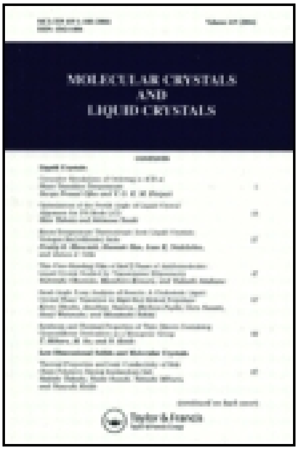

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BIAXIAL PERSISTENCE LENGTH IN NEMATIC LIQUID CRYSTALS

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Abstract Third Harmonic Generation studies for monodomain nematic solutions have recently shown that biaxial anchoring conditions can be induced on the surface of nematic liquid crystals. This biaxiality relaxes in the bulk within a distance from the surface that depends both on the material elastic constants and on the degree of induced biaxiality. We compute the biaxial persistence length and predict that, by continuously varying the biaxial anchoring condition, a first-order transition occurs in the bulk from a planar to a homeotropic distribution.

INTRODUCTION

The Landau-de Gennes' theory predicts[1] that the bulk free energy of nematic liquid crystals .requires a uniaxial bulk distribution to be minimized. However, it has been recently shown[2,3] that the peculiar molecular shape of some new polymeric nematics makes it possible to induce biaxial distributions on their boundaries.

Biaxial surface layers have been already predicted in the past[4,5,6], but here we derive an analytical expression for their thickness, the biaxial persistence length, and we predict a first-order transition which takes place in a half-space delimited by a biaxial plane boundary. This transition occurs between a *planar* and a *homeotropic* solution. Let us introduce a co-ordinate z, normal to the bounding plate, that we will take as $z = 0$. When the biaxial boundary distribution is spread in the $z = 0$ plane, the order tensor $\boldsymbol{Q}$ tends to become uniaxial in the bulk with director parallel to the bounding plate (*planar distribution*); if we now continuously modify the anchoring condition by increasing the z-eigenvalue of $\boldsymbol{Q}(0)$, the uniaxial bulk distribution remains planar until it suddenly jumps to a *homeotropic distribution* in which the director becomes parallel to $\boldsymbol{e}_z$ (*i.e.* perpendicular to the bounding plate).

We find the equilibrium distribution by minimizing the free energy functional

$$\mathcal{F}[\boldsymbol{Q}] := \int_{\mathcal{V}} \left(f_{\rm el}(\boldsymbol{Q}, \nabla\boldsymbol{Q}) + f_{\rm LdG}(\boldsymbol{Q})\right) {\rm d}v, \qquad (1)$$

where $\mathcal{V}$ is the half-space occupied by the nematic and $f_{\rm el}$ and $f_{\rm LdG}$ are, respectively, the elastic and internal parts of the free energy density. In the next section we describe our minimization procedure; in the third we identify the absolute minimizer of the free energy; finally, in the last section, we compute the analytical expression of the biaxial persistence length.

FREE ENERGY FUNCTIONAL

In this section we refer to the paper by Biscari and Virga[3], where all the approximations here used were introduced and discussed in detail.

Order tensor $\boldsymbol{Q}$

Our first simplification excludes the domain-like distributions from our study: since we consider the half-space represented by $z \geq 0$, and we impose the boundary condition $\boldsymbol{Q}\big|_{z=0} = \boldsymbol{Q}_0 =$ cons., that does not depend on the co-ordinates x and y, we take into account distributions depending only on z. This simplification does not prevent us from finding the minimum of the free energy functional, but hides the domain structures that usually arise when a first-order transition is approached.

Then, since the surface at $z = 0$ breaks the symmetry among all directions in space introducing the normal $\boldsymbol{e}_z$ to the bounding plate, we further take $\boldsymbol{e}_z$ as one of the eigenvectors of $\boldsymbol{Q}(z)$, while leaving the other two eigenvectors free to rotate in the plane (x, y):

$$\boldsymbol{Q}(z) = -\frac{s_0}{3}\left(u(z) - v(z)\sqrt{3}\right)\boldsymbol{e}_1(z)\otimes\boldsymbol{e}_1(z) - \frac{s_0}{3}\left(u(z) + v(z)\sqrt{3}\right)\boldsymbol{e}_2(z)\otimes\boldsymbol{e}_2(z) + \frac{2}{3}s_0\, u(z)\, \boldsymbol{e}_z\otimes\boldsymbol{e}_z,$$

where

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

The number of independent parameters needed to determine $\boldsymbol{Q}(z)$ is so reduced to three.

Internal potential $f_{\rm LdG}$

To treat the internal potential we use an approximation first introduced by Lyutsyukov[7]. In the standard Landau-de Gennes' expansion

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

with $b, c > 0$, and $a < 0$ in order to represent the nematic phase, the parameters $|a|$ and c turn out to be much greater than all other magnitudes in the free energy density. We can then consider the term $a\,{\rm tr}\,\boldsymbol{Q}^2 + c({\rm tr}\,\boldsymbol{Q}^2)^2$, and suppose that it must be minimized at any point, so introducing the constraint

$$\operatorname{tr} \boldsymbol{Q}^2(z) \equiv -\frac{2a}{c} =: \frac{2}{3}\, s_0^2, \tag{2}$$

and further reducing the number independent parameters in $\boldsymbol{Q}$ to two, since equation (2) can be also written as

$$u^2(z) + v^2(z) \equiv 1\,. \tag{3}$$

We will take the scalar u and the angle φ as independent. The parameter u, as equation (3) clearly shows, takes values in the interval $[-1, 1]$. It represents both uniaxial and biaxial distributions, and it is closely related to the value of the z-eigenvalue of the order tensor $\boldsymbol{Q}$, since $\mu_z = \frac{2}{3} s_0 u$. There are four special values of u related to uniaxial order tensors $\boldsymbol{Q}$; they are shown in Table I.

TABLE I Values of u that correspond to uniaxial distributions.

u	Uniaxial director	Degree of orientation
1	homeotropic	positive
1/2	planar	negative
−1/2	planar	positive
−1	homeotropic	negative

Elastic energy f_{el}

The most general elastic free energy, depending quadratically on the derivatives of $\boldsymbol{Q}$, is:

$$f_{\mathrm{el}}(\nabla \boldsymbol{Q}) = L_1 \left|\nabla \boldsymbol{Q}\right|^2 + L_2 \left(\operatorname{div} \boldsymbol{Q}\right)^2 + L_3 \sum_{ijk} Q_{ij,k}\, Q_{ik,j}\ ,$$

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 $K_2 = 4s_0^2 L_1$, $K_1 = K_3 = 2s_0^2(2L_1 + L_2 + L_3)$. As usual, this quadratic approximation is not able to distinguish between K_1 and K_3. To treat the materials in which those two elastic constants are different, one is forced to consider also higher-order terms in the elastic free energy density, depending not only on the derivatives of $\boldsymbol{Q}$, but also on the order tensor itself, as it has been done in [3].

Free energy functional $\mathcal{F}[\boldsymbol{Q}]$

With all the considerations above, the free energy functional (1) can be written as:

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

where

$$F_0 := \frac{K_2}{6}\,, \quad \gamma := \frac{4bs_0^3}{3K_2}, \quad \text{and} \quad \delta := \frac{4}{3}\, \frac{K_1 - K_2}{K_2}.$$

We remark that the combination of elastic constants we have denoted by δ needs not to be positive, but it is forced to verify $\delta > -1$ in order to make the functional $\mathcal{F}$ bounded from below.

EQUILIBRIUM DISTRIBUTIONS

The functional in (4) depends on the functions $u(z)$ and $\varphi(z)$, and is to be minimized subject to the boundary conditions $u(0) = u_0$ and $\varphi(0) = \varphi_0$, where u_0 and φ_0 are the parameters characterizing the imposed anchoring condition $\boldsymbol{Q}(0) = \boldsymbol{Q_0}$.

The Euler-Lagrange equation of (4) relative to the angle φ can be easily integrated to give $\varphi(z) \equiv \varphi_0$ for all $z \geq 0$, as in [3]. This fact can be explained by considering that, since the nematic is confined by only one bounding plate, it has no reason to spontaneously rotate its eigenvectors.

The second equilibrium equation in (4) can also be integrated to give

$$u'^2 = f(u) := \gamma \frac{(1-u)^2(1+u)(1+2u)^2}{1+\delta(1-u^2)}. \tag{5}$$

Equation (5) shows that, for every value of $u(0) = u_0$ there exist at most two minimizers of the free energy functional (with, respectively, positive and negative $u'(0)$). Actually, since $u(z)$ must tend to either $-\frac{1}{2}$ (corresponding to the planar prolate uniaxial distribution) or 1 (homeotropic prolate uniaxial distribution) when z goes to infinity to have a finite energy, only one minimizer can be found if $u_0 \in [-1, -\frac{1}{2}]$ (with $\lim\limits_{z\to\infty} u(z) = -\frac{1}{2}$), while two exist when $u_0 \in (-\frac{1}{2}, 1)$. The absolute minimizer can be determined by computing the free energies corresponding to both solutions: it then appears that the planar minimizer is preferred when u_0 is less than a critical value $u_0^{\rm cr}(\delta)$, at which a first order transition occurs and the homeotropic minimizer becomes the stable equilibrium configuration.

Figure 1 shows how $u_0^{\rm cr}$ depends on δ. When $\delta = 0$ (*i.e.* when $K_1 = K_2 = K_3$), the critical value is exactly $\frac{1}{2}$, as it could be expected: the planar and the homeotropic distributions share the same free energy value when the boundary condition is such that the bigger planar eigenvalue (say, μ_1) and the z-eigenvalue μ_z coincide at $z = 0$.

When $\delta < 0$, that is when the splay constant is greater than $K_1 = K_3$, $u_0^{\rm cr}$ increases, so indicating that the planar distribution is finally preferred even in some cases with $\mu_z > \mu_1$ at $z = 0$. The opposite situation arises when $\delta > 0$; in particular, the limit of $u_0^{\rm cr}(\delta)$ when $\delta \to +\infty$ (corresponding to $K_2 \ll K_1$, a situation that arises in most polymeric nematics) coincides with the result predicted in [3].

BIAXIAL PERSISTENCE LENGTH

To define a biaxial persistence length we use the following invariant biaxiality measure[8]:

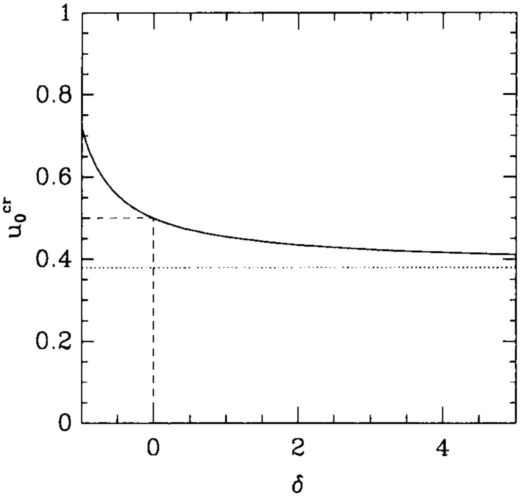

FIGURE 1 Critical value of the boundary parameter u_0.

$$\beta := \left(6\sqrt{3}\,|\mu_1 - \mu_2|\,|\mu_2 - \mu_z|\,|\mu_z - \mu_1|\right)^{1/3},$$

where μ_1, μ_2, and μ_z are the eigenvalues of the order tensor $\boldsymbol{Q}$. The parameter β so defined takes values in $[0, 1]$, being 0 if only and only if the order tensor $\boldsymbol{Q}$ is uniaxial. The constraints $\operatorname{tr}\boldsymbol{Q} = 0$ and $\operatorname{tr}\boldsymbol{Q}^2 = \frac{2}{3}s_0^2$ allow us to compute β in terms of the parameter u:

$$\beta(z) = 2^{\frac{2}{3}}\, s_0\, |4u^2(z) - 1|\, \sqrt{1 - u^2(z)},$$

confirming that $\beta = 0$ when either $u = \pm\frac{1}{2}$ or $u = \pm 1$.

Now we define the *biaxial persistence length* as:

$$L_B(u_0, \delta) := \frac{\beta(0)}{|\beta'(0)|}\ ;$$

equation (5) allows us to compute L_B analytically:

$$L_B(u_0, \delta) = \lambda\, \frac{|1 - 2u_0|\sqrt{(1 + u_0)\left(1 + \delta(1 - u_0^2)\right)}}{\left|u_0\left(3 - 4u_0^2\right)\right|}, \tag{6}$$

where $\lambda := \gamma^{-\frac{1}{2}}$ is a material characteristic length, usually of the order of the micron[3]. Figure 2 shows how the biaxial persistence length depends on the initial condition u_0 for three different values of δ: the continuous, dotted and dashed lines represent the cases when $\delta = 0$, $-\frac{1}{2}$, and 1, respectively.

Equation (6) and Figure 2 show that L_B vanishes when $u_0 = -1$ or $u_0 = \frac{1}{2}$, so indicating that biaxiality fades away most rapidly when the nematic is forced to reach its final uniaxial prolate distribution starting from an uniaxial oblate distribution on the surface. On the contrary, L_B diverges when $u_0 = \pm\sqrt{3}/2$, or $u_0 = 0$: this indicates that biaxiality survives most in the bulk when any of the

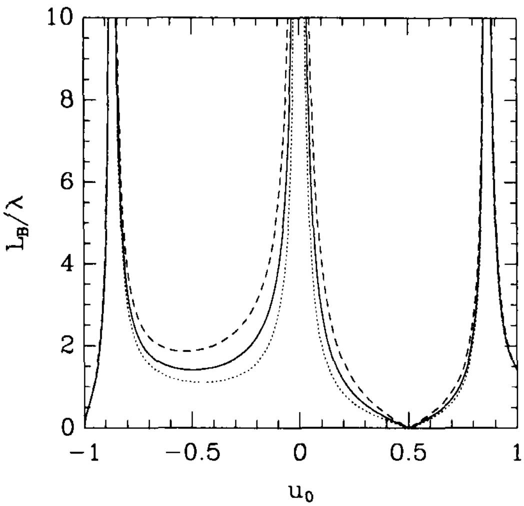

FIGURE 2 Biaxial persistence length.

three eigenvalues of the order tensor $\boldsymbol{Q}$ is set equal to 0 at the bounding plate.

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