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# Possibility of a deformed ground state in free standing nematic films

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**Résumé.** — On considère la possibilité d'existence de configurations distordues dans des films de cristaux liquides nématiques. Dans le cadre de la théorie de l'élasticité de Frank, les configurations stables sont celles qui ne sont pas distordues et compatibles avec les conditions aux limites. Quand on tient compte du terme de torsion contenant la constante $k_{13}$ et qu'on utilise l'énergie libre de Nehring-Saupe dans l'analyse de la stabilité des configurations nématiques, il apparaît que la structure déformée pourrait être plus stable que la structure non distordue si $k_{13}$ vérifie une relation particulière. Ce résultat, indépendant de l'épaisseur de l'échantillon, semble justifié par quelques résultats expérimentaux. Nous montrons que ce résultat étrange est dû à une simplification de la théorie élastique dans laquelle on néglige les termes qui dépendent du carré des dérivées deuxième de l'orientation moyenne des molécules du cristal nématique. Dans cet article, nous tenons compte de ces termes habituellement négligés. Nous montrons que les configurations distordues peuvent rester stables par rapport à la configuration non distordue seulement si la constante élastique $k_{13}$ est suffisamment grande et si l'épaisseur de l'échantillon est inférieure à une valeur critique. De plus, nous déterminons l'ordre de grandeur du rapport entre la nouvelle constante élastique, liée au terme élastique et qui dépend de la dérivée du deuxième ordre, et la constante élastique habituelle, en utilisant une théorie simple quasi microscopique.

**Abstract.** — The possibility of existence of distorted configurations in free standing nematic liquid crystal films is considered. In the framework of Frank elastic theory the stable configurations are always the undistorted ones, compatible with boundary conditions. When the mixed splay-bend elastic term with elastic constant $k_{13}$ is considered and the Nehring-Saupe free energy density used to analyse the stability of the nematic configurations, it seems that a splayed or bent structure could be more stable than the undistorted one, if $k_{13}$ satisfies a suitable relation. This result, which is independent of the sample thickness, seems justified by some experimental data. But we show that this strange result is due to an over-simplification of the elastic theory, in which terms depending on the square of the second order derivatives of the nematic molecular average orientation are neglected. In this paper we consider these usally neglected terms. We show that the distorted configurations can still be stable with respect to the undistorted one only if the elastic constant $k_{13}$ is large enough, and the sample thickness is smaller than a critical value. Furthermore the order of magnitude of the ratio between the new elastic constant, connected to the elastic term depending on the second order derivative, and the usual one is determined by using a simple quasi-microscopic theory.

## 1. Introduction.

The elastic behaviour of nematic liquid crystals is usually described in terms of the Frank elastic constants $k_{11}$, $k_{22}$ and $k_{33}$ connected with three fundamental deformations depending quadratically on the gradients of the average molecular orientation n̂ [1]. Recently attention has been drawn to the mixed splay-bend elastic constant $k_{13}$ [2, 3], associated with the term div (n̂ div n̂). This elastic contribution comes from a linear term in second order derivatives of n̂ and gives, using Gauss' theorem, only a surface contribution, which depends on the n̂-gradients [4]. Consequently it seems that it plays an important role in determining the equilibrium configuration only if weak anchoring situations are considered [5, 6]. Some years ago it was shown [7] that if the $k_{13}$-term is considered, the variational problem, connected with the minimization of the total free energy, has a discontinuous solution. This surface discontinuity has also been determined in a different way [8]. Furthermore it has been underlined [9] that the influence of surfaces must be carefully examined, since, near the boundaries it is necessary to take into account the spatial variation of the elastic constants [10], and of new terms which are zero in the volume. In this case the elastic problem becomes difficult to solve, but still a « surface discontinuity », localized over some molecular lengths, is expected [9].

In this paper we analyze another strange effect of the $k_{13}$-term on the nematic structure. More precisely we will show that if the ordinary elastic theory is considered the presence of the $k_{13}$-term would suggest that splayed structures are, from the energy point of view, favoured with respect to the undistorted one, independently of the sample thickness. But a deeper analysis shows that this result holds only if the sample thickness is smaller than a critical value, of the order of magnitude of the interaction range $r_N$ of the molecular forces giving rise to the nematic phase. This agrees with the fact that the sign of $k_{13}$, and obviously its magnitude, depend on the molecular shape, and hence splay or bend deformations can be favoured w.r.t. the undistorted one if the sample is very thin, as recently suggested [11]. Of course when the sample thickness is very large w.r.t. $r_N$ the equilibrium configuration does not depend on the molecular shape, and the undistorted configuration, compatible with the boundary conditions, is more stable.

In section 2 the usual elastic theory is considered. In this framework it is shown that a splayed structure can be stable w.r.t. the undistorted one if $k_{13}$ is negative and large enough. In section 3 a more general nematic free energy density, containing also terms which depend on the square of the second order derivatives, is used to determine the equilibrium configuration. It is shown that the new terms give a boundary distortion which simulate, from the macroscopic point of view, a « surface discontinuity » of the angle formed by n̂ with a fixed direction. This discontinuity is found to be of the same order as the one obtained with a different analysis [8]. Furthermore we will show that the free energy associated with these new terms is equivalent to a surface energy. We will also determine the critical thickness below which the splayed configuration is stable. This critical thickness, which is of the order of $r_N$, is different from zero only if $k_{13}$ is negative and large enough. Finally in section 4 the order of magnitude of the ratio between the new elastic constant, connected with the elastic term depending on the square of the second order derivative, and the usual one is determined by means of the simple Nehring-Saupe quasi-microscopic theory [4].

## 2. The role of the $k_{13}$-term.

Let us consider a freely suspended nematic film of thickness $d$. The $z$-axis is normal to the surfaces placed at $z = \pm d/2$, and $\theta$ is the tilt angle made by the director n̂ with the surface.

We consider the case in which the film surface free energy has a minimum for a tilt angle $\theta_0$ such that $0 < \theta_0 < \pi/2$, and is independent of the azimuthal angle, thus giving conic degeneracy. In the one constant approximation, and with the assumption that the director lies in a plane containing the surface normal $\hat{z}$, the Frank free energy density is given by

$$f_1 = (1/2) k \theta'^2 , \tag{1}$$

where $k$ is the average elastic constant and $\theta' = d\theta/dz$. In the absence of external fields the Euler-Lagrange equation, which gives the tilt angle $\theta(z)$ minimizing the bulk free energy, yields $\theta''(z) = 0$, i.e.

$$\theta'(z) = \text{constant} . \tag{2}$$

The solutions of equation (2), with the following three possible boundary conditions

$$\theta(d/2) = \theta(-d/2) = \theta_0 , \tag{3.1}$$

$$\theta(d/2) = -\theta(-d/2) = \theta_0 , \quad \text{and} \tag{3.2}$$

$$\theta(d/2) = \pi - \theta(-d/2) = \theta_0 , \tag{3.2'}$$

are

$$\theta_U(z) = \theta_0 , \tag{4.1}$$

$$\theta_S(z) = 2(z/d) \theta_0 , \quad \text{and} \tag{4.2}$$

$$\theta_B(z) = (\pi/2) + 2(z/d)(\pi/2 - \theta_0) , \tag{4.2'}$$

which are shown in figures 1a, 1b and 1c respectively. In the following we refer to solution (4.1) as U-solution (uniform or symmetric), to solution (4.2) as S-solution (splayed or antisymmetric), and to solution (4.2') as B-solution (bent) [12]. Solutions of both type (4.1) and (4.2) are possible because the conic degeneracy of the boundary conditions.
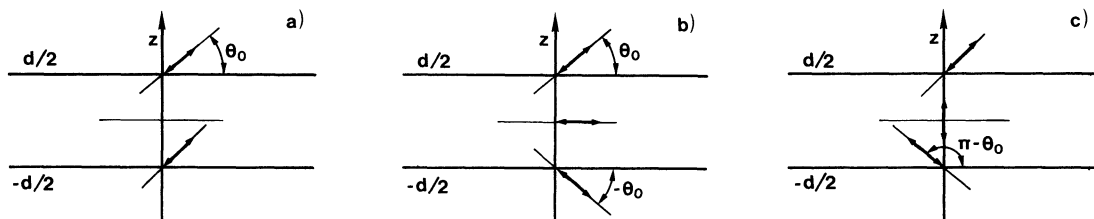


Fig. 1. — Three different configurations corresponding to the same surface energy : a) U-configuration, b) S-configuration, and c) B-configuration.

Obviously the different solutions correspond to different values of the free energy $F_U$, $F_S$ and $F_B$. If only the Frank energy term is taken into account the absolute minimum corresponds to the uniform solution $\theta_U(z)$, since $F_{U,1} = 0$, $F_{S,1} = 2(k/d) \theta_0^2$ and $F_{B,1} = 2(k/d)(\pi/2 - \theta_0)^2$.

Let us now consider the role of the term $k_{13} \text{div} (\hat{n} \, \text{div} \, \hat{n})$. It gives no contribution to the Euler-Lagrange equation, and therefore leaves the bulk equation (2) unchanged. In fact it can be integrated, and appears then as a surface term. The role of this term has been examined in many papers [7-9], and it seems now well established that it can give a strong distortion in a

thin boundary layer, whose thickness is of the order of few molecular diameters. This means that the « macroscopic » surface angle $\theta_0$ is different from the actual angle $\tilde{\theta}_0$ between the first molecular layer and the surface normal. Only rough evaluations of the ratio $\tilde{\theta}_0/\theta_0$ and of the energy associated with the distortion are avaible. However, in our case, it seems reasonable to assume that the surface energy is the same for all the solutions given by equations (4), since $\theta_0$ is the same. Under this assumption, only the bulk free energies of the solutions given by equation (4) are to be compared, in order to find the solution which minimizes the total free energy. By taking into account equation (2) it is easily found that the free energy density related to the $k_{13}$-dependent term is given by

$$f_{13} = k_{13}\, \theta'^2 \cos\,(2\,\theta)\,, \tag{5}$$

and that the bulk free energy per unit area is zero for U-solution (4.1) ($F_{U,1} = 0$), and

$$F_{S,1} = 2(k/d)\,\theta_0^2[1 + 2\,R \sin\,(2\,\theta_0)/(2\,\theta_0)]\,, \tag{6}$$

where $R = k_{13}/k$, for S-solution (4.2).

If $k_{13}$ is negative and large enough, this energy is negative, and gives the absolute minimum since

$$F_U > F_S\,. \tag{7}$$

This means that the distorted configuration is the preferred one. This result is not related to the one constant approximation, as shown in appendix A. We can note the following points :

i) the occurrence of solutions of both type (4.1) and (4.2) is related to the conic degeneracy, and is hardly expected for anchoring on a solid substrate : the choice between a distorted and an undistorted configuration is generally only allowed for freely suspended films. Some experimental evidence of a spontaneous distortion in films of this kind is found in literature [13, 14], but the effect appears as rather complicated, and can not be explained only in terms of the above oversimplified theory ;

ii) the dispersion forces give for the elastic constants the ratios $k_{11} : k_{22} : k_{33} : k_{13} = 5 : 11 : 5 : -6$ [4] ; with these values, S-configuration is the preferred one over a large $\theta_0$-range. This fact is related to the negative value of the constant $(k_{11} + 2\,k_{13})$ (see appendix A) ;

iii) if $k_{13}$ is positive and large enough, the B-configuration (4.2') is the preferred one for a suitable $\theta_0$-range. This fact is related to the negative value of the constant $(k_{33} - 2\,k_{13})$ [12].

Despite the above considerations, a more careful analysis is required, before we accept the possibility that a nematic liquid crystal could choose a distorted configuration if the boundary conditions allow for an undistorted one. In particular in the following we reconsider the assumption that the surface free energy is the same for the solutions (4.1) and (4.2). This is done by finding out a better solution, which leads a continuous variation of $\theta$ near the boundaries. This becomes possible when a higher order term is taken into account in the free energy expression.

## 3. Effect of the second order elasticity.

The presence of the $k_{13}$-term introduces a surface discontinuity of $\theta$ of the order $\Delta\theta = -R\theta_0$, as shown recently [8]. Since $\Delta\theta$ variation occurs on a thickness of the order of $r_N$, restriction of the free energy density in the Frank form may be questionable.

In fact $f_1$ is deduced by considering only slow nematic director variations on $r_N$. It is built writing, in general [15],

$$f_1 = L_{ijkemn} \, Q_{ij,k} \, Q_{em,n} \, , \tag{8}$$

where $Q_{ij} = S(n_i \, n_j - \delta_{ij}/3)$ is the tensor order parameter [1], and $L_{ijkemn}$ the usual elastic tensor. When the first derivatives of $\hat{n}$, or in our case of $\theta$, are not small on $r_N$, the second order derivatives can also play an important role. In order to have a well posed variational problem we write this new contribution as

$$M_{ijkemnpq} \, Q_{ij,ke} \, Q_{mn,pq} \, .$$

$M_{ijkemnpq}$ is the second order elastic tensor [16]. In the limit of small tilt angle [12] the nematic bulk free energy density can be written as

$$f_2 = (1/2)(k\theta'^2 + k^* \, \theta''^2) \, . \tag{9}$$

As we will show in section 4

$$k^*/k = b^2 \sim r_0 \, r_N \, , \tag{10}$$

where $r_0$ is a molecular length and $r_N$ the above introduced molecular range of the forces giving rise to the nematic phase. In the strong anchoring case the total free energy of the nematic is [17]

$$F_2 = (1/2) \int_{-d/2}^{d/2} (k\theta'^2 + k^* \, \theta''^2) \, \mathrm{d}z + k_{13}[(\theta\theta')_{d/2} - (\theta\theta')_{-d/2}] \, . \tag{11}$$

By minimizing (11) we obtain

$$b^2 \, \theta'''' - \theta'' = 0 \, , \tag{12}$$

where $b^2$ is defined in (10). Of course in the limit $k^* \to 0$ from equation (12) we reobtain equation (2).

Equation (12) must be solved with the boundary conditions (3.1) or (3.2) for the U or S configuration (coming from the strong anchoring hypothesis), and

$$b^2 \, \theta'' + R\theta = 0 \, , \tag{13}$$

for both configurations at $z = \pm d/2$ [18].

The general solution of (12) is

$$\theta(z) = A \, \mathrm{sh} \, x + B \, \mathrm{ch} \, x + Cx + D \, , \quad \text{where} \quad x = z / b \, . \tag{14}$$

In the following we are interested in the symmetric solution (U), for wich $A = C = 0$, and in the asymmetric one (S), having $B = D = 0$.

The U-solution is found to be

$$\theta_U(z) = [-R(\mathrm{ch} \, x/\mathrm{ch} \, X) + 1 + R] \, \theta_0 \, , \tag{15}$$

where $X = d/2b$ is usually very large w.r.t. one.

From (15) it follows that $\theta_U$ has a surface variation, occurring on a thickness $b$ near the boundary, given by :

$$\Delta\theta = \theta_0 - \theta_U \sim - R\theta_0 \, , \tag{16}$$

in agreement with previous estimation [8], and independent of $b$ (see Fig. 2a). By substituting (15) into (11) we obtain

$$F_{U,2}(\theta_0) = - (k/b) R^2 \, \text{th} \, X \theta_0^2 , \tag{17}$$

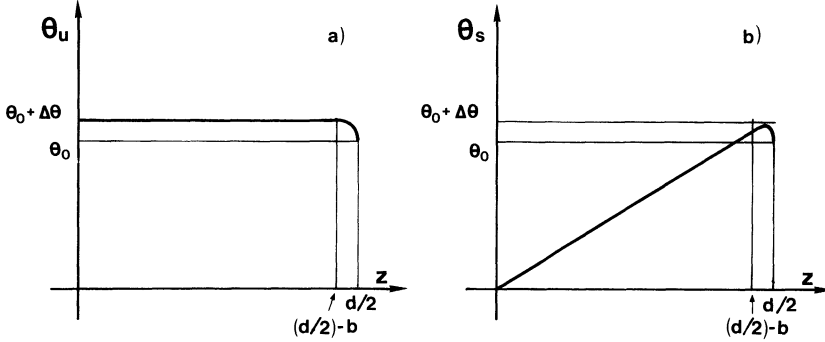where $\text{th} \, X \sim 1$, since $X \gg 1$.



Fig. 2. — Functions representing the tilt angle across the sample deduced by using second order elasticity for the undistorted configuration (a), and the distorted one (b). Both functions have a surface variation $\Delta\theta \sim - R\theta_0$, independent of $b$. The figure evidences the fact that the contribution to the free energy coming from the boundary layer is different in the two cases.

Equation (17) can be easily interpreted. In fact the « surface discontinuity » given by (16) occurs on a layer whose thickness is of the order of $b$. Hence the surface tilt angle gradient is approximatively given by $\theta' \sim (\Delta\theta/b) = - (R/b) \theta_0$. Consequently the Frank energy coming from this gradient is

$$F \sim 2 \int_{d/2 - b}^{d/2} (1/2) \, k (\Delta\theta/b)^2 \, dz = (k/b) R^2 \theta_0^2 , \tag{18}$$

which agrees with equation (17). The sign indicates only that the $\theta_U = \theta_0$ does not correspond to a minimum for $F_U$. The S-solution is then

$$\theta_S(z) = [- R (\text{sh} \, x/\text{sh} \, X) + (1 + R)(x/X)] \, \theta_0 . \tag{19}$$

$\theta_S(z)$ presents again a surface variation given by (16) (see Fig. 2b). The total free energy corresponding to the S-pattern is given by

$$F_{S,2}(\theta_0) = 2 (k/d)(1 + R)^2 \, \theta_0^2 - (k/b) R^2 \, \text{coth} \, X \theta_0^2 , \tag{20}$$

where $\text{coth} \, X \sim 1$. As in the U-case the latter term is equivalent to a surface contribution coming from the $\theta$-variation.

Taking into account the second order elasticity $F_S$ changes drastically, as it is easy to show. In fact from equation (6), valid in the small $\theta_0$-limit, we have

$$F_{S,1}(\theta_0) = 2 (k/d)(1 + 2 R) \, \theta_0^2 ,$$

i.e. a linear term $(1 + 2 R)$ is present. Hence $F_S$ can change its sign if $R$ is large enough and negative. On the contrary in equation (20) only the square of $(1 + R)$ appears. Consequently

if $d$ is large enough the S-configuration is never stable w.r.t. the U-one. This fact tells us simply that a bulk distortion always costs energy.

The S-configuration is favored w.r.t. the U-one if equation (7) holds, i.e. if

$$2 X/\text{sh}\, 2 X > [(1 + R)/R]^2 , \qquad (21)$$

from which we deduce that the S-pattern is stable only if $d < d_c$, given by equation (21) (see Fig. 3). This critical thickness is different from zero iff $R < - 1/2$. The critical thickness is, anyway, of the order of $b$. If dipolar interactions make a significant contribution to the intermolecular energies, $b$ can be quite large. Note that if $R \simeq - 1$, $d_c$ can become quite appreciable in magnitude.
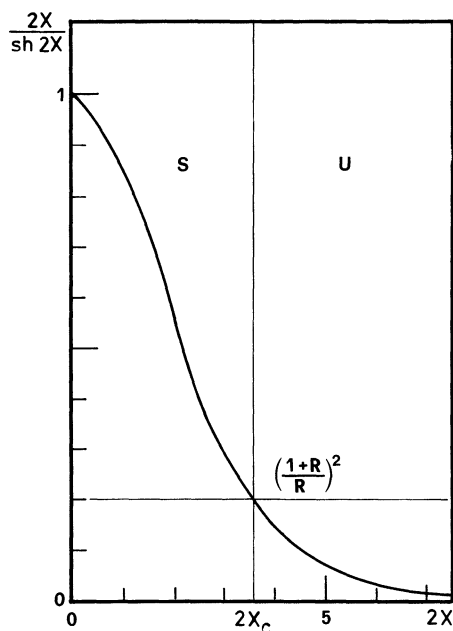


Fig. 3. — Phase diagram showing the regions where U or S configurations are stable. The critical thickness $d_c$ is different from zero, and hence the S-phase is stable in some $d$-range, only if $R < - 1/2$.

In the previous analysis we have considered the strong anchoring case. If this hypothesis does not work and the surface contribution is of the kind $(1/2)\, w\,(\theta_e - \theta_0)^2$, where $w$ is the anchoring strength and $\theta_e$ the orientation of the easy axis [19], equations (17) and (20) become

$$F_{U, 2} = w\,[- (L/b)\, R^2\, \text{th}\, X\theta_0^2 + (\theta_e - \theta_0)^2] , \qquad (17')$$

and

$$F_{S, 2} = w\,\{[2(L/d)(1 + R)^2 - (L/b)\, R^2\, \text{coth}\, X]\, \theta_0^2 + (\theta_e - \theta_0)^2\} , \qquad (20')$$

where $L = k/w$ is the anchoring extrapolation length.

Equations (17') and (20') show that when the $k_{13}$-term and second order elasticity are considered the effective easy axis has a tilt angle given by

$$\theta_{\text{eff}} = \theta_{\text{e}}/[1 - (L/b) R^2],\qquad (22)$$

and the effective anchoring energy is found to be [1]

$$w_{\text{eff}} = w[1 - (L/b) R^2]/(1 + R)^2.\qquad (23)$$

It is possible to deduce equation (23) also by considering Freedericksz transition [16].

By minimizing equations (17') and (20') w.r.t. $\theta_0$ we obtain $\theta_{0u}$ and $\theta_{0s}$. By substituting them into equations (17') and (20') and imposing condition (7) we deduce that the S-configuration is stable if equation (21) holds.

Our analysis is valid only if $F_u(\theta_{0u})$ and $F_s(\theta_{0s})$ correspond to minima of the total free energy, i.e. only if

$$1 - (L/b) R^2 > 0,\qquad (24)$$

which implies

$$w > (k/b) R^2.\qquad (25)$$

By supposing $R \sim 1$ [4], $k \sim 10^{-6}$ dyne [1] and $b \sim 10^{-6}$ cm [20], we obtain $w \sim 1$ erg/cm$^2$, which is of the order of the surface tension anisotropy [21]. Experimental determinations of $w_{\text{eff}}$ give values in the range $10^{-4} - 10^{-2}$ erg/cm$^2$ ; hence we conclude that these very small values arise from the difference between two large quantities.

## 4. Evaluation of the $k^*/k$ ratio.

In this section we estimate the order of magnitude of the ratio between the second order elastic constant $k^*$ and the usual one $k$. As known if the scalar order parameter $S$ is considered position independent, Frank energy, coming from $L_{ijklmn} Q_{ij,k} Q_{lm,n}$, can be written as [22]

$$f_1 = A_{ijke}\, n_{i,j}\, n_{k,e}\qquad (26)$$

where

$$A_{ijke} = \iiint_V q_{ij}\, u_k\, u_e\, r^2\, \mathrm{d}V,\qquad (27)$$

$$q_{ij} = [\partial^2 G/\partial n_i'\, \partial n_j']_{\hat{\mathbf{n}}' = \hat{\mathbf{n}}},\qquad (28)$$

$$\hat{\mathbf{u}} = \mathbf{r}/r.\qquad (29)$$

In (28) $G = G(\hat{\mathbf{n}}, \hat{\mathbf{n}}', \mathbf{r})$ is the two bodies interaction law. $G$ depends on the orientation of the

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[1] In fact from (20') we obtain for the surface tilt angle $\theta_s$

$$\theta_s = \theta_{\text{e}}/[1 - (L/b) R^2 + 2(L/d)(1 + R)^2] = \theta_{\text{eff}}/\{1 + 2(L/d)[(1 + R)^2/(1 - (L/b) R^2)]\},$$

where $\theta_{\text{eff}}$ is given by equation (22). In the usual elastic theory (where $k_{13} = k^* = 0$) the surface tilt angle is given by $\theta_s = \theta_{\text{easy}}/[1 + 2(L_{\text{eff}}/d)]$.

Comparing the obtained results we have for the effective surface anchoring energy expression (23).

two interacting bodies characterized by $\hat{n}$ and $\hat{n}'$ and from their relative position $\mathbf{r}$ [23-25, 9]. In the same way the second order elastic contribution $M_{ijklmnpq} Q_{ij,kl} Q_{mn,pq}$ writes

$$B_{ijklpq} \, n_{i,jk} \, n_{l,pq} \, , \tag{30}$$

where

$$B_{ijklpq} = \iiint_V q_{ij} \, u_k \, u_l \, u_p \, u_q \, r^4 \, dV \, . \tag{31}$$

In (27) and (31) the $V$-integration, in a first approximation, is performed over the region bounded by two spheres, whose inner radius is of molecular dimension $r_0$ and the outer radius $r_N$ is of the order of magnitude of the range of the nematic forces responsible of the nematic phase.

By decomposing tensor $A_{ijkl}$ appearing in equation (27) in the usual way [26], equation (26) can be rewritten in Frank form, where only splay, twist and bend distortions are present. The elastic constants are expressed in terms of $q_{ij}$.

If the two body interaction law is written as [23]

$$G(\hat{n}, \hat{n}', \mathbf{r}) = \sum_{a, a', c} J_{a, a', c}(r) (\hat{n}\hat{u})^a (\hat{n}' \, \hat{u})^{a'} (\hat{n}\hat{n}')^c \, , \tag{32}$$

where $a + a'$, $a + c$ and $a' + c$ are even numbers from symmetry considerations, we can compute, in a rough way, the elastic constants.

Routine calculations give for Frank elastic constants the expression [23]

$$k_i = (1/2) \sum_{a, a', c} J(a, a', c) \, N_i(a, a', c) \, , \tag{33}$$

where

$$J(a, a', c) = 4 \, \pi \int_{r_0}^{r_N} J_{a, a', c}(r) \, r^4 \, dr \tag{34}$$

and $N_i(a, a', c)$ do not depend on $r$, and are obtained integrating the angular part of the interaction law over $4 \, \pi$.

By operating in the same way we can rewrite expression (30) in a vectorial form, where only terms of the kind $(\Delta_2 \hat{n})^2$, $(\text{grad div } \hat{n})^2$ and so on appear. By means of equation (32) the second order elastic constants are found to be

$$k_i^* = (1/2) \sum_{a, a', c} J^*(a, a', c) \, N_i^*(a, a', c) \, , \tag{35}$$

where now

$$J^*(a, a', c) = 4 \, \pi \int_{r_0}^{r_N} J_{a, a', c}(r) \, r^6 \, dr \, , \tag{36}$$

and $N_i^*(a, a', c)$ is of the same order of magnitude of $N_i(a, a', c)$.

In the case of induced dipole-induced dipole interaction $J_{a, a', c}(r) = (1/r^6) \, C_{a, a', c}$ [4, 23], and trivial calculations give equation (10). Similar calculations show that in the case of $J_{a, a', c}(r) = (1/r^n) \, C_{a, a', c}$, with $n$ very large (8, 9...), $b \to r_0$, as expected, since only contact interactions are considered [27].

## 5. Conclusion.

In this paper we have considered the influence of the $k_{13}$-elastic constant on the nematic orientation. We have pointed out that if only the linear elasticity is considered a distorted structure seems stable w.r.t. the undistorted one, if a condition on the elastic constants is satisfied. This very strange result follows from the approximated expression of the free energy density employed in the analysis of the problem. If a more accurate free energy density is considered, in which quadratic terms in the second order derivatives are taken into account, the undistorted configuration is always stable for sample thickness large with respect to the nematic interaction range. In the limit of small thickness the undistorted configuration can be stable or not according to elastic constant ratio. In this limit the molecular shape can play an important role on the equilibrium configuration.

In fact, the found boundary distortion is of the same order of magnitude of the molecular dimensions, and the very fact of approaching the problem in terms of a continuum theory is questionable. For this reason we have limited our analysis to the case of small distortions. In this limit only one of the terms coming from equation (8) gives non negligible effects [17]. A more general analysis, with a detailed discussion of the other higher terms, seems of limited or doubtful usefulness to the authors.

In conclusion, the analysis given here confirms the fact, already point out in [7], that an acritical use of the $k_{13}$-dependent free energy terms can be misleading, and shows that physically consistent results can be obtained with the inclusions of the new term $\frac{1}{2} k^* \theta''^2$.

## Acknowledgement.

## Appendix A.

Let us reconsider the analysis given in section 2 in the general case, in which $k_{11} \neq k_{33}$, in order to show that the results are independent of the assumption $k_{11} = k_{33}$. The bulk free energy of the nematic is given by

$$F_1 = \int_{-d/2}^{d/2} \frac{1}{2} K(\theta) \, \theta'^2 \, dz + \frac{1}{2} k_{13} \{ [\sin (2\,\theta) \, \theta']_{d/2} - [\sin (2\,\theta) \, \theta']_{-d/2} \} \, . \quad (A.1)$$

The effective elastic constant is [28]

$$K(\theta) = k_{11} \cos^2 \theta + k_{33} \sin^2 \theta + k_f(\theta^2) = k_{11}(1 - h \sin^2 \theta) + k_f(\theta^2) \, . \quad (A.2)$$

The latter term in $K(\theta)$, $k_f(\theta^2)$, comes from the flexoelectric polarization. It is important when the Debye-length $L_D$ is large w.r.t. the length over which $\theta$ changes [29]. In the following we neglect it, since we are interested in $\theta$ variations occurring over the sample thickness, which is usually larger than $L_D$ [30]. In (A.2) $h = 1 - K_{33}/K_{11}$ is the relative elastic anisotropy.

The first term in (A.1) is minimum when $\theta(z)$ satisfies the equation :

$$K(\theta) \, \theta'^2 = C^2 \, , \quad (A.3)$$

where $C^2$ is an integration constant.

Let us consider the strong anchoring case where the surface tilt angles $\theta (\pm d/2)$ are fixed by the surface treatment and undependent of the bulk deformation. By putting

$$\theta_1 = \theta (- d/2) \quad \text{and} \quad \theta_2 = \theta (d/2) \tag{A.4}$$

from equation (A.3) we have

$$C = (1/d)\, I(\theta_1, \theta_2)\,, \tag{A.5}$$

where

$$I(\theta_1, \theta_2) = \int_{\theta_1}^{\theta_2} \sqrt{K(\theta)}\, d\theta \,. \tag{A.6}$$

The tilt angle is then given by

$$I(\theta_1, \theta(z))/I(\theta_1, \theta_2) = (z + d/2)/d \,. \tag{A.7}$$

By substituting equation (A.3) into equation (A.1), and using equation (A.5), we obtain for the total free energy :

$$F_1(\theta_1, \theta_2) = (1/2\, d)\, I(\theta_1, \theta_2) \times$$
$$\times \left\{ I(\theta_1, \theta_2) + k_{13}[\sin (2\, \theta_2)/\sqrt{K(\theta_2)} - \sin (2\, \theta_1)/\sqrt{K(\theta_1)}] \right\} \,. \tag{A.8}$$

The surface treatment only fixes the angle formed by $\hat{n}$ with the surface normal $\hat{z}$. Hence in our case there are two possible configurations corresponding to the same surface energy [12], i.e.

$$\theta_1 = \theta_2 = \theta_0 \tag{A.9}$$

shown in figure 1a, and

$$\theta_2 = - \theta_1 = \theta_0 \tag{A.10}$$

shown in figure 1b. As in section 2 we denote the configuration connected to (A.9) by U, and the other one connected to (11) by S.

In the U-case $I(\theta_1, \theta_2) = I(\theta_0, \theta_0) = 0$ ; $\theta(z) = \theta_0$ is constant in the layer and equation (A.9) gives

$$F_{U,1} = F(\theta_0, \theta_0) = 0 \,. \tag{A.11}$$

In the S-case $I(\theta_1, \theta_2) = I(- \theta_0, \theta_0) = 2\, I(0, \theta_0)$, as follows from (A.6) and (A.2). Now $\theta(z)$ changes across the sample and it is given by equation (A.7). The total free energy is

$$F_{S,1} = F(- \theta_0, \theta_0) = (2/d)\, I(0, \theta_0)[I(0, \theta_0) + k_{13} \sin (2\, \theta_0)/\sqrt{K(\theta_0)}] \,. \tag{A.12}$$

In the one constant approximation ($k_{11} = k_{33} = k$, hence $K(\theta) = k$ and $I(0, \theta_0) = \sqrt{k}\, \theta_0$) equation (A.12) becomes

$$F_{S,1} = (2\, k/d)\, \theta_0^2[1 + 2\, R \sin (2\, \theta_0)/(2\, \theta_0)] \,, \tag{A.13}$$

which agrees with equation (6).

The S-configuration is stable w.r.t. the U-one when $F_S < F_U$, i.e. when

$$I(0, \theta_0) + k_{13} \sin (2\, \theta_0)/\sqrt{K(\theta_0)} < 0 \,, \tag{A.14}$$

as follows from (A.11) and (A.12), since $I(0, \theta_0) > 0$ for any $\theta_0 \in (0, \pi/2)$. Equation (A.14) is independent of the sample thickness $d$. In the one constant approximation equation (A.14) becomes

$$1 + 2 R \sin (2 \theta_0)/(2 \theta_0) < 0 . \tag{A.15}$$

In the event that $\theta_0 \ll 1$ from equations (A.14), (A.15) we deduce that S-configuration is always stable if $R < -1/2$, i.e.

$$k_{13} < - k_{11}/2 . \tag{A.16}$$

If $\theta_0$ is not small equation (A.14) has to be used to find the relative stability of the S-configuration.

Previous analysis shows that, in the framework of the ordinary elastic theory the $k_{13}$-term could favour S-configuration, if it is negative and large enough. The critical value for this constant seems independent of the sample thickness, but dependent on $\theta_0$, as shows equation (A.14).

It is possible to estimate the importance of the new term $(k^*/2) \theta''^2$ introduced in section 3 w.r.t. the usual one $(k/2) \theta'^2$ by using the above results. In fact by means of equations (A.3) and (A.5) and taking into account equation (A.2), equation (9) can be written as

$$f_2 = (1/2)[k_{11}(1 - h \sin^2 \theta) + h^2(k^*/4 k_{11} d^2) I^2(\theta_1, \theta_2) \sin^2 (2 \theta)(1 - h \sin^2 \theta)^{-3}] \theta'^2 . \tag{A.17}$$

Equation (A.17) shows that

$$k^* \theta''^2/k\theta'^2 \sim h^2(k^*/k_{11} d^2) = h^2(r_0 r_N/d^2), \tag{A.18}$$

where equation (10) has been used. Hence the new term seems negligible. The analysis given in section 3 shows, on the contrary, that this term plays an important role when the effect of $k_{13}$ on the nematic structure is taken into account. As it is easy to understand, this surprising result, in which a very small term plays a very important role, is connected with the fact that the variational problem, is not well posed, when only the Frank energy is considered, in the sense that its solution is a discontinuous function.

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