This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

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

A surface-induced transition in polymeric nematics

Paolo Biscari; Epifanio G. Virga

Online publication date: 06 August 2010

To cite this Article Biscari, Paolo and Virga, Epifanio G.(1997) 'A surface-induced transition in polymeric nematics', Liquid Crystals, 22: 4, 419 — 425

To link to this Article: DOI: 10.1080/026782997209135

URL: http://dx.doi.org/10.1080/026782997209135

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1997, VOL. 22, NO. 4, 419–425

A surface-induced transition in polymeric nematics

by PAOLO BISCARI†*, EPIFANIO G. VIRGA‡

†Dipartimento di Matematica, Politecnico di Milano, Via Bonardi 9, 20133 Milan, Italy

‡Dipartimento di Matematica, Università di Napoli Federico II, Via Claudio 21, 80125 Naples, Italy

(*Received 27 June 1996; in final form 28 October 1996; accepted 1 November 1996*)

New polymeric liquid crystals can be treated as standard nematic liquid crystals when only their bulk properties are at issue, but they exhibit peculiar surface properties. The most striking one is that biaxial distributions may be induced on a confining surface. On continuously varying the surface anchoring conditions, we find a first-order phase transition from planar to homeotropic alignment in the bulk. Moreover, the decay towards these uniaxial states is radically different in the two cases: it is asymptotically exponential in the former, whereas it happens abruptly at a *finite* depth in the latter. There is precisely one surface biaxial distribution that induces bistability between these decay modes: it depends on the elastic constants in the Landau–de Gennes free energy functional. The analysis of the model we propose can prove useful in detecting the sign of the difference between splay and bend constants.

1. Introduction

A surprising result has recently been obtained by Matoussi, Berry, and Patterson [1] through non-linear optical measurements relying on third harmonic generation made on solutions of PBZT, a nematogenic polymer. They have observed a surface biaxial layer of thickness comparable with the wavelength of the incoming light, which in those experiments was approximately 1·5 and 2·0 microns.

Here we present a mathematical model which was essentially motivated by the observations just recalled. It is phrased within the Landau–de Gennes formalism and it aims at describing how a biaxial surface phase can decay towards a uniaxial phase in the bulk, which indeed minimizes the internal potential. We do not ask ourselves how the surface induces biaxiality: we accept it as a fact, although in [2] we have already proposed a model for it, which applies to uniaxial molecules. Thus, our work complements that of Sluckin and Poniewierski [3, 4], further pursued by L'vov, Hornreich, and Allender [5] and Kothekar, Allender, and Hornreich [6]. In the model studied by these authors, an anchoring energy of variable strength is acting on the surface; depending on the values of both the anchoring strength and the surface temperature, they found either uniaxial or biaxial phases to be energetically preferred within a surface layer, and they described the various possible transitions between them.

We find a transition too: the surface biaxiality decays in the bulk in one of two drastically different ways, depending on the boundary conditions prescribed on the plane delimiting a half-space. The order tensor $\mathbf{Q}$ employed in Landau–de Gennes theory is symmetric and traceless; when it has two equal eigenvalues, it represents a uniaxial state with the optic axis orthogonal to its eigenvectors with equal eigenvalues. In our model the normal to the plane boundary is everywhere taken as an eigenvector of $\mathbf{Q}$; a tensor subject to this constraint may represent uniaxial states with the optic axis either parallel or orthogonal to the surface, which we will refer to as *planar* and *homeotropic*, respectively.

It is shown below that the biaxial states prescribed on the surface can be divided into two classes: from one, these states decay *asymptotically* according to an exponential law to a planar uniaxial state, whereas from the other they reach a homeotropic uniaxial state abruptly at a *finite* depth. In both cases the surface biaxial state does not persist for long in the bulk, but the two decay modes, which become bistable for a definite boundary condition, are quite different. While the former mode could be easily anticipated, the latter one was of some surprise to us: it is very reminiscent of the scenario that Palffy-Muhoray, Gartland, and Kelly call *eigenvalue exchange* in [7]. They studied a hybrid nematic cell, which may become biaxial away from the bounding plates, where two different uniaxial states are enforced, with the optic axes at right angles (see also [8] for a similar study, under a simplifying assumption that made

---

*Author for correspondence.

the development purely analytical). However, what was a *uniaxial defect* (in the sense of [9]) right in the middle of the cell in their situation, is here a permanent state extending throughout the space from the singular plane where two eigenvalues of $\mathbf{Q}$ have come to a common value.

In Landau–de Gennes theory, the stable equilibrium distribution is arrived at by minimizing the free energy functional $\mathcal{F}[\mathbf{Q}]:=\int_{\mathcal{V}}(f_{\mathrm{el}}(\mathbf{Q},\nabla\mathbf{Q})+f_{\mathrm{LdG}}(\mathbf{Q}))\,\mathrm{d}v$, where $\mathcal{V}$ is the region in space occupied by the liquid crystal, and f_{el} and f_{LdG} are, respectively, the elastic and internal parts of the free energy density, which we will describe in detail in §2 below, where we also define the class of distributions we consider. Further, in §3 we study the minimizers of the free energy, and in §4 we compare their energies and find the absolute minimizer, thus arriving at the transition described above. Finally, in §5 we present the main conclusions of this paper.

2. Free energy functional

Since the minimization of the complete free energy functional in the whole manifold of order tensors is a formidable task, in this section we will look for a simpler class of distributions that, either by symmetry reasons or by physical considerations, appears to be fit to contain the absolute minimizer of our free energy functional.

Here the region $\mathcal{V}$ is to be the half-space that in Cartesian co-ordinates (x,y,z) is represented by $z\geqslant 0$; furthermore, we consider only boundary conditions independent of the co-ordinate x and y: $\mathbf{Q}|_{z=0}=\mathbf{Q}_0=\text{const.}$, so that, as a first simplification, we can take into account distributions depending only on the co-ordinate z.

2.1. *Internal potential*

To further restrict this class, we focus attention on the internal potential $f_{\mathrm{LdG}}(\mathbf{Q})$, usually defined as

$$f_{\mathrm{LdG}}(\mathbf{Q}):=a\,\mathrm{tr}\,\mathbf{Q}^2-b\,\mathrm{tr}\,\mathbf{Q}^3+\frac{c}{2}(\mathrm{tr}\,\mathbf{Q}^2)^2,$$

with $b,c>0$. As Lyutsyukov first noted [10], and Penzenstadler and Trebin then exploited [11], the parameter b is usually much smaller than both $|a|$ and c. In fact, b is responsible for the isotropic–nematic transition being first order, but most experiments show (see, e.g. [12], §2.3.1 and 2.3.4) that the latent heat of this transition is very small, so that the transition is only weakly first order.

These considerations allow us to minimize f_{LdG} in two steps. First we consider

$$f_{\mathrm{uni}}(\mathbf{Q}):=a\,\mathrm{tr}\,\mathbf{Q}^2+\frac{c}{2}(\mathrm{tr}\,\mathbf{Q}^2)^2.$$

We suppose f_{uni} to be strong enough to fix $\mathrm{tr}\,\mathbf{Q}^2$ equal to the value that makes it minimum. We regard this as a constraint, while retaining the term $-b\,\mathrm{tr}\,\mathbf{Q}^3$ in the free energy.

The minimum of f_{uni} depends on the sign of a: if $a\geqslant 0$, f_{uni} attains its minimum for $\mathbf{Q}=0$, which corresponds to the isotropic phase. On the contrary, when $a<0$ the minimizer satisfies

$$\mathrm{tr}\,\mathbf{Q}^2=-\frac{a}{c}=:\frac{2}{3}s_0^2.$$

Here and in the following, s_0 is taken as positive; it represents the *degree of orientation* preferred in the bulk. Note that, by fixing $\mathrm{tr}\,\mathbf{Q}^2$, we leave $\mathbf{Q}$ free to vary in a four-dimensional manifold, where every tensor is determined by one scalar and three angles, which determine both its eigenvalues and the orientation of its eigenvectors.

2.2. *Elastic energy*

We require the elastic free energy to be quadratic in the gradient of $\mathbf{Q}$, and at most quadratic in $\mathbf{Q}$. Under these assumptions, it was proven in [13] that f_{el} can be expressed as $f_{\mathrm{el}}(\mathbf{Q},\nabla\mathbf{Q})=f_2(\nabla\mathbf{Q})+f_3(\mathbf{Q},\nabla\mathbf{Q})+f_4(\mathbf{Q},\nabla\mathbf{Q})$, where f_3 is linear in $\mathbf{Q}$, while f_4 is quadratic. Explicit representations for the most general function f_{el} with these properties can also be found in [13], but they will not be needed here.

The function f_2 can be written as:

$$f_2(\nabla\mathbf{Q})=L_1|\nabla\mathbf{Q}|^2+L_2(\operatorname{div}\mathbf{Q})^2+L_3\sum_{ijk}Q_{ij,k}Q_{ik,j}, \tag{1}$$

where a comma denotes differentiation with respect to Cartesian co-ordinates, and L_1, L_2, and L_3 are related to Frank's elastic constants through $K_2=4s_0^2L_1$, $K_1=K_3=2s_0^2(2L_1+L_2+L_3)$. The second and third terms in equation (1) differ only by a surface term, so that, when a strong anchoring is prescribed on the boundary, f_2 introduces only two new elastic constants: namely L_1, and the combination $L_{23}:=L_2+L_3$. Actually, the second order approximation to f_{el} is unable to distinguish between K_1 and K_3. To overcome this problem we should consider also the higher order elastic terms, but here the opposite problem arises: f_3 has 6 additional constants, while f_4 has 13. To simplify the model, we must choose a criterion which selects the fewest new elastic constants able to separate K_1 from K_3. Table 4 of [13] collects all contributions to Frank's constants from a suitable mean field approximation to both f_3 and f_4. We see from it that among all 19 higher order elastic constants, only 9 contribute differently to K_1 than to K_3: precisely, 4 contribute more to K_1 than to K_3, whereas 5 do the opposite. To make economies, without preferring a single term to many, we choose those in the former group, assigning one and the same value to them, and we disregard all the others. Thus, we have

$$
\begin{aligned}
&f_3(\mathbf{Q},\nabla\mathbf{Q})\\
&\quad=\frac{\Lambda}{s_0}\left\{\mathbf{Q}\cdot(\operatorname{div}\mathbf{Q}\otimes\operatorname{div}\mathbf{Q})+\sum_{ijkl}Q_{ij}Q_{ik,l}Q_{jl,k}\right\},\\
&f_4(\mathbf{Q},\nabla\mathbf{Q})\\
&\quad=\frac{\Lambda}{s_0^2}\left\{\mathbf{Q}^2\cdot(\operatorname{div}\mathbf{Q}\otimes\operatorname{div}\mathbf{Q})+\sum_{ijklm}Q_{im}Q_{mj}Q_{ik,l}Q_{jl,k}\right\},
\end{aligned}
\tag{2}
$$

so that, by equation (39) of [13],

$$
\begin{aligned}
K_1&=2s_0^2\left(2L_1+L_{23}+\frac{20}{9}\Lambda\right),\\
K_2&=4s_0^2L_1,\\
K_3&=2s_0^2\left(2L_1+L_{23}-\frac{4}{9}\Lambda\right),
\end{aligned}
\tag{3}
$$

whence it follows that $\frac{1}{2}(K_1-K_3)=\frac{8}{3}s_0^2\Lambda$, where Λ need not be positive.

2.3. *Representation of the order tensor*

Since, on the one hand, the surface at $z=0$ breaks the symmetry among all directions in space introducing the normal $\mathbf{e}_z$ to the bounding plate as a special direction, and, on the other hand, all admissible configurations are already taken to depend only on z, we further assume that, in those that minimize the free energy, $\mathbf{e}_z$ is an eigenvector of $\mathbf{Q}(z)$ for every z, so that we can write:

$$
\begin{aligned}
\mathbf{Q}(z)=&-\frac{s_0}{3}(u(z)-v(z)3^{1/2})\mathbf{e}_1(z)\otimes\mathbf{e}_1(z)\\
&-\frac{s_0}{3}(u(z)+v(z)3^{1/2})\mathbf{e}_2(z)\otimes\mathbf{e}_2(z)+\frac{2}{3}s_0u(z)\mathbf{e}_z\otimes\mathbf{e}_z,
\end{aligned}
\tag{4}
$$

where

$$
\begin{cases}
\mathbf{e}_1(z)=\cos\varphi(z)\mathbf{e}_x+\sin\varphi(z)\mathbf{e}_y,\\
\mathbf{e}_2(z)=-\sin\varphi(z)\mathbf{e}_x+\cos\varphi(z)\mathbf{e}_y.
\end{cases}
\tag{5}
$$

In terms of the scalars u and v, the constraint on $\operatorname{tr}\mathbf{Q}^2$ can be written as:

$$
u^2(z)+v^2(z)=1,
\tag{6}
$$

which gives v in terms of u, and implies $u(z)\in[-1,1]$ for all $z\in[0,+\infty)$. For each u there are two values of v satisfying equation (6) which differ only in sign; they indeed represent the same physical state, as shown by equation (4), where a change in the sign of v has no effect on $\mathbf{Q}$, provided $\mathbf{e}_1$ and $\mathbf{e}_2$ are exchanged. Henceforth, to resolve this ambiguity, we take v as positive.

Among the distributions represented by a function u through equations (4) and (6), only four are everywhere uniaxial: namely, $u\equiv-\frac{1}{2}$, $u\equiv1$, $u\equiv-1$, and $u\equiv\frac{1}{2}$. The former two have a positive degree of orientation and optic axis along e_1 and e_z, respectively, while the latter two have a negative degree of orientation and optic axis along $\mathbf{e}_z$ and $\mathbf{e}_2$, respectively.

2.4. *Free energy functional*

Along the constraint in equation (6) the Landau–de Gennes potential reduces to

$$
f_{\mathrm{LdG}}=-\frac{2}{9}s_0^2bu(4u^2-3).
\tag{7}
$$

As b is positive, the minimum of f_{LdG} is $-\frac{2}{9}s_0^2$, and it is attained when either $u=-\frac{1}{2}$ or $u=1$, both corresponding to uniaxial states with the same (positive) degree of orientation, but different directors. Since the volume occupied by the liquid crystal is infinite, we need to subtract this constant from the free energy density to make the free energy functional converge when either $u\equiv-\frac{1}{2}$ or $u\equiv1$ from a point in the bulk onward to infinity.

With this warning in mind, we write the free energy functional, also resorting to equations (1) and (2), and to the above representation of $\mathbf{Q}$ in terms of u:

$$
\begin{aligned}
\frac{\mathcal{F}[u,\varphi]}{F_0}=&\int_0^{+\infty}(u'^2-\gamma u(4u^2-3)+\gamma)\mathrm{d}z\\
&+\beta\int_0^{+\infty}\left(\frac{u'^2}{1-u^2}+4\varphi'^2(1-u^2)\right)\mathrm{d}z\\
&+\nu\int_0^{+\infty}u(3+2u)u'^2\mathrm{d}z,
\end{aligned}
\tag{8}
$$

where

$$
\beta:=\frac{3L_1}{2L_{23}},\quad \nu:=\frac{4\Lambda}{9L_{23}},\quad F_0:=\frac{4}{9}L_{23}s_0^2,\quad\text{and}\quad \gamma:=\frac{bs_0}{2L_{23}}.
\tag{9}
$$

The functional in equation (8) depends on both u and φ. This latter is a function of z representing the twist of the eigenvectors of $\mathbf{Q}$, subject to the condition $\varphi(0)=\varphi_0$ at $z=0$, where φ_0 is the angle pertaining to the boundary distribution $\mathbf{Q}_0$. Since the equilibrium equation for φ reads as

$$
\varphi'(1-u^2)=\text{const.},
\tag{10}
$$

the free energy reduces to a functional of u only, which with a slight abuse of language we still denote by $\mathcal{F}[u]$. This functional is bounded from below, provided the function of u that multiplies u'^2 in its integrand is positive on the interval $[-1,1]$; being β positive, this is the case whenever ν satisfies $-\frac{1}{5}(1+\beta)<\nu<\frac{8}{9}(1+\beta)$, as can easily be seen. These inequalities, which henceforth are taken as valid, do not represent a severe constraint, as both

$$\beta \sim \frac{K_2}{K_1} \quad \text{and} \quad |\nu| \sim \frac{|K_1-K_3|}{K_1}$$

are much smaller than 1 for most polymers. For the same reason, we will minimize the first term in the functional and treat the other two as perturbations.

3. Free energy minimizers

In this section we study the minimizers of the dominant part of the free energy functional, that is minimizers of the functional obtained from equation (8) by letting $\beta=\nu=0$. Thus, we consider the following differential problem

$$\begin{cases} u''=\frac{3}{2}\gamma(1-4u^2) \\ u(0)=u_0\in[-1,1], \end{cases} \tag{11}$$

which, as can be seen, has either one or two solutions, as to whether u_0 is smaller or greater than $-\frac{1}{2}$. In both cases, the order tensor $\mathbf{Q}$ tends to become uniaxial in the bulk, but the two possible solutions are quite different in the resulting directors, since one is parallel to the bounding plate, while the other is orthogonal to it. The dividing case $u_0=-\frac{1}{2}$ is singular, since for $u=-\frac{1}{2}$ the potential f_{LdG} in the free energy functional attains its minimum, and so the equilibrium configuration $u\equiv-\frac{1}{2}$, which solves equation (11) for $u_0=-\frac{1}{2}$, is actually the absolute energy minimizer.

3.1. *Planar energy minimizer*

For every value of $u_0\neq-\frac{1}{2}$, there is one *planar* minimizer for which the distribution tends to become uniaxial in the bulk with the director in the same plane as the bounding plate. When $u_0>-\frac{1}{2}$ it is given by:

$$u_\parallel(z)=1-\frac{3}{2}\left[\frac{1-\exp\left(-\dfrac{z+z_0}{\lambda}\right)}{1+\exp\left(-\dfrac{z+z_0}{\lambda}\right)}\right]^2, \quad z\in[0,+\infty), \tag{12}$$

where

$$\lambda:=\left(\frac{L_{23}}{3bs_0}\right)^{1/2}$$

is a material characteristic length, and

$$z_0:=\lambda\log\frac{3^{1/2}+(2-2u_0)^{1/2}}{|3^{1/2}-(2-2u_0)^{1/2}|} \tag{13}$$

depends on the boundary data. When $u_0<-\frac{1}{2}$ the planar minimizer is given by:

$$u_\parallel(z)=1-\frac{3}{2}\left[\frac{1+\exp\left(-\dfrac{z+z_0}{\lambda}\right)}{1-\exp\left(-\dfrac{z+z_0}{\lambda}\right)}\right]^2, \quad z\in[0,+\infty). \tag{14}$$

It should be noticed that both functions in equations (12) and (14) tend asymptotically to $-\frac{1}{2}$ at infinity.

It is not easy to estimate the magnitude of λ, as there are not very many precise measurements of the elastic constants for polymeric liquid crystals. Its approximate order of magnitude should be 0·1 μm, as one can infer using the data given in [14] for L_{23} (see p. 177), and taking $b=6\times10^4\,\mathrm{J\,m^{-3}}$ as for MBBA. Nevertheless, estimating λ is not so crucial here, as the thickness of the layer where the surface biaxial state appreciably persists in the bulk, which we call the *biaxial persistence length*, depends also on u_0 and can be considerably greater than λ. The biaxial persistence length associated with $u_\parallel$ is defined by

$$L_\parallel:=\left|\frac{u_0}{u'_\parallel(0)}\right|; \tag{15}$$

it follows from equations (12) and (14) that

$$L_\parallel=\frac{9|u_0|\lambda}{(5-2u_0)(1-u_0)|1+2u_0|}. \tag{16}$$

Figure 1 shows how $L_\parallel$ depends on the boundary data u_0.

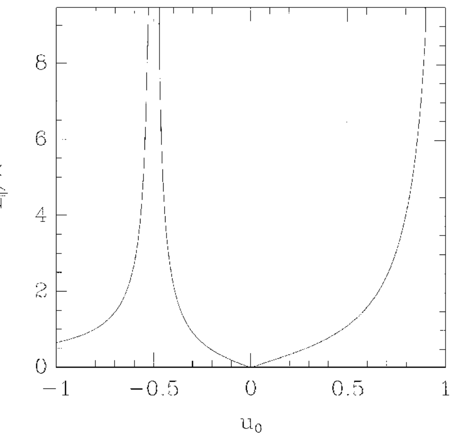

Figure 1. Dependence on the surface state u_0 of the biaxial persistence length $L_\parallel$ for the planar energy minimizer $u_\parallel$.

Substituting $u_{\parallel}$ in equations (6) and (4), we can easily recover the three eigenvalues of the order tensor **Q** as functions of z: figure 2 shows the result for $u_0=\tilde{u}_0$, a critical value we shall define in the next section.

3.2. *Homeotropic energy minimizer*

When $u_0>-\frac{1}{2}$, there is also a *homeotropic* minimizer where the distribution becomes uniaxial with director perpendicular to the bounding plate (i.e. parallel to $\mathbf{e}_z$) at a finite distance from the surface: it is described by the function

$$u_{\perp}(z)=\begin{cases}1-\dfrac{3}{2}\left[\dfrac{\exp\left(\dfrac{z_0-z}{\lambda}\right)-1}{\exp\left(\dfrac{z_0-z}{\lambda}\right)+1}\right]^2 & \text{if } z\in[0,z_0],\\ 1 & \text{if } z\in[z_0,+\infty),\end{cases} \tag{17}$$

where z_0 is defined as in equation (13). If we now define the biaxial persistence length associated with this solution as $|u_0/u'_{\perp}(0)|$, we find that it is indeed equal to $L_{\parallel}$, so that there would be one and the same biaxial persistence length for both minimizers. For the homeotropic minimizer, however, this length can exceed z_0, thus losing its meaning, since by equation (17), $\mathbf{Q}(z)$ is fully uniaxial for $z\geqslant z_0$. This is the case for $u_0\in[-\frac{1}{2},u_0^{(1)}]$, and $u_0\in[u_0^{(2)},1]$, where both $u_0^{(1)}$ and $u_0^{(2)}$ are computed numerically: $u_0^{(1)}=-0{\cdot}4505$, $u_0^{(2)}=0{\cdot}5323$. Thus, we define the biaxial persistence length associated with $u_{\perp}$ as:

$$L_{\perp}:=\min\left\{\left|\frac{u_0}{u'_{\perp}(0)}\right|,z_0\right\} \tag{18}$$

which is illustrated in figure 3 for $u_0>-\frac{1}{2}$.

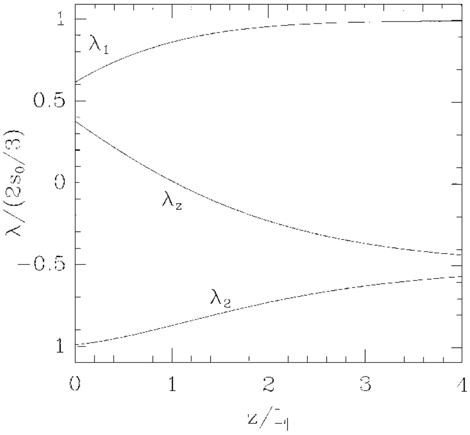

Figure 2. Eigenvalues of the order tensor **Q** for the planar minimizer $u_{\parallel}$.

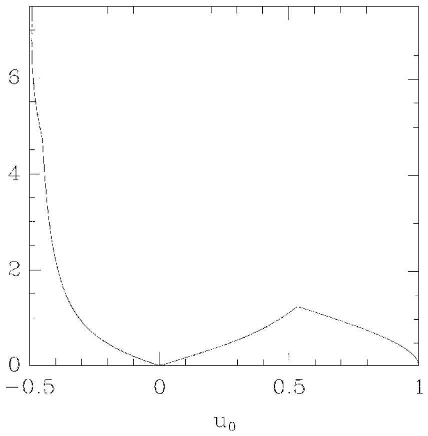

Figure 3. Dependence on the surface state u_0 of the biaxial persistence length $L_{\perp}$ for the homeotropic energy minimizer $u_{\perp}$.

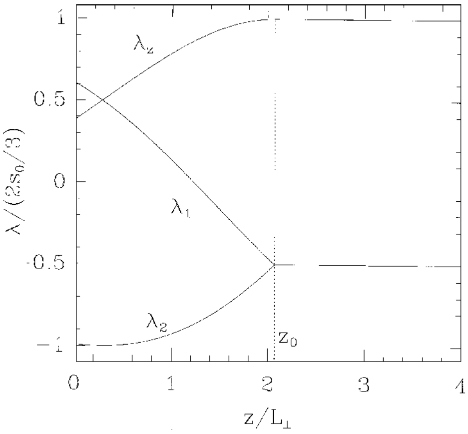

Figure 4. Eigenvalues of the order tensor **Q** for the homeotropic minimizer $u_{\perp}$.

Figure 4 bears for $u_{\perp}$ the same information as figure 2 does for $u_{\parallel}$; it also corresponds to the same value of u_0 employed above. At variance with the former, the latter exhibits two eigenvalue exchanges at a finite depth. First, λ_1, the largest eigenvalue at $z=0$, crosses λ_z at $z=z_0-\lambda\log(2+3^{1/2})$: at this plane there is a uniaxial defect, where the degree of orientation s is negative. Second, λ_1 crosses λ_2 at the distance $z=z_0$ from the bounding plate. At this plate there is a uniaxial state with a positive degree of orientation; since the internal potential here attains its minimum, this state persists for all $z>z_0$. Note that although $u_{\perp}$ is differentiable at $z=z_0$, both λ_1 and λ_2 are not.

4. Comparing energies

Now that we have two relative minimizers, we must compare their free energies to decide which is the stable equilibrium configuration. Including the corrections due to the perturbations generated by both the splay and the higher order elastic contributions, the free energies of the two minimizers are:

$$
\begin{aligned}
&\mathscr{F}[u_\perp]\\
&:=\frac{F_0}{\lambda 3^{1/2}}\left\{\frac{(2-2u_0)^{3/2}}{5}(3+2u_0)\right.\\
&\quad+\frac{\beta}{2}\left([32(1-u_0)]^{1/2}+\log\frac{3-u_0-2(2-2u_0)^{1/2}}{1+u_0}\right)\\
&\quad\left.+\frac{[2(1-u_0{}^3]^{1/2}\nu}{315}(140u_0^3+480u_0^2+573u_0+382)\right\}\\
&\mathscr{F}[u_\parallel]\\
&:=\frac{F_0}{\lambda}\left\{\frac{6}{5}+\left[2-\frac{1}{2\times 3^{1/2}}\log(7+4\times 3^{1/2})\right]\beta+\frac{33}{35}\nu\right\}\\
&\quad-\mathscr{F}[u_\perp].
\end{aligned}
\tag{19}
$$

To arrive at these formulae the constant appearing in equation (10) has been set equal to zero, as required by minimizing the energy functional in equation (8). This, in particular, implies that the twist of the eigenvectors of **Q** around $\mathbf{e}_z$ is constant throughout the half-space, provided u remains away from both -1 and 1, where **Q** becomes uniaxial along $\mathbf{e}_z$.

As above, let first $\beta=\nu=0$. Figure 5 shows the graphs of both $\mathscr{F}[u_\parallel]$ and $\mathscr{F}[u_\perp]$: it is clear that, by continuously increasing u_0 from $-\frac{1}{2}$, a first order transition from the planar to the homeotropic configuration occurs at the critical value $\tilde{u}_0=0{\cdot}3796$ which we found numerically. This transition between such deeply different equilibrium configurations is first order. When the boundary condition reaches its critical value, macroscopic domains, where homeotropic and planar distributions alternate, are likely to arise.

The observations reported in [1] clearly refer to the case where the asymptotic uniaxial state in the bulk is planar, and so u_0 must make $u_\perp$ more energetic than $u_\parallel$. A glance at figure 1 suffices to show that our analysis is able to explain the thickness of the surface initial biaxial layer observed in [1], though the transition predicted here still remains to be seen.

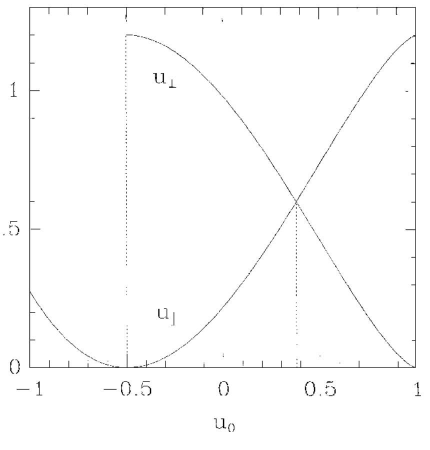

Figure 5. The free energy of both the planar and homeotropic minimizers as a function of the surface state u_0.

If we include the perturbations to the free energy due to both the splay and the higher order elastic terms, the first order transition is found to happen at $u_0=u_0^{\text{crit}}$, with $u_0^{\text{crit}}=\tilde{u}_0+0{\cdot}2683\beta+0{\cdot}3405\nu+o(\beta,\nu)$.

This critical value of u_0, that is, the value at which two deeply different equilibrium solutions both become stable, could bear information about the sign of ν, i.e. about the sign of K_1-K_3. In fact, for most polymeric liquid crystals not only are both β and $|\nu|$ much smaller than 1, but also they satisfy $\beta\ll|\nu|\ll 1$, so that the sign of ν coincides with the sign of $u_0^{\text{crit}}-\tilde{u}_0$.

5. Conclusions

Moving from recent new experimental evidence for a biaxial surface layer, we have studied the decay towards a uniaxial state in the bulk. Our analysis was especially intended for polymeric liquid crystals, as pointed out in introducing the various approximations made here. We strove to let the elastic constants in the Landau–de Gennes free energy remain distinct from one another, and also to let the higher order corrections to the basic second order terms play a rôle, so that Frank's constants K_1 and K_3 would not coincide. The main outcome of the paper is to predict a bulk transition driven by the surface biaxial states. We were not content with describing this qualitatively and have also shown how the difference between K_1 and K_3 can influence its onset.

Also away from the transition, our analysis was rather telling: it showed precisely how the biaxial persistence length, which is our estimate for the thickness of the surface biaxial layer, would depend on both material constants and the surface biaxial state.

References

[1] Mattoussi, H., Berry, G. C., and Patterson, G. D., 1996, *J. Polym. Sci. B*, **34,** 925.

[2] Biscari, P., Capriz, G., and Virga, E. G., 1994, *Liq. Cryst.*, **16,** 479.

[3] Sluckin, T. J., and Poniewierski, A., 1985, *Phys. Rev. Lett.*, **55,** 2907.

[4] Sluckin, T. J., and Poniewierski, A., 1986, *Fluid Interfacial Phenomena*, edited by C. A. Croxton, (Chichester, UK: Wiley), pp. 215–253.

[5] L'vov, Y., Hornreich, R. M., and Allender, D. W., 1993, *Phys. Rev. E*, **48,** 1115.

[6] Kothekar, N., Allender, D. W., and Hornreich, R. M., 1994, *Phys. Rev. E*, **49,** 2150.

[7] Muhoray-Palffy, P., Gartland, E. C., and Kelly, J. R., 1994, *Liq. Cryst.*, **16,** 713.

[8] Biscari, P., Capriz, G., and Virga, E. G., 1993, *Boundary-Value Problems for Partial Differential Equations and Applications*, edited by C. Baiocchi and J. L. Lions (Paris: Masson), pp. 313–318.

[9] Biscari, P., and Guidone Peroli, G., 1997, to appear in *Comm. Math. Phys.*

[10] Lyuksyutov, I. F., 1978, *Sov. Phys. JETP*, **48,** 178.

[11] Penzenstadler, E., and Trebin, H.-R., 1989, *J. Phys. France*, **50,** 1027.

[12] De Gennes, P. G., and Prost, J., 1993, *The Physics of Liquid Crystals* (Oxford: Clarendon Press).

[13] Longa, L., Monselesan, D., and Trebin, H.-R., 1987, *Liq. Cryst.*, **2,** 769.

[14] Donald, A. M., and Windle, A. H., 1992, *Liquid Crystalline Polymers*, (Cambridge: Cambridge University Press).