constant, and is defined by

$$k[\phi(z); z] = \int_{-d/2}^{d/2} (z'-z)^2 D[\phi(z); z, z']\,\mathrm{d}z'. \tag{62}$$

In the bulk, $k[\phi(z); z]$ does not depend explicitly on z if $f[\phi(z), \phi(z'); z, z']$ is sufficiently peaked around $z'=z$, and hence $k = k[\phi(z)]$. Since in equation (61) there are no terms linear in $\mathrm{d}\phi/\mathrm{d}z$ or in $\mathrm{d}^2\phi/\mathrm{d}z^2$, it follows that the contributions to the elastic energy connected to the spontaneous splay (k_1), or to the splay–bend (K_{13}) elastic constants cancel each other. Hence they cannot be the source of the sub-surface deformation. Let us consider now the homogeneous part of the total energy. It is given by equation (49), that we rewrite as

$$\mathcal{F}_{\mathrm{bu}} = \int_{-d/2}^{d/2} G[\phi(z); z]\,\mathrm{d}z \tag{63}$$

where

$$G[\phi(z); z] = \int_{-d/2}^{d/2} F[\phi(z); z, z']\,\mathrm{d}z'. \tag{64}$$

In the bulk, i.e. for z different from $\pm d/2$ more than a few molecular dimensions, G reduces to a constant if $f[\phi(z), \phi(z'); z, z']$ is sufficiently peaked around $z = z'$. For the sake of simplicity let us consider the case in which the nematic sample occupies the $z \geqslant 0$ half space. In this case equations (63) and (64) write

$$\mathcal{F}_{\mathrm{bu}} = \int_{0}^{\infty} G[\phi(z); z]\,\mathrm{d}z \tag{65}$$

and

$$G[\phi(z); z] = \int_{0}^{\infty} F[\phi(z); z, z']\,\mathrm{d}z'. \tag{66}$$

In the limit of small sub-surface deformation, for z close to the limiting surface we have

$$\phi(z) = \phi_0 + \left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)_0 z + \ldots \tag{67}$$

whereas in the bulk $\phi(z) = \phi_{\mathrm{b}}$. Substituting equation (67) into (66) and the result into (65) we obtain

$$\mathcal{F}_{\mathrm{bu}} = \mathcal{F}_{\mathrm{bu}}(\phi_0) + \mathcal{R}(\phi_0)\left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)_0 \tag{68}$$

where

$$\mathcal{F}_{\mathrm{bu}}(\phi_0) = \int_{0}^{\infty} G(\phi_0; z)\,\mathrm{d}z \tag{69}$$

and

$$\mathcal{R}(\phi_0) = \int_{0}^{\infty} z \left\{\frac{\partial G[\phi(z); z]}{\partial \phi(z)}\right\}_{\phi(z)=\phi_0} \mathrm{d}z. \tag{70}$$

A simple analysis reported elsewhere [21, 22] shows that $\mathcal{R}(\phi_0) = R\sin(2\phi_0)$, where R still depends on ϕ_0, but it does not vanish for $\phi_0 = 0$ and for $\phi_0 = \pi/2$. Hence equation (68) becomes

$$\mathcal{F}_{\mathrm{bu}} = \mathcal{F}_{\mathrm{bu}}(\phi_0) + R\sin(2\phi_0)\left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)_0. \tag{71}$$

From equation (71) we can conclude that the homogeneous part of the total energy can be separated into an intrinsic anchoring energy $\mathcal{F}_{\mathrm{bu}}(\phi_0)$ and a term having the same structure as that of the K_{13}-elastic term proposed by Nehring and Saupe. It follows that R could be interpreted as an 'effective' splay–bend elastic constant. However, this 'effective' elastic constant is not useful for an elastic description of a nematic close to a substrate, because the relevant variational problem is ill posed [4–6].

It is possible to analyse the problem from another point of view. In the simple case under consideration the total energy is given by

$$\mathcal{F}_{\mathrm{b}} = \int_{0}^{\infty} \left\{ G[\phi(z); z] + \frac{1}{2} k[\phi(z); z]\left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)^2 \right\} \mathrm{d}z. \tag{72}$$

Let us consider strong anchoring on the limiting surface: $\phi(0) = \phi_0$. The nematic profile is obtained as usual by minimizing $\mathcal{F}_{\mathrm{b}}$ written above. The Euler–Lagrange equation for $\phi(z)$ is found to be

$$k[\phi(z); z]\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2} + \frac{1}{2}\frac{\partial k}{\partial \phi}\left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)^2 + \frac{\partial k}{\partial z}\frac{\mathrm{d}\phi}{\mathrm{d}z} - \frac{\partial G}{\partial \phi} = 0. \tag{73}$$

In the simple case in which k is $\phi(z)$-independent, this differential equation reduces to

$$k(z)\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2} + \frac{\partial k}{\partial z}\frac{\mathrm{d}\phi}{\mathrm{d}z} - \frac{\partial G}{\partial \phi} = 0. \tag{74}$$

Since G depends on ϕ by means of $\cos^2\phi$, the Euler–Lagrange equation may be rewritten finally as

$$k(z)\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2} + \frac{\partial k}{\partial z}\frac{\mathrm{d}\phi}{\mathrm{d}z} + \mathcal{U}(\phi, z)\sin(2\phi) = 0 \tag{75}$$

where

$$\mathcal{U}(\phi, z) = \frac{\partial G}{\partial(\cos^2\phi)}. \tag{76}$$

Equation (75) shows that:

(i) $\mathcal{U}(\phi, z)$ acts as an external distortion field,
(ii) if a deformation is already present, the z-dependence of the elastic constant also gives rise to a distortion.

Since $\mathcal{U}$ and $\partial k/\partial z \neq 0$ applies only in a surface layer whose thickness is of the order of the range of the forces responsible for the nematic phase, we can conclude that $\mathcal{U}$ and $\partial k/\partial z$ are sources of sub-surface deformations. Hence, in order to avoid ill posed problems, it is better to take into account the distorting effects of the incomplete nematic interaction by means of a delocalized surface field due to the spatial variation of the elastic constant and to the uniform part of the free energy density. Only in the case in which this quantity is $\phi(z)$-independent, and the sub-surface deformation disappears.

9. Conclusion

We have presented a non-local description of a nematic liquid crystal. By supposing a generic intermolecular interaction law, the total energy of the nematic sample has been formally evaluated by means of a generalized non-local functional. Minimizing this functional, we have shown that the actual nematic profile is a solution of an integral equation which substitutes the well known Euler–Lagrange equation used in the elastic theory. The existence of sub-surface deformation has been discussed by means of this integral equation. The non-local description has been made in the case of weak or strong anchoring, with or without an external field. We have also considered the elastic description of nematic liquid crystals and shown that the source of the sub-surface deformation is the tilt dependence of the homogeneous part of the total energy.

During this work we had useful discussions, with S. Faetti, P. Galatola, C. Oldano, A. Strigazzi and E. Virga. Many thanks are due also to H. Yokoyama and P. I. C. Texeira for reprints of their papers sent to us before publication.

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