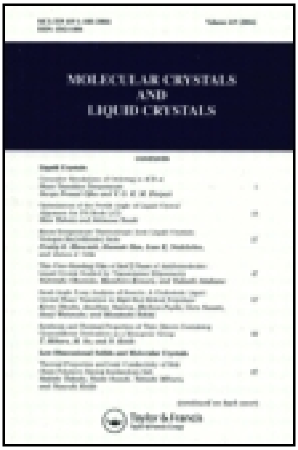

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Distortion in the Surface Layers of Nematic Liquid Crystals: An Elastic Constant Approach

G. Barbero [a] & C. Oldano [a]
[a] Dipartimeto di Fisica del Politecnico and CISM-MPI, Corso Duca degli Abruzzi, 24, 10129, Torino, Italy

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Distortion in the Surface Layers of Nematic Liquid Crystals: an Elastic Constant Approach

G. BARBERO and C. OLDANO

Dipartimeto di Fisica del Politecnico and CISM-MPI, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy

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A strong boundary distortion of the director field $\hat{n}(\mathbf{R})$ near the boundary surface of nematics is evidenced and theoretically discussed in terms of elastic constants. The sources of the distortion are the diffuse nature of the surface tension, the spontaneous splay, which is different from zero in a boundary layer of thickness comparable with the range of molecular interactions, and the surface-like free energy term k_{13} div($\hat{n}$ div $\hat{n}$). In the distorted layer a drastic change of $\hat{n}(\mathbf{R})$ with respect to the surface normal $\hat{k}$ occurs. As a consequence, the surface alignment may appear homeotropic from a macroscopic point of view, even in the case where the short range nematic–substrate interactions give an obliquely oriented surface layer, as suggested by recent experiments of P. Guyot-Sionnest, H. Hsiung and Y. R. Shen.

1. INTRODUCTION

One of the main topics in the physics of interfacial phenomena is the surface-induced orientation of liquid crystals. Despite its theoretical and practical interest and the great deal of work devoted to this problem, it is at present rather poorly understood. Nevertheless, some results seem well established. In particular:

1) The surface tension of a nematic–vapor and nematic–isotropic interface depends on the angle θ_s between the average molecular orientation (director $\hat{n}$) and the surface normal $\hat{k}$. Depending on the molecular properties of the nematic and on its temperature, the equilibrium director may be parallel, orthogonal or obliquely oriented with respect to $\hat{k}$.[1–3]

2. Both theory and experiments have evidenced the diffuse nature of the interface, with a gradual variation of the order parameter S and possibly of the density and of the polar order.[4–7] A critical behavior of such effects near the nematic–isotropic transition temperature has been evidenced.[8,9]

A further effect consisting of a strong distortion of the director field near the boundary surface has been suggested by the authors of this paper.[10,11] This effect is quite different from the well-known distortions found in films with different anchoring or acted on by external fields. In fact it is related to the free-energy term $k_{13}\mathrm{div}(\hat{n}\ \mathrm{div}\ \hat{n})$ introduced by Oseen[12] and by Nehring and Saupe.[13,14] Further, the main distortion is expected to occur in a few molecular layers and only if the surface director is obliquely oriented with respect to $\hat{k}$.

In Reference 10 it is shown that in the framework of the continuum theory the distortion can be described as a boundary discontinuity $\Delta\theta$ of the angle θ defining the direction of $\hat{n}$. In Reference 11 a rough evaluation of $\Delta\theta$ is given, and it is pointed out that for a more correct analysis the theory of Nehring and Saupe must be properly extended to take into account the expression of the free energy near the boundaries. Such extension is the main purpose of this paper. The authors are quite conscious of the intrinsic limitation of an approach where a distortion involving few molecular layers is discussed in terms of elastic constants, i.e., in terms of a free energy expansion involving director derivatives $n_{i,j}$. This approach is fully justified only if the distortion is small over the interaction range of the molecular forces giving rise to the nematic phase. This condition is not always fulfilled near the boundary surface, according to our estimation[10,11] and also according to the experimental data of Shen et al.[15] However, some considerations suggest that such a very simple approach may be of some interest and usefulness:

1. An experimental technique, based on optical second harmonic generation, is now available, which is able to probe the surface molecular alignment with the sensitivity of a monolayer.[15] This gives an experimental meaning to the concept of the surface director, which was introduced in Reference 11 as a purely analytic concept. The first results seem to confirm the boundary distortion[16];
2. The very existence of the considered boundary distortion was suggested by an analysis of the k_{13}-dependent free energy, i.e., in the framework of an elastic-constant approach; and
3. Although the main distortion is expected to occur in a few molecular layers, a long-range tail of the distortion is certainly present, which may be correctly evaluated in terms of a continuum theory.

Obviously the results obtained with this approach can be quantitatively applied only to the cases of relatively small distortions. For higher distortions only qualitative estimations are possible.

2. THEORY

Let us summarize the essential lines of the molecular approach to the bulk elastic constant given in Reference 13. The starting point is the assumption of a two-body interaction of the type

$$f(\hat{n},\hat{n}',\mathbf{r})d^3\,\mathbf{R}d^3\,\mathbf{R}' \tag{1}$$

between the volume elements $d^3\mathbf{R}$, $d^3\mathbf{R}'$, where $\hat{n}$ and $\hat{n}'$ are the directors at $\mathbf{R}$ and $\mathbf{R}'$, respectively, and $\mathbf{r} = \mathbf{R}' - \mathbf{R}$. In order to express the excess energy associated with a given director distortion in terms of elastic constant, we write

$$\hat{n}' = \hat{n} + \Delta\hat{n} \tag{2}$$

$$f(\hat{n},\hat{n} + \Delta\hat{n},\mathbf{r}) = f_o + f_i\Delta n_i + \tfrac{1}{2}f_{ij}\,\Delta n_i\,\Delta n_j + 0(3); \tag{3}$$

where

$$f_o = f(\hat{n},\hat{n},\mathbf{r}),\quad f_i = (\partial f/\partial n_i')_{\Delta\hat{n} = 0},\quad f_{ij} = (\partial^2 f/\partial n_i'\,\partial n_j')_{\Delta\hat{n} = 0}.$$

By furtherly assuming (4)

$$\Delta n_i = n_{i,l}(\mathbf{R})r_l + n_{i,lm}(\mathbf{R})r_l r_m + 0(r^3). \tag{5}$$

We obtain

$$f = f_o + f_i n_{i,l} r_l + \tfrac{1}{2}[f_i n_{i,lm} + f_{ij} n_{i,l} n_{j,m}]\, r_l r_m + 0(r^3).$$

Here $r = |\mathbf{r}|$, $i,j,l,m = 1,2,3$ and the Einstein summation convention over repeated indices is used. The energy density $F(\mathbf{R})$ at the point $\mathbf{R}$ is obtained by integrating $f/2$ over $\mathbf{r}$.

Equation (5) shows that the terms $f_i\, n_{i,lm}$, which depend on the second order derivatives of the director field $\hat{n}$ ($\mathbf{r}$), can give a contribution to f comparable with the terms $f_{ij}\, n_{i,l}\, n_{j,m}$, which are quadratic in the first order derivatives. An expansion up to higher order terms is possible but of doubtful usefulness, as explained below (point 1).

For nematic liquid crystals, which have $D_{\infty h}$ symmetry (a full symmetry axis, without polarity and without screw sense), the energy density may be written, after a rearrangement of the terms:

$$\begin{aligned} F = F_o &+ \tfrac{1}{2}[\mathrm{k}_{11}(\operatorname{div}\hat{n})^2 + k_{22}(\hat{n}\cdot\operatorname{rot}\hat{n}) + k_{33}(\hat{n}X\operatorname{rot}\hat{n})^2] \\ &- (k_{22} + k_{24})\operatorname{div}(\hat{n}\operatorname{div}\hat{n} + \hat{n}X\operatorname{rot}\hat{n}) + k_{13}\operatorname{div}(\hat{n}\operatorname{div}\hat{n}) \end{aligned} \tag{6}$$

where $k_{11},k_{22},k_{33},k_{24}$ are the well-known elastic constants of Frank's phenomenological approach. The last term is the one which gives the boundary distortion. In Reference 13 it is shown that the dispersion forces give for $k_{\mathrm{ii}}(i = 1,2,3)$ and k_{13} values of the same order of magnitude. Since the k_{13}-dependent boundary distortion essentially depends on the ratio k_{13}/k_{ii}, it seems interesting to consider other types of interactions. For this purpose, it is useful to write[17]:

$$f(\hat{n},\hat{n}',\mathbf{r}) = -\sum_{aa'b} J_{a.a'.b}(r)\quad A^a\, A'^{a'}\, B^b \tag{7}$$

where the sum is over a suitable set of integer values of a, a', and b which depend on the type of the molecular interactions and where $A = \hat{n}\cdot\hat{r}$, $A' = \hat{n}'\cdot\hat{r}$ and

$B = \hat{n} \cdot \hat{n}'$. The symmetry $f(\hat{n},\hat{n}',\mathbf{r}) = f(-\hat{n},\hat{n}',\mathbf{r}) = f(\hat{n},-\hat{n}',\mathbf{r}) = f(-\hat{n},-\hat{n}',\mathbf{r})$implies that $a + b$, $a' + b$ and $a + a'$ are even.

The formal expressions of the elastic constants [see Equation (10) below] show that the terms with $a' = 0$ do not contribute to k_{13}. In particular the Maier–Saupe interaction, where only terms with $a = a' = 0$ appear, gives $k_{11} = k_{22} = k_{33} = k$, $k_{24} = -(3/2)k$, $k_{13} = 0$.

New terms in the expression of the free energy F are expected at a point R near a boundary surface, owing to the lower symmetry of the problem. If we explicitly assume that the plane defined by $\hat{n}(\mathbf{R})$ and $\hat{k}$ is a symmetry plane, only a new term appears, having the structure:

$$k_1 \text{div } \hat{n}. \tag{8}$$

As is well known, this term gives a splay distortion. The spontaneous splay constant k_1 is identically zero in the bulk for apolar nematics, whereas it is generally different from zero in the boundary layers.

Obviously the quantities $F_o, k_{ii}, k_{24}, k_{13}, k_1$ are no longer constants: an explicit dependence on the distance from the boundary surface and on the angle $[\hat{n}(\mathbf{R}), \hat{k}]$ is expected. A formal expression of these quantities in terms of the molecular interaction law is only possible if further simplifying assumptions are made.

In the following we consider only the interactions between the molecules of the nematic and neglect the order parameter or density variations. Furthermore:

1. The integration over $\mathbf{r}$ is performed within a sphere of radius r_1, by assuming the contribution of the outside region to the energy density at point $\mathbf{R}$ to be negligible. The thickness of the boundary layer is assumed coincident with the "interaction range" r_1. The expansions (4) and (5) where only second order terms are retained, are fully justified if the director changes slowly within the interaction range r_1. Since strong changes $\Delta\hat{n}$ can occur in the boundary layer, only some very particular limiting cases may be quantitatively analyzed. This is the main limitation of the present theory. An expansion up to higher order terms is possible but not useful in our opinion. The fact that the bulk elastic constants become $\mathbf{R}$- and $\hat{n}$-dependent suggests that substantial improvements of the present theory must be obtained by searching for a different and more direct analysis of the boundary problem.
2. In Reference 13 $d^3\mathbf{R}$ and $d^3\mathbf{R}'$ are volume elements containing many molecules. Since we are looking for very short range distortions, it seems preferable to consider as a starting point the interaction between two molecules.[17,18] In order to avoid the necessity of performing thermodynamic averages over the molecular directions, we simply assume that the molecular long axis at point $\mathbf{R}$ is in the direction of $\hat{n}(\mathbf{R})$. Obviously, this is equivalent to the assumption $S = 1$, where S is the order parameter. The formal features of the results are not affected by this simplifying assumption (and by the fact that the entropy term is neglected, since the interaction energy instead of the free energy is considered). More precisely $d^3\mathbf{R}$ is the molecular volume, and the integration over $\mathbf{r}$ is performed outside of the sphere of radius r_o, where r_o is of the order magnitude of the molecular dimensions.

In order to justify the very crude assumption above, let us recall that the analysis of the possible boundary distortion given in References 10 and 11 is based on the very existence of the k_{13}-dependent energy term: Only the formal feature of the energy terms and the order of magnitude of the corresponding parameters are of interest for what concerns the present analysis.

With the above assumption one straightforwardly obtains:

$$F_o = -\frac{1}{2}\sum_{aa'b} X(0,2), \tag{9}$$

$$k_1 = -\frac{1}{4}\sum_{aa'b} \mathrm{a}'[\mathrm{X}(-1,3) - X(1,3)],$$

$$k_{13} = -\frac{1}{4}\sum_{aa'b} a'\ [X(0,4) - X(2,4)],$$

$$k_{11} = -\frac{1}{4}\sum_{aa'b}\left\{-[b + (3/2)a'(a' + 1)]\ X(0,4) + \left[b + \left(\frac{3}{4}\right)a'(a' + 3)\right] X(2,4)\right.$$
$$\left. + \left(\frac{3}{4}\right)a'(a' - 1)\ X(-2,4)\right\}, \tag{10}$$

$$k_{22} = -\frac{1}{4}\sum_{aa'b}\left\{-[b + \tfrac{1}{2}a'(a' - 3)]\ X(0,4) + \left[b + \left(\frac{1}{4}\right)a'(a' - 5)\right] X(2,4)\right.$$
$$\left. + \left(\frac{1}{4}\right)a'(a' - 1)\ X(-2,4)\right\},$$

$$k_{33} = -\frac{1}{4}\sum_{aa'b}\{-[2b + a'(a' + 3)]\ X(2,4) + a'(a' + 1)\ X(0,4)\},$$

where

$$X(i,j) = \iiint_{V} J_{a,a',b}(r)\ (\hat{n}\cdot\hat{r})^{a+a'+i}\ r^{j+}\ dr\ d\Omega. \tag{11}$$

In the bulk, V is the region between the spherical surfaces $r = r_0$ and $r = r_1$, and the solid angle $d\Omega$ must be integrated over 4π. In the boundary region, V is only the part of the region between $r = r_0$ and $r = r_1$ which is inside the boundary surface of the nematic.

3. DISCUSSION

Let us consider a semi-infinite nematic in the region $z < r_1$ of a Cartesian coordinate system. The bulk and the boundary layer correspond to $z < 0$ and $z > 0$, respectively. For $z > 0$ the integrals (11) explicitly depend on z and on the angle θ between $\hat{n}(z)$ and $\hat{k}$. Despite the complexity of the energy–density expression some definite and very simple conclusions may be deduced.

The quantities k_1 and k_{13} are related to energy terms which are linear in the first and second order derivatives of $\hat{n}$, respectively. These terms are obviously not minimized by a uniform $\hat{n}$-field, and can therefore be sources of distortion. In the bulk no distortion appears, since $k_1 = 0$, and the distorting effects of the k_{13}-dependent terms cancel each other, owing to the particular structure of the resulting expression, which may be exactly integrated and gives only boundary effects.

Notice that k_1 and k_{13} are identically zero if $a' = 0$. The two distortion sources are absent if the interaction law does not depend on the direction $\hat{r}$ of $\mathbf{r}$, i.e., on the relative position of the molecules (type I interactions), whereas they are generally present in the opposite case (type II interactions, which explicitly depend on $\hat{r}$).

This fact may be easily understood by the following very simple argument. Let us consider a molecule m_R at point $\mathbf{R}$, directed along $\hat{n}$, acted upon by all the molecules within the interaction sphere r_1, which are assumed perfectly aligned along a unique direction $\hat{n}'$. In order to obtain nematic order the minimum energy of m_R must occur for $\hat{n} = \hat{n}'$. However, for type II interactions this minimum is obtained by averaging all two-body energies whose minimum occurs, in general, for $\hat{n}'$ obliquely oriented with respect to $\hat{n}$, whereas all type I two-body interactions give a minimum for $\hat{n} = \hat{n}'$. If now some surrounding molecules are absent, because m_R is near a boundary surface, the minimum of the interaction energy generally occurs for $\hat{n} \neq \hat{n}'$ for type II interactions, whereas for type I interactions it is always $\hat{n} = \hat{n}'$.

Two points must be emphasized: i) The above argument is valid even in the case where only nearest-neighbor interactions are present, a case where a quantitative analysis can hardly be performed in the framework of the present theory; ii) the quantity F_o gives the surface tension of the free surface of nematics. Its anisotropic part determines the director orientation of a freely suspended film.[19] By expressing F_o as a function of z, we have evidenced the diffuse nature of the surface tension, a fact which may be a further source of boundary distortion. As shown by Equation (9), F_o is isotropic and cannot give distortions if only type I interactions are present.

The starting point for a quantitative analysis is the expression of the total energy of the boundary layer:

$$\mathcal{F} = \int_0^{z_1} F(z,\theta(z))dz, \tag{12}$$

where

$$F(z,\theta) = F_o(z,\theta) - k_1(z,\theta)\sin\theta\dot{\theta} + \tfrac{1}{2}k(z,\theta)\dot{\theta}^2 - \tfrac{1}{2}k_{13}(z,\theta)\sin(2,\theta)\,\ddot{\theta}, \tag{13}$$

$$k(z,\theta) = [k_{11}(z,\theta) + 2k_{13}(z,\theta)]\sin^2\theta + [k_{33}(z,\theta) - 2k_{13}(z,\theta)]\cos^2\theta \tag{14}$$

where the dot means derivation with respect to z.

The director profile $\theta(z)$ is obtained by minimizing $\mathcal{F}$. The Euler equation of the variational problem is:

$$\partial F/\partial\theta - (d/dz)(\partial F/\partial\dot{\theta}) + (d^2/dz^2)(\partial F/\partial\ddot{\theta}) = 0. \qquad (15)$$

Equation 13 is only of the second order, since $\ddot{\theta}$ is linearly contained in F. As noticed in Section 2, only the case of small distortions may be quantitatively treated.

To this purpose, we notice that near a free surface the profiles $\theta(z) = 0$ and $\theta(z) = \pi/2$ are solutions of Equation (15), for evident symmetry considerations. Let us assume that the solution $\theta = 0$ corresponds to a minimum of $\mathcal{F}$. A small distortion may be obtained by imposing a boundary condition $\theta(r_1) = \theta_1$, with $\theta_1 \ll 1$. This can be achieved by a suitably treated substrate, under the assumption that the nematic–substrate forces are only acting on the first molecular layer. An expansion of $F(z,\theta)$ in a power series of θ, up to θ^2, gives:

$$F = F_0(z,0) + \tfrac{1}{2}(\partial F_0/\partial\theta)_0\,\theta^2 - k_1(z,0)\theta\,\dot{\theta}$$
$$+ \tfrac{1}{2}[k_{33}(z,0) - 2k_{13}(z,0)]\dot{\theta}^2 - k_{13}(z,0)\theta\ddot{\theta} \qquad (16)$$

The Euler equation becomes:

$$(d/dz)[k_{33}(z,0)\dot{\theta}] = [(\partial F_0/\partial\theta)_0 + \dot{k}(z,0) - \ddot{k}_{13}(z,0)]\,\theta, \qquad (17)$$

which confirms the previous qualitative analysis: k_1, k_{13} and the anisotropic part of F_0 are the sources of the boundary distortion. By considering the r-dependence of the quantities F_0, k_1, k_{13}, given by Equation (9), we expect that the three distorting terms are of the same order of magnitude. The same equation suggests that for interactions with a power law of the type r^{-5} (as, for instance, the electric quadrupole interactions) or r^{-6} (dispersion forces) the main contribution to the distortion comes from several molecular layers.

A most important point is the evaluation of the order of magnitude of the θ-change through the boundary layer. To this purpose, we notice that the coefficients of θ in Equation (17) play the same role of a magnetic field directed along z. These "fields" are present only in the boundary layer, since in the bulk $k_1(z,0) = 0$, $k_{13}(z,0) = k_{13}$ and F_0 is independent of θ. For a rough estimation of their effects, we assume that these fields are non-zero and constant only in a suitably chosen average interaction length $\bar{r}$, of the order of magnitude of a few molecular layers. By further assuming $k_{33}(z,0) = k_{33}$ we may associate the three fields with a coherence length ζ, which plays the role of the magnetic coherence length.[21] The ratio $\bar{r}/\zeta$ gives the order of magnitude of the boundary distortion. For the evaluation of the length ζ_{13} associated with k_{13}, it seems reasonable to assume that $k_{13}(z,0)$ decreases from the bulk value k_{13} to a surface value $k_{13}/2$. This gives $-\ddot{k}_{13} = k_{13}/(4\bar{r}^2)$. From the definition of coherence length,[21] we obtain $\zeta_{13} = (-k_{33}/\ddot{k}_{13})^{1/2}$, and

$$\bar{r}/\zeta_{13} = \tfrac{1}{2}(k_{13}/k_{33})^{1/2}. \qquad (18)$$

For $k_{13} \approx k_{33}$ this gives $\Delta\theta \approx \frac{1}{2}\theta_1$, independent of $\bar{r}$ where $\Delta\theta = 1\theta_{\text{bulk}} - \theta_1$. The same order of magnitude is found in Reference 10, with a different computation method. At present we have no means to evaluate the k_1-induced distortion. In order to compute the coherence length ζ_0 associated with the other term, we assume that $(\partial F_0/\partial\theta)\bar{r}$ gives the anisotropic part $\gamma_\parallel - \gamma_\perp$ of the surface tension γ, computed by assuming an undistorted director field.[19,20,22] This gives:

$$\bar{r}/\zeta_0 = [(\gamma_\parallel - \gamma_\perp)\bar{r}/k_{33}]^{1/2}. \tag{19}$$

By assuming, as a rough estimation, $\gamma_\parallel - \gamma_\perp \approx 1$ erg/cm^2, $\bar{r} \approx 10^{-6}$ cm, $k_{33} \approx 10^{-6}$ erg/cm, we obtain $\bar{r}/\zeta_0 \approx 1$, which means $\Delta\zeta/\theta_1 \approx 1/2.7$. In the previous analysis the substrate is assumed as perfectly flat and both angles θ_1 and φ_1 which define the surface director are assumed constant. As evidence, a possible domain structure with randomly oriented φ_1-angles would give $\theta_{\text{bulk}} = 0$ for $z \to \infty$. The tilted surface anchoring observed in Reference 16 is not incompatible with a macroscopically homeotropic alignment. We also expect that the surface distortion plays a major role in determining the bulk alignment in the case of a highly irregular surface, as for instance in the case of glasses coated with obliquely evaporated SiO.

As a final comment, we observe that the terms associated with k_1 and F_0 must be taken into account in any attempt to measure the elastic constant k_{13} or to evaluate the effects of the corresponding free-energy term.

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