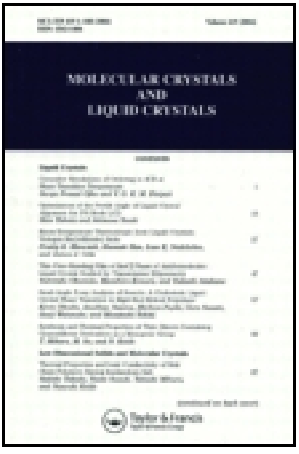

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The K_{13} Surface-Like Elastic Constant: Analysis of the Predictions of Different Theoretical Models

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The K_{13} Surface-Like Elastic Constant: Analysis of the Predictions of Different Theoretical Models

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In recent years two very different theoretical approaches have been proposed to by-pass the mathematical difficulties related to the problem of finding the director-field in a nematic liquid crystal when the surface-like elastic constant K_{13} is different from zero. Barbero *et al.* expanded the free energy functional up to the fourth order in the director derivatives and showed that, under these conditions, the minimisation problem now becomes correctly set from the mathematical point of view. A strong subsurface director distortion on a length scale of the order of the molecular length is predicted by using this approach. Hinov and V. Pergamenshchik consider the subsurface strong distortion as an artefact of theory and propose an alternative method to account for the effect of K_{13}. In this paper we analyze the consequences of these different theoretical approaches in the case of a nematic layer with a tilted director orientation at one interface and in the presence of a magnetic field. In this special case (tilted alignment), we show that, *for every value of* K_{13}, the Hinov-Pergamenshchick method predicts very unusual phenomena, whilst no anomalous macroscopic phenomenon is predicted by the second order elastic theory. According to this latter theory, the macroscopic behaviour of the system is demonstrated to be fully equivalent to that predicted by the first order Frank theory ($K_{13} = 0$) if the actual easy axis at the interfaces and the anchoring energy are substituted by an "effective easy axis" and an "effective anchoring energy." A simple experimental method to test the different predictions of the two theories is proposed.

Keywords: liquid crystals, elastic constants, fluid surfaces and interfaces with fluids

I. INTRODUCTION

The macroscopic behaviour of nematic liquid crystals (NLC) is described by the director ***n*** which denotes the average molecular orientation. The space variation of the director can be obtained by minimizing the Frank elastic free energy.[1] Nehring and Saupe,[2] in 1971, showed that a new term must be added to the free energy. This new contribution, which is proportional to the surface-like elastic constant K_{13}, explicitly contains second-order derivatives of the director and, thus, behaves as a surface free energy contribution. Oldano and Barbero,[3] in 1985, showed that this new surface contribution makes the free energy unbounded from below so that no minimum of the free energy can be found. Under these conditions a discontinuity of the director-field is predicted to exist at the interfaces.[4–6] Oldano and Barbero showed that this mathematical discontinuity is due to an oversimplification of the surface problem and it tends to simulate an actual strong director distortion which occurs in a very thin subsurface layer of molecular characteristic length. In this greatly distorted subsurface layer, the director derivatives assume very high values and, thus, one expects higher order elastic contributions in the expansion of the free energy to play a considerable role. According to this idea, Barbero *et al.*[7,8] generalize the Frank theory of elasticity by making a power expansion of the free elastic energy density of nematic L.C. up to the fourth order in the director derivatives. In the following we will refer to this elastic theory as the "**second order elastic theory**." The second order free energy is bounded from below and possesses a minimum corresponding to a well defined director distortion. The director-field is now represented by a continuous function but there is a sharp variation close to the interfaces within a thickness of the order of the molecular length. In the case of homeotropic or planar easy alignment of the director at the interface, *the main effect of this subsurface distortion has been demonstrated to be an apparent reduction of the surface anchoring energy coefficient W*. Although in my opinion this solution probably accounts for the main effects of the surface-like elastic constant K_{13}, it cannot be considered as a definitive solution for the K_{13}-problem. In particular there are some important points which still remain open to theoretical investigation:

1. A power expansion of the free energy as a function of the director derivatives is justified only if the length scale of the director distortion is much higher than the molecular scale length. This is certainly not the case as far as the strong subsurface distortion is concerned and, thus, the role that elastic contributions of order higher than the second order may play is not clear.

2. Very close to the interfaces the free energy density differs greatly from the bulk expression. In particular the elastic constants become position-dependent and new elastic contributions must be considered.[9]

3. The second order free energy density introduces new higher order surface contributions which are not taken into consideration, but which, in principle, still make the free energy unbounded from below. Therefore it is not clear how disregard of these higher order surface contributions affects the main theoretical predictions.

More recently Barbero *et al.*[9] made a different semiquantitative analysis of this problem by also accounting for the spatial variation of elastic constants near the interfaces and for the symmetry breaking due to the presence of the interface which produces new elastic subsurface contributions. Using a modified first order elastic form for the free energy near the interfaces, in the case of planar or homeotropic surface anchoring, the authors show that all the subsurface elastic effects are fully equivalent to a renormalization of the anchoring energy. Therefore they conclude that the macroscopic properties of nematic L.C. can be correctly analyzed by using the standard Frank elastic free energy (without K_{13}) for the bulk and an effective surface anchoring potential for the surface free energy which implicitly accounts for the effects of K_{13} and for other elastic subsurface contributions. According to this interesting point of view, the standard theoretical and experimental procedure which consists in disregarding the surface elastic constant seems to be fully justified.

However, in this case, too, the use of an elastic form for analyzing the subsurface free energy is questionable.

A very different solution to the problem of the surface-like elastic constant K_{13} was proposed some years ago by Hinov[10,11] which made the *a priori* assumption that discontinuities of the director-field at the interfaces are unphysical and the director-field which minimizes the free energy must be searched in the class of continuous solutions of the bulk Euler-Lagrange equations. More recently V. M. Pergamenshchik[12] reached the same conclusion on the basis of better founded physical arguments. The main idea of V. M. Pergamenshchik is that the presence of a strong subsurface distortion is an artifact of theory because the theory consists in a power expansion of the free energy that is stopped at a finite order. According to Pergamenshchik, the truncation procedure at any finite order automatically produces surface elastic contributions and a solution for the director-field which is characterized by surface discontinuities, whilst a complete resummation over all the higher order terms should bound the free energy from below in such a way that director distortions with a very short characteristic length are no longer possible. To clarify this point of view, he considers a simple model of surface anchoring potential and shows that, if this surface potential is expanded in terms of the surface derivatives up to a finite order, the same mathematical problems related to K_{13} occur: in particular the free energy becomes unbounded from below. From this example V. M. Pergamenshchik infers that truncation of the free energy expression at a finite order automatically also produces unphysical strong subsurface distortions in the case of the K_{13} elastic constant, whilst a complete resummation over all higher order terms should avoid any subsurface strong distortion. Therefore he suggests that the true director-field must be searched in the class of *continuous functions* which solve the bulk Euler-Lagrange equation related to the first order elastic free energy. Although this point of view coincides with that of Hinov,[10,11] the Pergamenshchik boundary conditions differ substantially from those proposed by Hinov (see note (31) in Reference 12). However we can easily show that the Hinov boundary conditions do not always correspond to a minimum of the free energy in the class of continuous solutions of the bulk Euler-Lagrange equations. Therefore in the following we shall consider only the Pergamenshchik theoretical approach and we will refer to this theoretical procedure as the "**first order elastic theory**."

The previous argument is stimulating, but, in my opinion, there are no sound physical reasons for excluding the possibility of the occurrence of strong subsurface director distortions, whilst there are simple symmetry arguments that make the presence of these distortions probable when the orientation of the director at the interface is tilted.[6,9] In his paper Pergamenshchik criticizes the physical consistency of the existence of strong subsurface distortions occurring on a molecular length scale δ. He shows that the presence of this strong distortion produces an enormous negative subsurface free energy density localized in the subsurface layer. The free energy per unit surface area related to this source is estimated to be of the order of $F_{13} \approx -K_{13}/\delta$ which is much higher than the positive elastic contribution from any long-range bulk distortion. By using the reasonable values $K_{13} = 10^{-7}$ erg/cm and $\delta \approx 20$ Å we find $F_{13} \approx 0.5$ erg/cm^2. This negative surface free energy corresponds to a *negative* "surface tension" and, thus, Pergamenshchik concludes that a freely suspended nematic L.C. should be unstable and should spontaneously increase its surface area to reduce the surface free energy in complete disagreement with the experimental evidence. However, this argument is not correct since the distortion of the director-field is not the main source of excess of surface free energy at an interface. In particular, there is always a standard contribution to the surface free energy due to modified interactions between molecules close to the interface. This contribution has been calculated, for instance, by Parsons[13] for Van der Waals interactions and has been found to be $\gamma \approx 30$ erg/cm^2 for the free surface of typical nematic L.C., in satisfactory agreement with experimental values of surface tension. Therefore the surface tension of a freely suspended nematic L.C. is given by $\gamma_{tot} = \gamma + F_{13} \approx \gamma$ which is always positive and, thus, no exotic behaviour is predicted by the second order elastic theory as far as surface tension is concerned. Furthermore, the analysis of simple models of microscopic molecular interactions in nematic liquid crystals shows that, near the interface, due to the different local symmetry of the system, a uniform director orientation does not minimize the interaction energy between molecules if the director at the surface is tilted.[6,9] Under these conditions (tilted surface director orientation), there are well-founded physical arguments for expecting a great subsurface director distortion to actually occur within a few molecular layers. Note that a similar strong distortion has been observed in an experimental case.[14] Therefore, in my opinion, there are no well-founded physical reasons for excluding the presence of strong subsurface distortions close to the interfaces of a NLC. However, due to the approximations of the second order elastic theory, the actual shape of subsurface distortions may differ greatly from that predicted by this theory.

In this paper we are interested in comparing the predictions of the first order and the second order elastic theories. A recent theoretical analysis of consequences of the first order theory in the case of the Freederickz transition in a homeotropic or planar nematic layer has been published.[15] Very unusual phenomena were predicted in the case where $|K_{13}| > K_{11}/2$ or $|K_{13}| > K_{33}/2$, whilst only quantitative effects were predicted for $|K_{13}| < K_{11}/2$ or $|K_{13}| < K_{33}/2$. This makes it somewhat difficult to verify this theory in this latter case. In a recent paper we proposed an experimental method which should make it possible to test unambiguously the correctness of both the theories for $|K_{13}| < K_{11}/2$ or $|K_{13}| < K_{33}/2$. This method requires very high precision measurements of threshold Freederickz fields and surface director orientation which may be at the limit of actual experimental accuracy. In this paper we analyze a different geometry which, in principle, makes it possible to take more accurate measurements concerning the surface-like elastic constant. A simple analysis of the surface-like elastic contribution [see Equation (2)] shows that the greatest effects of K_{13} should occur in the case where the easy orientation of the director at the interfaces is tilted with respect to the normal to the surfaces. Therefore in this paper we analyze the case of a nematic LC with a tilted easy orientation at the surface in the presence of a magnetic field and we compare the predictions of the first order elastic model with those of second order elasticity. In Section 2, we analyze the predictions of the first order elastic theory and we show that this theory always predicts the existence of unusual macroscopic effects *for each value of the surface-like elastic constant*. In particular, a director distortion is also prediced to occur in the nematic layer in the special case where the orientation of the magnetic field is parallel to the director easy axis at the surface. Furthermore, no displacement of the director from the easy axis is expected to occur when the magnetic field makes a given angle with the easy axis. In Section 3 we repeat the same analysis using the second order elastic theory and we show that, in this case, no new macroscopic effect is predicted to occur. In particular the macroscopic physical behaviour of the system is exactly the same as that predicted by the Frank elastic theory (Equation (2) with $K_{13} = 0$) if one defines an apparent macroscopic easy axis and an "effective" anchoring energy. This conclusion is in full agreement with previous theoretical results obtained in Reference 8 and with the point of view to be found in Reference 9. The considerable qualitative differences between the predictions of the two theoretical models in the case of a tilted anchoring at the interface suggest simple and accurate experimental methods to test the correctness of the two proposed theoretical models. Section 4 is devoted to a discussion of these theoretical results and to conclusive remarks.

2. PREDICTIONS OF THE FIRST ORDER ELASTIC THEORY

Consider a NLC layer of thickness d, sandwiched between two parallel plates as shown schematically in Figure 1. We suppose that the easy director alignment at both the bounding plates lies in the vertical x-z plane and makes an angle β_0 with respect to the normal z to the plates. For the sake of simplicity we assume the same anchoring energy at both the plates. A magnetic field **H** is applied along an axis which makes an angle α with the normal to the plates. In order to simplify the mathematical calculations, we make the following simplifying assumptions: i) the bulk elastic constants K_{11} and K_{33} have the same value K ($K_{11} = K_{33} = K$); ii) the magnetic coherence length $\xi = (K/\chi_\alpha)^{1/2}/H$ is much smaller than the thickness d of the nematic layer, where χ_α denotes the anisotropy of the magnetic susceptibility and H the intensity of the magnetic field; iii) the displacement of the director at both the plates with respect to the easy axis is very small and, thus, the surface anchoring potential can be written in the very general form:

$$W(\theta_s) = \frac{W}{2}(\theta_s - \beta_0)^2, \tag{1}$$

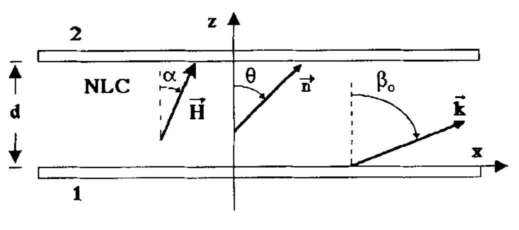

FIGURE 1 Schematic view of a nematic LC layer sandwiched between two parallel plates. d is the thickness of the layer, $\theta = \theta(z)$ is the angle between the director **n** and the orientation of the easy axis, α is the angle which the magnetic field **H** makes with the z-axis and β_0 is the easy angle at both the surfaces.

where W is the anchoring energy coefficient and θ_s is the angle which the director makes with the z-axis orthogonal to the surface. Note that in the literature authors often use the Rapini expression[16] to express the anchoring energy potential: $W(\theta_s) = W \sin^2(\theta_s - \beta_0)/2$. One can easily show that this expression is not the most general form for the surface potential; in particular, the symmetry of the interface makes other more complex contributions possible[17] which have been effectively observed in experiments.[18–21] On the other hand, we must emphasize that the theoretical predictions concerning the effects of a finite value of the surface-like elastic constant can greatly depend on what expression is assumed for the anchoring potential (see the Appendix of Reference 22). Therefore, to avoid model-dependent theoretical results, we do not make any assumption as to the actual form of the surface potential except the condition that $\theta_s = \beta_0$ must represent a minimum for this surface potential according to Equation (1). Condition (iii) is equivalent to hypothesizing that the anchoring extrapolation length $L_{ext} = K/W$ is much smaller than the magnetic coherence length ξ. Both conditions (ii) and (iii) can be easily satisfied in practical experimental conditions with magnetic fields lower than 10 KG. For instance one can easily perform an experiment by choosing the cell geometry, the magnetic field intensity and the kind of solid plates in such a way that: $d \approx 100–200\ \mu m$, $\xi(H) \approx 1–5\ \mu m$ and $L_{ext} \approx 100–300$ Å. As far as assumption (i) is concerned, we note that the same qualitative phenomena which are described in this paper can also be shown to exist if $K_{11} \neq K_{33}$, but, in this case, the theoretical expressions become very complicated. Therefore, to make the theoretical results clearer, here we prefer to avoid this unessential complication.

Under previous assumptions, the first order elastic free energy per unit surface area is:

$$F_2 = \frac{1}{2}\int_0^d [K\theta'^2 - \chi_\alpha H^2 \cos^2(\theta - \alpha)]\, dz + \frac{1}{2} W(\theta_1 - \beta_0)^2 + \frac{1}{2} W(\theta_2 - \beta_0)^2 - \frac{K_{13}}{2}(\theta_2' \sin 2\theta_2 - \theta_1' \sin 2\theta_1), \quad (2)$$

where K is the bulk elastic constant, K_{13} is the surface-like elastic constant, χ_α is the anisotropy of diamagnetic susceptibility, H is the intensity of the magnetic field, $\theta = \theta(z)$ is the angle between the director and the easy axis z, and W is the anchoring energy coefficient. The primes denote differentiation with respect to z and the subscripts 1 and 2 correspond to quantities measured at the surfaces $z = 0$ and $z = d$, respectively. Equation (2) has been obtained by making the standard assumption that the director-field always remains in the vertical x-z plane which contains the easy axis and the magnetic field. Under this assumption (planar distortion), the director-field is given by $\mathbf{n} \equiv [\sin\theta(z), 0, \cos\theta(z)]$. The Euler-Lagrange equation for the bulk director distortion is:

$$\theta'' - \frac{\sin 2(\theta - \alpha)}{2\xi^2} = 0 \quad (3)$$

For $\xi \ll d$, the director distortion remains almost entirely confined within two thin subsurface layers of characteristic thickness $\approx 3\xi$, whilst the director orientation is virtually parallel to the magnetic field in the remaining portions of the nematic layer. The director distortions close to the two interfaces are identical and, thus, we can restrict our attention to the region $0 \leq z \leq d/2$ where the first integral of Equation (3) becomes:

$$\theta' = -\frac{\sin(\theta - \alpha)}{\xi}, \tag{4}$$

where we have considered the case $-\pi/2 + \beta_0 < \alpha < \pi/2 + \beta_0$ and we have exploited the condition $d/\xi \gg 1$. The free energy per unit surface area is obtained by substituting Equation (4) in Equation (2) and by accounting for the symmetry of the director-field with respect to the centre $z = d/2$ of the nematic layer ($\theta_1 = \theta_2$, $\theta(z) = \theta(d - z)$). After some straightforward calculation we find:

$$F_2 = 2K\left[g_0 - \frac{1}{\xi}\cos(\theta_1 - \alpha) + \frac{(\theta_1 - \beta_0)^2}{2L_{\text{ext}}} - \frac{R}{2\xi}\sin 2\theta_1 \sin(\theta_1 - \alpha)\right], \tag{5}$$

where $g_0 = -1/\xi(d/2\xi - 1)$ is an unessential isotropic contribution, $L_{\text{ext}} = K/W$ is the extrapolation length and $R = K_{13}/K$ is the surface-like adimensional coefficient. The equilibrium value of the director surface angle θ_1 at the lower interface must minimize the free energy F_2 and, thus, it satisfies the boundary condition:

$$\frac{1}{\xi}\sin(\theta_1 - \alpha) + \frac{1}{L_{\text{ext}}}(\theta_1 - \beta_0) - \frac{R}{\xi}\left[\cos 2\theta_1 \sin(\theta_1 - \alpha) + \frac{\sin 2\theta_1}{2}\cos(\theta_1 - \alpha)\right] = 0. \tag{6}$$

Equation (6) predicts very unusual behaviour. Consider, for instance, the special case where the magnetic field is parallel to the easy axis ($\alpha = \beta_0$). We can easily verify that, for $R \neq 0$ and $\beta_0 \neq 0$, the expected solution $\theta_1 = \beta_0 = \alpha$ never satisfies Equation (6); this means that *a bulk distortion and a displacement of the director from the easy axis is always predicted by the first order elastic theory when the magnetic field is applied parallel to the easy axis if the easy director alignment is tilted.* In order to carry out a better analysis of this unexpected behaviour we shall consider the case where $\alpha = \beta_0 \ll 1$ and $\theta_1 \ll 1$, where Equation (6) gives:

$$\theta_1 = \beta_0 + \frac{R\beta_0}{\left[1 - 2R + \dfrac{\xi}{L_{\text{ext}}}\right]} \approx \beta_0 + \frac{L_{\text{ext}}}{\xi} R\beta_0, \tag{7}$$

where we have exploited condition (iii) ($L_{\text{ext}} \ll \xi$). According to Equation (7), the displacement of the director from the easy axis and, thus, the amplitude of the distortion in the bulk, is proportional to the intensity of the applied magnetic field ($1/\xi = (\chi_a/K)^{1/2}H$). A more unexpected consequence of Equation (6) is that the director at the surface remains parallel to the easy axis ($\theta_1 = \beta_0$) for each value of the magnetic field if the m.f. is oriented along the direction which corresponds to the special angle α given by:

$$\alpha = \beta_0 - \operatorname{atan}\left[\frac{R \sin 2\beta_0}{2(1 - R\cos 2\beta_0)}\right]. \tag{8}$$

For given values of β_0 and R, Equation (8) always provides a unique solution for α lying in the interval $-\pi/2 + \beta_0 < \alpha < \pi/2 + \beta_0$. In the case of homeotropic anchoring ($\beta_0 = 0$) and planar anchoring ($\beta_0 = \pi/2$) one obtains the obvious result $\alpha = \beta_0$. *In the case of tilted anchoring* α *is always different from* β_0 *for* $R \neq 0$ and, thus, for each value of the surface-like elastic constant K_{13}. Note that, unlike the case of homeotropic or homogeneous planar alignment where the first order theory predicts anomalous symmetry breaking distortions[15] only in the case in which $|R| > \frac{1}{2}$, in the present case of tilted easy director alignment, does the same theory predict exotic behaviour *for each value of the adimensional coefficient R.*

Effects such as those described by Equations (7) and (8) could be easily detected by using standard experimental methods. In particular, a measure of the surface director orientation versus the intensity of the magnetic field by means of reflectometric methods should supply a simple test of the validity of the theory.[23,24] However, we should like to remind the reader that a number of experimental investigations have been performed by using transmission-light methods in the same experimental conditions that correspond to the geometry of Figure 1, but anomalous effects of this kind have never been found. In particular a very accurate and standard method for measuring the easy tilt angle in a nematic layer is the "magnetic null method."[25] According to this method, which is currently used, a homogeneously oriented nematic layer is rotated in a magnetic field until the orientation is found where a measured physical property such as the layer capacitance or the optical retardation is found to be independent of the strength of the magnetic field. This special orientation corresponds to the easy director orientation. This method is very sensitive and, to the best of my knowledge, no unusual effects have been observed so far.

We note that the theoretical procedure followed in this Section is that proposed by Pergamenshchik.[12] Although the point of view of Reference 12 is practically coincident with that of Hinov,[10,11] the Hinov-boundary conditions differ substantially from those in Reference 12 and give somewhat different theoretical predictions showing anomalous behaviours of the same kind as those in Equations (7) and (8). However, the Hinov boundary conditions do not correspond to a minimum for the free energy and, thus, their physical meaning is not clear (see note (31) in Reference 12).

3. PREDICTIONS OF THE SECOND ORDER ELASTIC THEORY

In this Section we analyze the predictions of the second order theory for the same geometry as in Figure 1. A general analysis of this problem by means of the second order theory is practically impossible since the expression of the second order free energy density contains 35 new elastic constants that make it practically impossible to solve the mathematical problem. For this reason we restrict our attention here to the special case of small values of angles θ, β_0 and α ($\theta \ll 1$, $\beta_0 \ll 1$ and $\alpha \ll 1$) where only one bulk elastic constant K^* plays an important role.[7,8] According to Barbero *et al.* (see note 7 in Reference 26), we disregard the second order surface elastic constant and we write the free energy per unit surface area in the form:

$$F = F_2 + F_4 = \frac{1}{2}K\left\{\int_0^d \left[\delta^2(\theta'')^2 + (\theta')^2 - \frac{1}{\xi^2}\left(1 - \frac{(\theta-\alpha)^2}{2}\right)\right] dz\right\} + \frac{K}{2}\left[\frac{(\theta_1-\beta_0)^2}{L_{ext}} + \frac{(\theta_2-\beta_0)^2}{L_{ext}} - 2R(\theta_2\theta_2' - \theta_1\theta_1')\right], \quad (9)$$

where F_2 and F_4 are the first order and second order free energies per unit surface area, respectively, and $\delta = (K^*/K)^{1/2}$ is a characteristic length of the order of typical molecular dimensions ($\approx$20 Å) where K^* is the second order elastic constant. Minimization of Equation (9) with respect to small variations of $\theta(z)$ gives the following Euler-Lagrange equation for the director-field in the bulk:

$$\delta^2\theta^{IV} - \theta'' + \frac{\theta - \alpha}{\xi^2} = 0, \quad (10)$$

where the superscript IV denotes the fourth derivative with respect to z.

3a. Nematic Layer in the Absence of a Magnetic Field

In order to get a better understanding of the following results concerning the behaviour of this system in the presence of an external magnetic field, we first consider the simplest case where no magnetic field is applied to the system and, thus, the last contribution in Equation (10) vanishes ($\xi \to \infty$). This situation has been already investigated in Reference 26 in the case of a strong anchoring at both the interfaces. The general solution of Equation (10), with $\xi \to \infty$, is a symmetric function with respect to the centre of the layer which is given by:

$$\theta(z) = A + B\cosh\left[\frac{z - \frac{d}{2}}{\delta}\right], \quad (11)$$

where A and B are two unknown coefficients which can be obtained by solving the following boundary conditions at the lower plate $z = 0$:

$$\delta^2\theta_1''' - (1 - R)\theta_1' + \frac{\theta_1 - \beta_0}{L_{ext}} = 0 \tag{12}$$

and

$$\delta^2\theta_1'' - R\theta_1 = 0 \tag{13}$$

By substituting Equation (11) in Equations (12) and (13) we easily find:

$$\theta(z) = \frac{\beta_0 L_{eff}}{(1 - R)L_{ext}} + \frac{R\beta_0 L_{eff}}{(1 - R)^2 L_{ext}} \frac{\cosh\left(\dfrac{z - \frac{d}{2}}{\delta}\right)}{\cosh\left(\dfrac{d}{2\delta}\right)}, \tag{14}$$

where we have defined the "*effective extrapolation length*" L_{eff} by:

$$\frac{1}{L_{eff}} = \frac{1}{(1 - R)^2}\left[\frac{1}{L_{ext}} - \frac{R^2}{\delta}\operatorname{tgh}\left(\frac{d}{2\delta}\right)\right] \approx \frac{1}{(1 - R)^2}\left[\frac{1}{L_{ext}} - \frac{R^2}{\delta}\right] \tag{15}$$

which corresponds to the "*effective anchoring energy*":

$$W_{eff} = \frac{K}{L_{eff}} \approx \frac{W - \dfrac{KR^2}{\delta}}{(1 - R)^2} \tag{16}$$

The physical meaning of L_{eff} and W_{eff} will become clear in Section 3b. Equation (14) shows that, if the surface easy axis is tilted ($\beta_0 \neq 0$), a strong subsurface director distortion occurs within a very thin layer close to the interfaces even in the absence of the magnetic field. In this distorted layer the director passes rapidly from the surface value $\theta(0) = A + B = \beta_0 L_{eff}/(1 - R)^2 L_{ext}$ to the bulk value $\theta_{bulk} = A = \beta_0 L_{eff}/(1 - R)L_{ext}$. The total variation of the director angle across the subsurface distorted layer is, then, $\Delta\theta = B = R\beta_0 L_{eff}/(1 - R)^2 L_{ext}$. Therefore, in the absence of external magnetic fields, too, the second order elastic theory predicts that a short range director distortion will always occur close to both the interfaces of the nematic layer if $\beta_0 \neq 0$ and $R \neq 0$.

On preliminary analysis, this behaviour would appear to be in a complete disagreement with normal experimental evidence. However we can easily show that this is not true. In fact we emphasize that the strong director distortion which is predicted by Equation (14) occurs on the molecular scale length δ ($\delta \approx 20$ Å) which is practically inaccessible to standard experimental methods. In particular, optical methods are practically insensitive to director distortions which occur on a much smaller length scale than the optical wavelength λ ($\lambda \approx 5000$ Å $>> \delta$). Therefore, a nematic layer with the director distortion given by Equation (14) is practically indistinguishable from a nematic layer which is uniformly aligned along the bulk angle $\theta_{bulk} = B$. This means that, if we analyze this sample with optical methods, such as, for instance, the conoscopic technique or the "magnetic null method," we find that the director is uniformly oriented along an "*effective macroscopic easy axis*" making the following effective angle with the z-axis:

$$\beta_0^* = \theta_{bulk} = \frac{\beta_0 L_{eff}}{(1 - R)L_{ext}} . \tag{17}$$

Therefore, according to the second order elastic theory, the experimental value of the easy orientation in the case of a tilted alignment does not represent the true director orientation at the interface. *Apart from this new interpretation of the physical meaning of the macroscopic easy axis, we note that no apparent disagreement between the prediction obtained by using this theory and the experimental evidence is found in this case.*

3b. Nematic Layer in the Presence of a Magnetic Field

In this sub-Section we analyze the case where a magnetic field of intensity H is applied on the nematic L.C. layer at angle α with respect to the vertical z-axis (see Figure 1). As in the case investigated in Section 2, we restrict our attention to the simplest case $\xi << d$ where the long range distortion is confined within two thin sub-surface layers of characteristic thickness ξ. The general solution of Equation (9) in the semispace $0 < z < d/2$ which satisfies the boundary condition $\theta(z) \approx$ constant $= \alpha$ for $z/\xi \rightarrow \infty$, is given by:

$$\theta(z) = Ae^{-\lambda_1 z} + Be^{-\lambda_2 z} + \alpha, \tag{18}$$

where

$$\lambda_1 = \sqrt{\frac{1 - \sqrt{1 - \frac{4\delta^2}{\xi^2}}}{2\delta^2}} \approx \frac{1}{\xi} \tag{19}$$

and

$$\lambda_2 = \sqrt{\frac{1 + \sqrt{1 - \frac{4\delta^2}{\xi^2}}}{2\delta^2}} \approx \frac{1}{\delta} \tag{20}$$

with $\lambda_2 >> \lambda_1$. Coefficient A in Equation (18) is the amplitude of the standard macroscopic slow solution which is predicted by the first order elastic theory, whilst coefficient B is the amplitude of the short range second order distortion. Coefficients A and B can be obtained by substituting Equation (18) in the boundary conditions (12) and (13) that become:

$$\delta^2(-\lambda_1^3 A - \lambda_2^3 B) + (1 - R)(\lambda_1 A + \lambda_2 B) + \frac{A + B + \alpha - \beta_0}{L_{ext}} = 0 \quad (21)$$

and

$$\delta^2(\lambda_1^2 A + \lambda_2^2 B) + -R(A + B + \alpha) = 0. \quad (22)$$

We note that $A \neq 0$ and $B \neq 0$ for $\alpha = \beta_0$. This means that both the short range and the long range director distortions are always present when the magnetic field is applied parallel to the easy axis. This unexpected behaviour is apparently analogous to that already found in Section 2. However, according to the previous discussion in Section 3a, this behaviour is not in contrast with the experimental evidence if one considers that, from the macroscopic point of view, the nematic L.C. layer behaves as if the macroscopic easy axis was oriented along the effective easy angle β_0^* given by Equation (17) with the effective extrapolation length given by Equation (15). To make this important point clearer we shall solve the linear equation system (21), (22). Disregarding small contributions of the order δ^2/ξ^2, we find:

$$A = \frac{\beta_0^* - \alpha}{1 + \frac{L_{eff}}{\xi}} \quad (23)$$

and

$$B = \frac{R\left(\frac{L_{eff}\alpha}{\xi} + \beta_0^*\right)}{(1 - R)\left(1 + \frac{L_{eff}}{\xi}\right)}. \quad (24)$$

Therefore, apart from a strong subsurface distortion which cannot be seen by standard macroscopic techniques, the A coefficient which corresponds to the slow macroscopic distortion of characteristic thickness ξ, correctly vanishes when the magnetic field is oriented along the apparent macroscopic easy axis ($\alpha = \beta_0^*$ in Equation (23)). Therefore no special macroscopic phenomenon is found in this case in contrast with the predictions of the first order elastic theory. The macroscopic effective surface director angle can be defined as the limit for $z \to 0$ of the macroscopic director distortion which is given by: $\theta(z) = Ae^{-\lambda_1 z} + \alpha$ (see Figure 2). Therefore, the macroscopic surface director angle is given by:

$$\theta_1 = \beta_0^* + (\beta_0^* - \alpha)\frac{L_{eff}}{\xi} \quad (25)$$

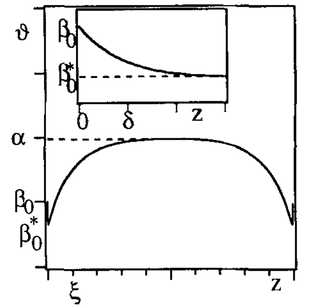

FIGURE 2 Director angle versus distance z from the lower surface for a magnetic field oriented at the angle α and for the easy director angle $\beta_0 = \alpha/2$. The magnetic coherence length is $\xi = d/10$, $\delta/\xi = 1/100$ and $R = 0.4$. A strong anchoring is assumed for both the interfaces. Insert: Details of the director angle very close to the lower surface ($z < 3\delta$). β_0^* and β_0 represent the macroscopic and the microscopic surface easy director angles, respectively. Note that the strong director distortion is practically invisible on the macroscopic scale length of Figure 2.

Note that the solution of the same elastic problem using the first order elastic theory with $R = 0$ (see Equation (6)) and for small angles, is: $\theta(z) = A'e^{-z/\xi} + \alpha$, where $A' = (\beta_0 - \alpha)/(1 + L_{ext}/\xi)$. The surface director angle is, then, $\theta_1 = A' + \alpha = \beta_0 + (\beta_0 - \alpha)L_{ext}/\xi$. If we compare these theoretical results for A' and θ_1 with those in Equations (23) and (25), we see that, from the macroscopic point of view, the second order elastic theory predicts the same behaviour predicted by the first order Frank theory (with $R = 0$) if we make the substitution of β_0 and L_{ext} with the corresponding macroscopic easy angle β_0^* and the effective extrapolation length L_{eff}. This conclusion is a complete agreement with the theoretical conclusions reached by Barbero *et al.*[8] in the case of homeotropic and planar anchoring and lends further support to the main idea in Reference 9 according to which the K_{13} elastic contribution behaves as a new anchoring source which only modifies the surface anchoring potential. Note that Equation (16) retains its physical meaning of an effective anchoring energy coefficient only if $|KR^2/\delta| < W$. In the opposite case, W_{eff} becomes negative and this means that the angle β_0 represents a maximum for the surface free energy and, thus, the actual easy axis is different from β_0.

4. DISCUSSION AND CONCLUSIONS

In this paper we have investigated the effects of the surface-like elastic constant on the behaviour of a nematic layer. Calculations have been performed by using two different theoretical procedures which have been proposed in the literature: the *first order elastic theory* and the *second order elastic theory*. Similar analyses have already been performed in the case of homeotropic or planar alignment in the presence of an orthogonal magnetic field.[8,15] In this case, the first order theory was shown to predict very spectacular effects (symmetry breaking distortions, spontaneous distortion) if $|K_{13}| > (K_{11}/2)$ or $|K_{13}| > (K_{33}/2)$ and only quantitative effects otherwise. In these conditions (homeotropic or planar alignment), the second order theory always predicts a renormalization of the anchoring energy and no exotic phenomenon. From a simple analysis of the structure of the surface elastic contribution one can expect that the most important contribution of the surface elastic constant occurs when the director easy alignment is tilted. For this reason, in this paper, we have investigated the predictions of the two theoretical models in the case of a nematic layer with a tilted director alignment and in the presence of a tilted magnetic field. In this case the first order theory always predicts unusual new phenomena for each value of the surface-like elastic constant. In particular this theory predicts that a director distortion must also occur in the case where the magnetic field is parallel to the easy axis, while no displacement of the director from the easy axis is expected to exist if the magnetic field makes a special angle with the easy axis. Both these phenomena are fully unexpected and could be easily detected by using reflectometric methods to measure the surface director orientation versus the intensity of the magnetic field.

The second order theory predicts the presence of a very sharp director distortion within a thin subsurface layer with a characteristic thickness of the order of a characteristic molecular length superimposed to the standard long range distortion generated by a magnetic field. In this paper we show that this apparently unusual behaviour is not in disagreement with the experimental evidence. Furthermore our theoretical results confirm the main conclusions in Reference 9 according to which the effects of the surface-like elastic constant are fully equivalent to a new anchoring source which only renormalizes the anchoring energy function and the easy axis orientation.

Our theoretical results suggest a simple and accurate experimental method for testing the validity of the two different theoretical procedures which have been proposed to by-pass mathematical difficulties connected with the problem of surface-like elastic constants. In particular, using reflectometric methods, one can measure the surface director angle versus the intensity of the magnetic field when the magnetic field is parallel to the easy axis. Under these experimental conditions, the first order elastic theory predicts a displacement of the director from the easy axis which is proportional to the intensity of the magnetic field and to the adimensional ratio R between the surface-like elastic constant and the bulk elastic constant, whilst the second order theory predicts no displacement of the director. Therefore measurement of the response of the surface angle to the magnetic field makes it possible to perform a direct and simple test concerning the validity of these theories. Using optical reflectometric methods[23,24] together with a time-modulation of the magnetic field and a synchronous detection-method one could easily measure variations of the surface director angle as small as 0.1 degrees if the easy surface angle is in the 20–70 degrees range. Note that the proposed method is a "null" method and, thus, it is virtually unaffected by the accuracy on the material parameters. Therefore this method is much more sensitive and accurate than the one we recently proposed[22] based on the measurement of the Freederickz threshold field for a homeotropic or planar layer. The possible results of this experiment are: a) no displacement of the director at the surface is observed. In this case, one can conclude either that $R = 0$ or that the first order elastic theory does not satisfactorily describe the actual physical behaviour of nematic LC. Since molecular theories predict that K_{13} should be different from zero[27] and of the same order of magnitude as the bulk elastic constants, this experimental result should lend some support to the second order elastic theory. b) A displacement of the director proportional to the magnetic field is observed. Such results would be direct evidence that the main consequences of the present form of the second order theory are not verified. In this case measurement of the linearity coefficient might provide the value of the K_{13}-elastic constant and justify the theoretical assumption in References 10–12.

The second order elastic theory is found to be consistent with the standard experimental evidence and provides a new interesting interpretation of the macroscopic meaning of the surface anchoring potential and of the easy axis in a tilted nematic layer. To the best of our knowledge the exotic effects predicted by the first order theory have not been observed. Furthermore, on the basis of symmetry arguments[9] and of the analysis of molecular interactions, there are well-founded physical reasons for expecting a strong subsurface distortion to occur close to the interfaces of a tilted nematic layer. Therefore, in our opinion, the second order elastic theory should provide a better description of the physics of the nematic surfaces. However we wish to emphasize that, although the main consequences of the second order elastic theory are probably correct, this theory is highly approximate (see the Introduction) and an accurate determination of the subsurface distortion and of the related anchoring source cannot be obtained by using an elastic theory but only with a direct analysis of microscopic molecular interactions in the subsurface layer.

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