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On the K_{13} surface-like elastic constant
An experimental method to test different theoretical models

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Oldano and Barbero showed that, due to the presence of the surface-like elastic constant K_{13} in the expression of the elastic free energy density, F_2, in a nematic liquid crystal, the functional F_2 is unbounded from below and thus it is impossible to find an equilibrium director distortion. In particular, they showed that the surface-like elastic constant favours a discontinuity of the director-field at the interfaces. In recent years two quite different theoretical approaches have been proposed to eliminate the mathematical difficulties related to the K_{13} problem. Barbero *et al.*, expanded the free energy functional F up to the fourth order in the director derivatives and showed that the minimization problem becomes mathematically well posed. A strong subsurface director distortion on a length scale of the order of the molecular length is predicted by using this approach. This point has been critized by V. Pergamenshchik who considers the subsurface strong distortion as an artefact of theory and proposes an alternative method to account for the effect of K_{13}. This method is virtually coincident with that already proposed by Hinov on the basis of an a priori assumption. In this paper we discuss some direct consequences of these two different approaches and we propose two simple experimental measurements which should lead to different results depending on which model is the correct one, allowing in this way a test of the different theoretical models.

1. Introduction

The macroscopic behaviour of a nematic liquid crystal (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]. In 1971 Nehring and Saupe [2] showed that a new term must be added to the free energy. This new contribution, 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. In 1985, Oldano and Barbero [3] showed that due to this new surface contribution, the free energy is unbounded from below so that no minimum of the free energy can be found. Therefore, the probem of finding the correct director-field in the NLC is not well posed if the surface contribution is present. The same kind of mathematical difficulty arises if the surface free energy depends explicitly on the first surface derivative of the director. In all these cases, a discontinuity of the director-field at the interfaces is expected to exist [4–6]. Barbero *et al.* [7–8], showed that the free energy becomes bounded from below if higher order terms up to the fourth order in the director derivatives are retained in the expression of the bulk free energy density. In the following, according to Barbero *et al.* we will denote this theory as the second order elastic theory. In this case, the free energy is shown to have a minimum in correspondence to a well-defined director distortion. The director-field is thus represented by a continuous function, but it exhibits a sharp variation close to the

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interfaces within a thickness of the order of the molecular length. *The main effect of this subsurface distortion is a large apparent reduction of the surface anchoring energy coefficient W.* Anyway, the above solution of the problem cannot be considered as definitive. In particular:

(i) A power expansion of the free energy as a function of the director derivatives is justified only if the length scale of director distortion is much higher than the molecular scale length. Therefore a correct analysis of strong subsurface distortions should be made by using microscopic theories of molecular interactions close to the interface.
(ii) Very close to the interfaces, the free energy density can differ largely from the bulk expression. In particular, the elastic constants become position-dependent and new elastic contributions must be considered [9].
(iii) The second order free energy density introduces new higher order surface contributions which are neglected but which, in principle, still make the free energy unbounded from below.

More recently, Barbero *et al.* [9], reanalysed the problem by accounting also for the spatial variation of elastic constants near the interfaces and for the symmetry breaking due to the presence of the interface by retaining an elastic form for the free energy near the interfaces. Also this analysis shows that all these subsurface elastic effects are fully equivalent to a renormalization of the anchoring energy. Therefore, they conclude that one can completely disregard the K_{13} elastic constant in the expression of the bulk free energy and account for its effects by defining a new effective anchoring potential.

A very different solution to the problem of the surface-like elastic constant K_{13} has been proposed by Hinov [10–11] which makes 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 found in the class of continuous solutions of the bulk Euler–Lagrange equations. More recently Pergamenshchik [12] reached the same conclusion on the basis of better founded physical arguments. The main idea of Pergamenshchik is that the presence of a strong subsurface distortion is an artefact of theory due to the fact that the theory consists in a power expansion of the free energy closed at a finite order. He shows that the truncation procedure at any finite order automatically produces a solution for the director-field which is characterized by a strong subsurface distortion. According to Pergamenshchik, a complete resummation over all the higher order terms should bound the free energy from below in such a way that director distortions with very short characteristic length are no longer possible. In order to clarify this point of view, Pergamenshchik considers a simple model of surface anchoring which does not allow for a subsurface strong deformation. He 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 case, Pergamenshchik infers that truncation of the free energy expression at any finite order automatically produces unphysical strong subsurface distortions also in the case of the K_{13} elastic constant, whilst a complete resummation over all higher order terms should eliminate any subsurface strong distortion. Therefore he suggests that the true director-field must be found in the class of *continuous functions* which minimize the standard first order elastic free energy.

The previous argument is stimulating, but not conclusive. In fact, the analysis of simple models of microscopic molecular interactions in a NLC shows that, near the interface, due to the symmetry breaking, it is actually possible that the uniform director orientation does not represent a minimum of free energy if the director at the surface is tilted at an angle $\theta \neq 0$ or $\theta \neq \pi/2$. Under these conditions, there are sound physical arguments to expect that a strong subsurface director distortion actually occurs within a few molecular layers. Note that a similar strong distortion has been found in some experimental cases [13]. Therefore we cannot exclude that subsurface strong distortions really occur close to the interfaces of a NLC. Finally, we notice that presently there is no consensus over whether the K_{13} term in the free energy exists at all [14]. Therefore, the problem of K_{13} is still open and new theoretical and experimental investigations are needed.

In a recent paper, Pergamenshchik *et al.* [15], analyse the Fréedericksz transition for a NLC layer in a magnetic field using the theoretical approach of [12]. They found that, if the K_{13} elastic constant is greater than $K_{33}/2$, the director-field should exhibit an unusual *parity-breaking configuration and a spontaneous bulk distortion should occur also in the absence of a magnetic field if the thickness is lower than a critical value* d_c. Note that a spontaneous bulk director distortion was predicted some years ago by Madhusudana *et al.* [16], for a conical anchoring at the interfaces by using the same theoretical procedure of [12]. If $|K_{13}|$ is lower than $K_{33}/2$, the K_{13} elastic constant only modifies the Fréedericksz threshold field and no parity breaking configuration is possible.

In the homeotropic case, the fourth order elasticity predicts a variation of the Fréedericksz threshold field which corresponds to an apparent decrease of the surface anchoring potential, but *no spontaneous bulk distortion.* A similar behaviour is expected in the case of conical degenerate anchoring at both the interfaces [17].

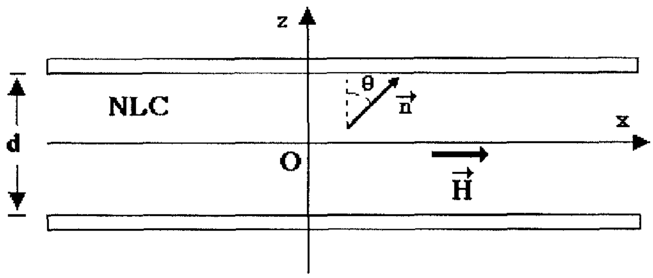
According to Pergamenshchik *et al.* [15], the experimental evidence of a spontaneous deformation, or of parity breaking director configurations, could give strong support to the analysis of [12]. However, to the best of our knowledge, these anomalous parity breaking director distortions have never been observed, although a lot of experiments concerning the Fréedericksz transition have been performed. This negative result could be interpreted as the experimental evidence either that the K_{13} constant for the NLC samples investigated so far by this experimental method is never larger than $K_{33}/2$, or that the Pergamenshchik method for calculating the bulk director-field is not correct.

In the present paper, we assume that $|K_{13}| < K_{33}/2$ and we pose the question whether effects related to a finite value of K_{13} can be experimentally observed. We propose two simple experimental measurements for which the Barbero and Pergamenshchik models predict different experimental results. Therefore, these experiments should supply a direct test for the validity of the two different theoretical approaches.

2. Threshold of the Fréedericksz transition

2.1. *Predictions of the Pergamenshchik model*

Consider a NLC layer of thickness d, sandwiched between two parallel plates in the presence of a magnetic field $\mathbf{H}$ oriented along the x axis parallel to the plates (see figure). We suppose that the anchoring of the director at the two interfaces is along the z axis, perpendicular to the plates (homeotropic anchoring). This is just the geometry analysed in [15] and [8]. Here we consider the case $K_{33} > 2K_{13}$ for which no spontaneous distortion is predicted. Let xyz be an orthogonal reference system with the origin at the



Schematic view of a nematic LC layer sandwiched between two parallel plates. Here d is the thickness of the layer, $\theta=\theta(z)$ is the angle between the director **n** and the orientation of the easy axis, and **H** is the magnetic field.

centre of the layer. By neglecting second order elasticity, the free energy (per unit area) of this system is given by [15]

$$F_2=\frac{1}{2}\int_{-d/2}^{d/2}[K_{33}\beta^2(\theta)\theta'^2-\chi_a H^2\sin^2\theta]\,dz$$
$$+W(\theta_1)+W(\theta_2)-\tfrac{1}{2}K_{13}(\theta_2'\sin 2\theta_2-\theta_1'\sin 2\theta_1), \tag{1}$$

where $\beta(\theta)=(1+\eta\sin^2\theta)^{1/2}$, $\eta=(K_{11}-K_{33})/K_{33}$ is the relative anisotropy of elastic constants. K_{11}, K_{33} and K_{13} are elastic constants, χ_a 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, $W(\theta)$ is the anchoring energy function (assumed to be the same on both interfaces), the primes denote differentiation with respect to z and the subscripts 2, 1 correspond to quantities measured at the surfaces $z=d/2$ and $z=-d/2$, respectively. In typical NLC, $\eta<0$. The exact functional dependence of $W(\theta)$ is not known, but it is usually assumed to be given by the Rapini form [18] $W(\theta)=W\sin^2\theta/2$, where W is the anchoring energy coefficient. This functional dependence is not rigorous and there are some experimental results [19–22] which indicate that the true anchoring energy is not represented by the Rapini form. It should be emphasized that assumptions concerning the functional dependence of $W(\theta)$ on the polar angle θ can greatly affect any possible measurement concerning the K_{13} elastic constant. Therefore, an unambiguous measurement of K_{13} requires that no a priori assumption on $W(\theta)$ is made. We will discuss in detail this important point in appendix A. For this reason, we restrict our attention to the special case where the surface polar angles θ_1 and θ_2 are very small and thus the anchoring energy is well represented by its parabolic approximation near the equilibrium angles $\theta_1=0$ and $\theta_2=0$

$$W(\theta)=\frac{W}{2}\theta^2, \tag{2}$$

where W is the anchoring energy coefficient. Note that the conditions $\theta\ll 1$ is always satisfied at the threshold of the Fréedericksz transition.

By using the procedure outlined in [12], Pergamenshchik *et al.* [15], calculated the threshold field for the Fréedericksz transition which is given by the implicit equation

$$u=\frac{Wd}{2K_{33}(1-2R)}\cot u, \tag{3}$$

where $u=d/2\xi$, where ξ is the magnetic coherence length. In the limit of strong enough anchoring ($Wd \gg K_{33}$), equation (3) becomes

$$H_c = H_\infty \left[1 - \frac{2L_{eff}}{d}\right], \tag{3 a}$$

where $H_\infty = \pi/d(K_{33}/\chi_a)^{1/2}$ is the Fréedericksz threshold field for strong anchoring ($W=\infty$) and where we have defined the effective extrapolation length

$$L_{eff} = \frac{K_{33}(1-2R)}{W}, \tag{4}$$

with $R=K_{13}/K_{33}$. For $R=0$, L_{eff} reduces to the ordinary extrapolation length $L_{ext}=K_{33}/W$. Therefore, as far as the Fréedericksz threshold is concerned, the effect of the K_{13} elastic coefficient is equivalent to a renormalization of the anchoring energy coefficient W. Note that, although the Hinov and Pergamenshchik approaches are based on the same assumption that the director-field must satisfy the Euler–Lagrange equation also at the two boundaries, equation (3) and equation (4) do not coincide with Hinov's results (equation (43) in [10]), since Hinov boundary conditions differ crucially from those proposed by Pergamenshchik (see the discussion in the note (31) of [12]). In particular, the Hinov solution for the director-field does not correspond to a minimum of the free energy in the class of continuous functions which solve the bulk Euler–Lagrange equations.

2.2. *Predictions of the second order elasticity*

The equilibrium solution for the director-field, as predicted by the second order elastic theory, exhibits a strong distortion near the two interfaces superposed to a standard long range distortion in the bulk. By neglecting surface contributions of higher order in the surface derivatives, Barbero and Strigazzi [8] found that the threshold field is still given by equation (3) and (3 *a*), but with a different definition of the effective anchoring energy coefficient and of the extrapolation length. In particular, L_{eff} becomes (in the homeotropic case)

$$L_{eff} = \frac{K_{33}}{W_{eff}}, \quad \text{with} \quad W_{eff} = \frac{[W-(K_{33}R^2/\delta)]}{(1-R)^2} \tag{5}$$

and where δ is the characteristic length of the strong subsurface distortion which is of the order of a few molecular lengths and is given by $\delta=(K^*/K_{33})^{1/2}$, where K^* is the second order elastic constant. As in the previous case, the main effect of K_{13} is a renormalization of the anchoring energy coefficient.

We notice that measurement of the Fréedericksz threshold field alone does not allow one to distinguish between the two previous models, since this measurement gives only the effective anchoring energy and thus, the parameters W and R cannot be obtained separately. However we will show that it is possible to discriminate experimentally between the two models if one (or some) more independent measurement(s) is (are) made on the same system. In the following § we discuss the predictions of the two models in the limiting case of high magnetic fields ($H \gg H_c$).

3. Behaviour in high magnetic fields ($H \gg H_c$)

3.1. *Predictions of the Pergamenshchik model*

For $H \gg H_c$, the characteristic length of the director distortion close to the interfaces of the layer is $\xi=(K_{33}/\chi_a H^2)^{1/2} \ll d$. Under these conditions, $\theta(0) \approx \pi/2$ and $\theta'(0) \approx 0$ and the bulk director distortion which minimizes the functional F_2 of equation (1) is easily found to satisfy the following equation [semi-infinite nematic layer]

$$\frac{d\theta}{dz}=\pm\frac{\cos\theta}{\xi\beta(\theta)},\tag{6}$$

where the signs + and − refer to the regions $z\in[-d/2, 0]$ and $z\in[0, +d/2]$, respectively. By substituting equation (6) in equation (1) with $\theta_1=\theta_2$ and $\theta'_1=-\theta'_2$ (this symmetric solution is correct in our hypothesis that $K_{13}<K_{33}/2$ [15]), after some straightforward calculations we find

$$F_2=2\left[\chi_a H^2\int_0^{+d/2}\left(\cos^2\theta-\frac{1}{2}\right)dz+W(\theta_2)+\frac{K_{13}}{2\xi\beta(\theta_2)}\sin 2\theta_2\cos\theta_2\right].\tag{7}$$

By using equation (6) and the boundary conditions $\theta(0)=\pi/2$ and $\theta(+d/2)=\theta_2$, the integral in equation (7) gives

$$F_2=F_0-\frac{K_{33}\beta(\theta_2)}{\xi}\left[1-\frac{2R\cos^2\theta_2}{\beta^2(\theta_2)}\right]\sin\theta_2-\frac{K_{33}\arcsin(\sqrt{(-\eta)}\sin\theta_2}{\xi\sqrt{(-\eta)}}+2W(\theta_2),\tag{8}$$

where $\eta<0$ and F_0 is a constant contribution which does not depend on the surface angle θ_2. In the limit of rather strong anchoring ($L_{\text{eff}}\ll\xi$, $\theta_2\ll 1$), equation (8) can be expanded up to the second order in the small angle θ_2:

$$F_2=F_0-\frac{2K_{33}}{\xi}[1-R]\theta_2+W\theta_2^2.\tag{9}$$

The equilibrium surface angle, which minimizes the free energy per unit surface F_2, is given by

$$\theta_2=\frac{K_{33}(1-R)}{W\xi}=\frac{L_{\text{eff}}(1-R)}{\xi(1-2R)}=\frac{\gamma}{\xi},\tag{10}$$

where we have defined the coefficient $\gamma=L_{\text{eff}}(1-R)/(1-2R)$ and where L_{eff} is given by equation (4). Note that our analysis is made on the hypothesis that $R<1/2$ and, in this case, equation (10) does not exhibit divergences. For $R>1/2$, the analysis of the director-distortion is different [15]. Equations (3) and (10) suggest that, if the Pergamenshchik method is correct, the surface-like elastic constant K_{13} can be obtained by measuring the Fréedericksz threshold field and the surface director angle in the high magnetic fields limit *on the same nematic LC layer*. Both measurements can be performed by using standard optical or capacitive methods [19–22]. The measurement of the threshold field H_c (equations (3) and (3 *a*)) allows one to obtain the effective extrapolation length L_{eff}, if the thickness d and the material parameters K_{33} and χ_a are known. Then, by measuring the surface director angle θ_2 for high enough magnetic fields, and by using equation (10), we can obtain the experimental value of the coefficient γ and, thus, the unknown parameter

$$R=\frac{K_{13}}{K_{33}}=\frac{(\gamma/L_{\text{eff}})-1}{(2\gamma/L_{\text{eff}})-1}.\tag{11}$$

We should remember that our theoretical calculations have been made under the assumption that $R<1/2$ and, thus, equation (11) is correct for $1/2<\gamma/L_{\text{eff}}<\infty$, where equation (11) represents a monotonically increasing function of γ/L_{eff}. It is important to emphasize that equation (11) has been obtained by making no a priori assumption concerning the functional dependence of the anchoring energy function $W(\theta)$ and, thus, it is a rigorous theoretical result if the Pergamenshchik procedure is correct. Furthermore, the validity of the approximation given by equation (2) can always be directly checked in the experiment. In fact, this approximation is well justified as far as the experimental value of the surface director angle θ_2 is found to be proportional to the applied magnetic field H as predicted by equation (10).

In the following sections we will show that the Barbero–Strigazzi model of second order free energy gives a completely different behaviour if $R \neq 0$ and, thus the measurement of both the Fréedericksz threshold and the surface director angle for high enough magnetic fields can represent a simple test of consistency of the two alternative theoretical approaches.

3.2. *Predictions of the second order elasticity*

The second order free energy contains 35 second order elastic constants. This makes the utilization of this expression impractical in the general case. However, in the limit of small director angles, the second order elastic free energy reduces to only one bulk elastic term characterized by *the second order elastic constant* K^*. In the case of high magnetic fields ($H \gg H_c$), the polar director angle in the bulk becomes very close to the value $\pi/2$ and thus, in principle, one should retain all 35 second order elastic constants. However, the analysis given in [8] shows that second order terms give a relevant contribution to the free energy only in a very thin subsurface layer of thickness $\delta = (K^*/K_{33})^{1/2}$, which is expected to be comparable with a typical molecular dimension ($20\,\text{Å} \ll \xi$). Therefore, if we restrict our attention to the case of small surface tilt angles (as in the previous discussions), the director angle is very small in the whole transition layer where the second order elasticity plays a relevant role. In the subsurface layer near the upper surface of the NLC layer, the bulk Euler–Lagrange equation for the director angle is given by the linearized equation [8]

$$\delta^2 \theta^{\mathrm{IV}} - \theta'' - \frac{\theta}{\xi^2} = 0, \tag{12}$$

where the superscript IV and primes denote the fourth and second derivatives with respect to z, respectively, and δ is given by

$$\delta = \left(\frac{K^*}{K_{33}} \right)^{1/2}. \tag{13}$$

At the upper surface, the solution of equation (12) must satisfy the boundary conditions [8]

$$\delta^2 \theta_2''' - \theta_2'(1-R) - \frac{W\theta_2}{K_{33}} = 0 \tag{14}$$

and

$$\delta^2 \theta_2'' - R\theta_2 = 0. \tag{15}$$

The general solution of equation (12) is given by the superposition of the usual long range distortion with characteristic length $\approx \xi$ and a strong subsurface distortion with characteristic length $\approx \delta \ll \xi$. This solution is

$$\theta(z) = A \exp(\lambda_2 x) + B \cos \lambda_1 x + C \sin \lambda_1 x, \tag{16}$$

where

$$\lambda_1=\sqrt{\left(\frac{-1+\sqrt{(1+(4\delta/\xi)^2)}}{2\delta^2}\right)}=\frac{1}{\xi}\left[1+O\left(\frac{\delta^2}{\xi^2}\right)\right]$$

and

$$\lambda_2=\sqrt{\left(\frac{1+\sqrt{(1+(4\delta/\xi)^2)}}{2\delta^2}\right)}=\frac{1}{\delta}\left[1+O\left(\frac{\delta^2}{\xi^2}\right)\right] \tag{17}$$

and where $x=z-d/2$. Substituting equation (16) in equations (14) and (15) with $\lambda_1\approx 1/\xi$, $\lambda_2\approx 1/\delta$ and $\lambda_1\ll\lambda_2$, we obtain

$$A=-\left(\frac{K_{33}(1-R)(R/\xi)}{W-(K_{33}R^2/\delta)}\right)C \quad \text{and} \quad B=-\left(\frac{K_{33}[(1-R)^2/\xi]}{W-(K_{33}R^2/\delta)}\right)C. \tag{18}$$

The solution (16) holds within the thin subsurface layer of thickness h given by a few characteristic lengths $\delta(\delta<h\ll\xi)$. Behind this layer, the second order elasticity becomes completely negligible ($\delta^2\theta^{\mathrm{IV}}\ll\theta''$) and the director-field must satisfy equation (6). Therefore the value of the unknown coefficient C can be obtained by imposing that the subsurface director field given by equation (16) satisfies equation (6) at $z=d/2-h$. For $\delta<h\ll\xi$ we find

$$\theta'\left(\frac{d}{2}-h\right)=\frac{A}{\delta}\exp\left(-\frac{h}{\delta}\right)-\frac{B}{\xi}\sin\left(\frac{h}{\xi}\right)+\frac{C}{\xi}\cos\left(\frac{h}{\xi}\right)\approx\frac{C}{\xi}. \tag{19}$$

Then, substituting equation (19) in equation (6) with $\theta(d/2-h)\ll 1$, we find $C=-1$ which, when substituted in equation (18), gives

$$A=\frac{L_{\text{eff}}}{\xi}\left(\frac{R}{1-R}\right) \quad \text{and} \quad B=\frac{L_{\text{eff}}}{\xi}. \tag{20}$$

In order to compare the high magnetic field case with the threshold-field condition, we must define the meaning of 'surface director angle' in the context of a macroscopic theory. According to standard models of the surface anchoring, the 'surface director angle' has to be considered as the limit for $z\to+d/2$ of the bulk slow director distortion, rather than the true surface angle (see, for instance (24) and (25)). As a matter of fact, both light transmission and capacitive methods are practically insensitive to director distortions which occur on a few molecular layers below the surface. In this context, the 'macroscopic' surface angle is given by

$$\theta_2=B=\frac{L_{\text{eff}}}{\xi}=\frac{\gamma}{\xi}, \tag{21}$$

where $\gamma=L_{\text{eff}}$ and L_{eff} is the fourth order effective extrapolation length defined in equation (5). Equations (21) and (3), with L_{eff} given by equation (5), are formally coincident with those which are obtained by using the Frank elastic energy without the K_{13} contribution, but assuming that the surface anchoring energy is W^{**} in place of W. Therefore, according to the second order elastic theory, the main effect of K_{13} is a renormalization of the anchoring energy coefficient and of the extrapolation length (see equation (5)). The same conclusion has been recently reached by Barbero *et al.* [9], who generalized equation (5) by accounting for the space variation of elastic constants and for the symmetry breaking at the interfaces. According to the theoretical expressions given in equations (3) and (22), we see that if we measure the extrapolation length L_{eff} by the threshold field (equations (3) and (3 *a*)) and the experimental γ coefficient defined in equation (21) by measuring the surface angle versus the magnetic field, we must find $\gamma = L_{\text{eff}}$. By substituting this result in equation (11) we see that it is equivalent to $K_{13} = 0$.

Similar results can be obtained in the case where the surface interactions produce a homogeneous planar alignment of the director along the x-horizontal axis and the magnetic field is oriented along the z axis. In the latter case, equations (3), (4), (5), (10) and (21) still hold if we make the substitutions $R \rightarrow -R$ and $K_{33} \rightarrow K_{11}$.

4. Discussion and conclusions

In the previous sections we have seen that if the Pergamenshchik conjecture is correct, the simultaneous measurement of the effective extrapolation length by means of the Fréedericksz threshold and of the γ-coefficient, which relates the surface angle to the magnetic coherence length ξ, allows us, in principle, to measure R and thus the K_{13} elastic constant through equation (11). On the other hand, if the predictions of the second order theory are correct, the same measurement should give a vanishing value of the right term in equation (11) and thus an apparent zero value of K_{13} in agreement with the main conclusions of [9]. These results have been obtained by making no special assumption about the anchoring energy function and, thus, they can be considered as rigorous theoretical results (see appendix *A*). Furthermore, we remark that the measurements proposed here are performed on the same nematic LC layer and in the same region of the sample. This is an important requisite to obtain unambiguous results on the value of K_{13}. In fact, under normal experimental conditions, it is very difficult and may be impossible to obtain the same anchoring energy values at different points in a same sample. The possible cases are two in number:

(i) The measured value of the right-hand side of equation (11) is found to be different from zero. In this case, we could infer that the second order theory *in the present form* is not able to describe in a satisfactory way the main experimental results. Therefore, this experimental result should give some support to the Pergamenshchik conjecture.

(ii) The measured value of the right-hand side of equation (11) is zero (within the experimental accuracy). In this case, the possible interpretations of the experiment are either that the K_{13} elastic coefficient is zero or that the second order theory is correct. Theoretical calculations of K_{13} seem to indicate that K_{13} should be different from zero and of the same order of magnitude as other first order elastic constants. Therefore this experimental result should give strong support to the main consequences of the second order elastic theory, according to which the main effects of K_{13} can be virtually accounted for by a renormalization of the anchoring energy potential. However, since in this case the contribution to the anchoring energy comes essentially from a very thin interfacial layer, equation (5) has only a semiquantitative character (higher order terms in the free energy may not be negligible) and a microscopic model of surface interactions is needed to obtain a more accurate value for the effective anchoring energy coefficient W_{eff}.

As shown in previous sections, a very important condition to obtain unambiguous theoretical results is that the surface polar angle is very small—also in the high magnetic field limit— so that *only the parabolic region of the surface potential is explored.* On the other hand, in a real experiment, the surface angle cannot become too small if we want to avoid large experimental errors. Therefore, one must reach some sort of compromise. Possible suitable values of the experimental parameters should be $L_{\mathrm{eff}} \approx 1/20\, d$ and $d/30 \leqslant \xi \leqslant d/6$. These conditions can be satisfied by a proper choice of the kind of surface treatment, the intensity of the magnetic field, the thickness of the nematic layer and the temperature. In this experiment, the greater experimental error is related to the measurement of the extrapolation length by means of the Fréedericksz threshold. Due to the relative large uncertainty of the elastic (≈ 3 per cent) and magnetic (≈ 3 per cent) constants of the NLC given in the literature, the maximum accuracy on the extrapolation length measured by the threshold field for $L_{\mathrm{eff}} \approx 1/20\, d$ can be estimated to be of the order of 30 per cent. A better accuracy should be obtained by measuring directly the threshold field H_{∞} in high anchoring conditions, for instance by repeating the same measurement for a NLC cell with a much higher thickness in such a way that $L_{\mathrm{eff}}/d \ll 1$. Another parameter which should be measured with a very high accuracy is the thickness d of the NLC layer [19]. By assuming that the experimental uncertainty on H_c and on H_{∞} is 0·5 per cent [19], we can estimate a relative accuracy on the experimental value of the extrapolation thickness of ≈ 10 per cent (if $L_{\mathrm{eff}} \approx d/20$). The obtainable accuracy on the experimental value of the γ coefficient ($\gamma = \theta_2 \xi$) measured by using high precision light transmission methods [20] can be estimated to be ≈ 5 per cent. The relative error on the parameter R of equation (11) is

$$\Delta R = \left(\frac{\Delta\gamma}{L_{\mathrm{eff}}} + \frac{\gamma}{L_{\mathrm{eff}}}\frac{\Delta L_{\mathrm{eff}}}{L_{\mathrm{eff}}}\right) \Bigg/ \left(\frac{2\gamma}{L_{\mathrm{eff}}} - 1\right)^2 . \tag{22}$$

So far, no experimental evidence for symmetry breaking distortions or spontaneous distortions in NLC layers has been reported in the literature, both in the case of planar and homeotropic alignment. This seems to indicate that $-1/2 < R < 1/2$ [15] and thus $3/4 < \gamma/L_{\mathrm{eff}} < \infty$. Equation (22) shows that the error ΔR greatly increases for $\gamma/L_{\mathrm{eff}} < 1$, corresponding to $R < 0$. In the case $R < 0$, the error greatly reduces if we make the same kind of measurements by studying the Fréedericksz threshold for a homogeneous planar alignment where all previous equations still hold if we make the substitution $R \to -R$ and $K_{33} \to K_{11}$. Therefore, to estimate the error on R, we can restrict consideration to the case $0 < R < 1/2$ which corresponds to $1 < \gamma/L_{\mathrm{eff}} < \infty$. In this case, the maximum error ΔR_{max} is expected for the case $\gamma/L_{\mathrm{eff}} = 1$ ($R = 0$), whilst a vanishing error ΔR is expected for $\gamma/L_{\mathrm{eff}} \to \infty (R \to 1/2)$. By assuming the relative errors $\Delta L_{\mathrm{eff}}/L_{\mathrm{eff}} \approx 0{\cdot}1$ and $\Delta\gamma/L_{\mathrm{eff}} \approx 0{\cdot}05$, the maximum error is $\Delta R_{\mathrm{max}} = 0{\cdot}15$.

In principle, the same kind of measurement should also be performed by using an electric field in place of the magnetic field. However, electric field interactions with nematic LC are much more complex than magnetic interactions. In particular, many different effects such as ordoelectricity, flexoelectricity, surface polarization, ionic electric conduction, etc., can influence experimental results and generate some ambiguity as far as the interpretation of experimental results is concerned.

We finally remark that an experimental measurement of K_{13} has been recently performed by Madhusudana and Pratibha by using a hybrid nematic layer of the NLC PCH-7 in the presence of a magnetic field [16]. These authors analysed the experimental results by using the Pergamenshchik procedure and found that their results gave a value of K_{13} comparable with the other elastic constants K_{33} and K_{11}. According to our previous discussion, this experimental result could be interpreted as the experimental evidence that the predictions of the fourth order elastic theory are not correct [8, 9]. However, to obtain their experimental results, the authors explicitly assume that the surface anchoring energy follows the Rapini–Popoular expression. This assumption is not well justified, since it has been found that the true anchoring potential has often a more complex shape [19–22]. In the appendix *A* we will show that the measured value of K_{13} can be greatly affected by this assumption. Therefore any experimental measurement of K_{13} which makes use of a priori hypotheses on the functional form of the anchoring potential is intrinsically ambiguous.

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Appendix A

In this appendix we show that an a priori choice of the surface anchoring function automatically induces wrong theoretical and experimental results concerning the K_{13} elastic constant. For the sake of simplicity we consider the simple case of the high magnetic field limit and make the simplifying assumption of isotropic elastic constants ($K_{11}=K_{33}=K$). This assumption does not modify our main conclusions, but only simplifies the mathematical analysis. Under these assumptions the free energy per unit surface area is

$$F_2=F_0-\frac{2K}{\xi}[1-R\cos^2\theta_2]\sin\theta_2+2W(\theta_2). \qquad \text{(A 1)}$$

The surface free energy is minimized if

$$\frac{K\cos\theta_2}{\xi}=\frac{W'(\theta_2)}{[(1+2R)-3R\cos^2\theta_2]}, \qquad \text{(A 2)}$$

where $W'(\theta_2)$ denotes the derivative of $W(\theta_2)$ with respect to the surface polar angle θ_2. For $R=0$, equation (A 2) reduces to the well-known result given by the Frank elastic theory

$$\frac{K\cos\theta_2}{\xi}=W'(\theta_2). \qquad \text{(A 3)}$$

The question is the following: is it possible to measure R utilizing equation (A2) if the functional dependence of the anchoring potential $W(\theta_2)$ is not known? The answer to this question is negative. In fact we can always define an effective anchoring potential $W_{\text{eff}}(\theta_2)$ by putting

$$W'_{\text{eff}}(\theta_2)=\frac{W'(\theta_2)}{[(1+2R)-3R\cos^2\theta_2]}. \qquad \text{(A 4)}$$

By symmetry arguments we know that, if the surface is not ferroelectric, $W(\theta_2)$ must be a function of $\cos^2\theta_2$, that is an even function of $\cos\theta_2$. This means that $W'(\theta_2)=g(\theta_2)\sin\theta_2$, where $g(\theta_2)$ is an odd function of $\cos\theta_2$. Therefore $W_{\text{eff}}(\theta_2)$, given by equation (A 4), is still an even function of $\cos\theta_2$, since

$$W_{\text{eff}}(\theta_2)=\int\frac{g(\theta_2)\sin\theta_2}{[(1+2R)-3R\cos^2\theta_2]}\,d\theta_2=W_{\text{eff}}(\cos^2\theta_2). \qquad \text{(A 5)}$$

Note that $W_{eff}(\theta_2)$ is still consistent with the general expression which is expected for a surface anchoring potential. Therefore, from this simple case, we infer that the effect of a finite value of the coefficient R can be simulated by assuming a different form for the surface anchoring potential. This means that, in this case, one cannot find a correct experimental value for the R parameter and thus for the surface-like elastic constant K_{13} if the form of the anchoring function $W(\theta_2)$ is not known. In fact, the main effect of this elastic constant, is a renormalization of the unknown anchoring energy function. In order to clarify this point further, consider the particular case where $R=0$, but the surface anchoring potential is not represented by the simple Rapini–Popoular form. In this case, if one attempts to fit the experimental results by assuming the Rapini form $W(\theta_2)=W\sin^2\theta_2/2$ for the anchoring potential and an unknown value of R, an experimental value of R which is different from zero can automatically be obtained. Otherwise, we notice that the analysis of experimental data under the assumption $R=0$ can give deviations from the Rapini potential also in the case where the true surface potential is of the Rapini form. This means that all previous experimental measurements of the polar anchoring energy functions [19–22] should be fully revised if $R\neq 0$ and the Pergamenshchik procedure is correct. Although our analysis concerns only a special case (high magnetic fields), we think that our main results can be generalized to most experimental conditions. Therefore, we think that an unambiguous measurement of the anchoring energy potential should always be performed by looking at the case of small surface angles for which the anchoring energy function has the known parabolic shape of equation (2).

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