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A conjecture on the Mada theory for nematic liquid crystal-surface interaction

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Résumé. — Nous discutons une nouvelle théorie proposée par Mada sur l'interaction surface-cristal liquide nématique. Nous soulignons certaines anomalies dans son calcul, et présentons les conditions aux limites correctes pour son modèle. En outre nous analysons le seuil de la transition de Fredericksz en fonction de l'épaisseur de l'échantillon et la dépendance en température de l'angle d'inclinaison à la paroi.

Abstract. — We discuss a recent theory proposed by Mada about the nematic liquid crystal-surface interaction. We point out certain anomalies in his calculation and we present the correct boundary conditions for his model. Furthermore we analyse the Fredericksz threshold vs. sample thickness and the pretilt angle vs. temperature with the revised theory.

1. Introduction.

The director in a nematic liquid crystal (NLC) has a well-defined angle with respect to the normal to an interface. This angle (the so-called pretilt angle) is determined by the NLC-surface interaction and the distortion in the bulk. At the present, very little is known about the mechanism responsible for the surface anchoring energy [1]. Excellent reviews on the continuum theory, taking into account the surface problems, are due to Kléman [2], Parsons [3], Yang [4] and Cognard [5]. In a recent paper, Mada [6] has analysed the NLC-surface interaction by introducing a surface free energy of the form :

$$\bar{A} = \bar{A}_d + \bar{A}_e \quad (1)$$

where $\bar{A}_d$ is the surface deformation energy per unit area, defined as

$$\bar{A}_d = \frac{1}{2}(\mathbf{n} \cdot \mathbf{d})^2 [\bar{K}_1 (d_i d_j \partial_i n_j)^2 + \bar{K}_2 (d_j \partial_i n_j)^2] \quad (2)$$

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and $\bar{A}_e$ is the energy related to the easy axis [2], that is

$$\bar{A}_e = -\frac{1}{2} \Delta\pi \{ (\mathbf{n} \cdot \mathbf{d})^2 - \frac{1}{3} \} . \quad (3)$$

In (2) and (3) $\mathbf{n}$ is the nematic director, $\mathbf{d}$ the easy axis (that is normal or parallel to the surface [7]), $\bar{K}_i$ are surface elastic constants, while $\Delta\pi$ is the anisotropic energy of surface alignment. Therefore equation (1) implies $\bar{A} = \bar{A}(n_i, \partial_j n_i)$.

Very recently Chiarelli *et al.* [8] report measurements on the pretilt angle vs. temperature, and they show that it is possible to interpret the experimental data both with Parson's [3] and Mada's [6] theories.

However, as pointed out in reference [8], these two theories are based on very different physical mechanisms.

In this letter we will show that Mada's theory must be revised. In fact the anisotropic interactions between a substrate and a NLC not only determine the direction of the easy axis on the substrate [7], but locally affect the orientational order of the liquid crystal [5], and then, as known, the order parameter on the boundary is greater than that in the bulk [9]. Therefore the elastic constant near the bounding walls are different from those in the volume.

Consequently, the general theory proposed by Mada seems correct from a phenomenological point of view. But the boundary conditions given by him are not valid (Sects. 3 and 4), and then the agreement with the experimental data is not significant (Sects. 5 and 6).

Furthermore a surface free energy depending on the derivative of the director along the normal to the substrate is connected with a long range distortion associated to $\bar{A}$, as we will show (Sect. 3).

But as shown by Sheng [10] if the sample thickness is $\gtrsim 1 \mu\text{m}$ the direct interaction between the bounding walls is negligible, in the sense that they interact only by means of the volume term (i.e. the surface effect is a local phenomenon), and then in these cases the boundary conditions connect the volume free energy only with a surface energy, contrary to the examined theory (see Sect. 3). On the other hand, if the sample is very thin, a direct influence between the walls is possible, but in this case a continuum theory does not seem very useful [11].

2. On the boundary conditions of Mada.

With the aim of demonstrating that the boundary conditions given by Mada are not correct, we consider the total free energy associated to the nematic director distortion. If $A(n_i, \partial_j n_i)$ is the free energy density in the bulk [2], the total free energy of a sample limited by a surface S is given by

$$F(\mathbf{n}) = \iiint_V A(n_i, \partial_j n_i) dV + \oint_S \bar{A}(n_i, \partial_j n_i) d\sigma . \quad (4)$$

Mada solved the problem in the usual way by minimizing (4) with respect to variations of n_i , and gives the following equation :

$$\partial_j \left\{ \frac{\partial A}{\partial (\partial_j n_i)} \right\} - \frac{\partial A}{\partial n_i} = 0 , \quad \forall \mathbf{P} \in V \quad (5)$$

and the boundary condition

$$\partial_j \left\{ \frac{\partial \bar{A}}{\partial (\partial_j n_i)} \right\} - \frac{\partial \bar{A}}{\partial n_i} - \nu_j \frac{\partial A}{\partial (\partial_j n_i)} = 0 , \quad \forall \mathbf{P} \in S \quad (6)$$

where ν is the outward normal to the surface.

Equation (5) is the well known Euler-Lagrange equation for functional (4). In this case the boundary condition is determined by the requirement that

$$\delta F = \delta n_i \left\{ \frac{\partial F}{\partial (\delta n_i)} \right\}_{\delta n_i=0} = 0, \quad \forall \delta n_i.$$

A simple analysis shows that if $\mathbf{n}$ is a solution of equation (5) with the boundary conditions (6), then δF is given by :

$$\delta F = \oint_S \partial_j \left\{ \delta n_i \frac{\partial \bar{A}}{\partial (\partial_j n_i)} \right\} d\sigma, \quad (7)$$

that is, generally, different from zero. In fact by using (2) and (3) we have :

$$\frac{\partial \bar{A}}{\partial (\partial_j n_i)} = \frac{\partial \bar{A}_d}{\partial (\partial_j n_i)} = (\mathbf{n} \cdot \mathbf{d}) \{ \bar{K}_1 d_i d_\beta \partial_\alpha n_\beta + \bar{K}_2 \partial_i n_\alpha \} d_j d_\alpha \neq 0.$$

Consequently only for some δn_i do we have $\delta F = 0$. But $\delta F = 0$ is a necessary condition for F to be stationary, and hence equations (5) + (6) do not give a stable configuration for the functional (4) (see Appendix 1).

3. Correct boundary conditions for Mada's theory.

Now we deduce the correct boundary conditions for the theory of Mada and we show that they differ strongly from that proposed by the above-mentioned author.

We consider a NLC layer of thickness d confined between $z = -d/2$ and $z = +d/2$ of a Cartesian coordinate system. The z -axis is normal to the cell plates, and the x -axis is parallel to them. Furthermore we suppose that the director always lies in the (x, z) plane. The tilt angle between the director $\mathbf{n}$ at the position z and the z -axis is denoted by ϕ . By the hypothesis of uniform alignment on the wall, $\mathbf{n}$ is invariant with respect to translations parallel to the x -axis and then $\mathbf{n} = \mathbf{n}(z)$ only (which implies $\phi = \phi(z)$). Based on the elastic continuum theory [2] of NLC, the total free energy of the system per unit area in the (x, y) plane can be written as :

$$F(\phi) = \int_{-d/2}^{d/2} A(\phi, \phi_z) dz + \bar{A}_1(\phi, \phi_z) + \bar{A}_2(\phi, \phi_z) \quad (8)$$

where the subscript z means differentiation with respect to z , and $\bar{A}_b(\phi, \phi_z) \equiv \bar{A}_b[\phi_b(\phi_z)_b]$, $b = 1 \rightarrow z = -d/2$ and $b = 2 \rightarrow z = +d/2$. The last two terms in equation (8) describe the interfacial energy per unit area as functions of ϕ and ϕ_z , while $A(\phi, \phi_z)$ given by Franck's formula, is the free energy density associated with ϕ_z .

In this case $\phi(z)$ is the solution of the equation

$$\frac{\partial A}{\partial \phi} - \left(\frac{\partial A}{\partial \phi_z} \right)_z = 0 \quad \forall z \in (-d/2, d/2) \quad (9)$$

and the first variation of (8) is

$$\delta F = \left\{ \left[-\frac{\partial A}{\partial \phi_z} + \frac{\partial \bar{A}}{\partial \phi} \right] \eta + \frac{\partial \bar{A}}{\partial \phi_z} \eta_z \right\}_1 + \left\{ \left[\frac{\partial A}{\partial \phi_z} + \frac{\partial \bar{A}}{\partial \phi} \right] \eta + \frac{\partial \bar{A}}{\partial \phi_z} \eta_z \right\}_2 \quad (10)$$

where η is an arbitrary function.

From equation (10) we deduce the mixed boundary condition, involving also the variation η , as

$$\left(-\frac{\partial A}{\partial \phi_z} + \frac{\partial \bar{A}}{\partial \phi}\right)_1 \eta_1 + \left(\frac{\partial \bar{A}}{\partial \phi_z}\right)_1 \eta_z(1) + \left(\frac{\partial A}{\partial \phi_z} + \frac{\partial \bar{A}}{\partial \phi}\right)_2 \eta_2 + \left(\frac{\partial \bar{A}}{\partial \phi_z}\right)_2 \eta_z(2) = 0. \quad (11)$$

In a planar deformation (no twist) with uniform boundary conditions, as in (8), the free energy density $A(\phi, \phi_z)$ is given by [2, 12]

$$A(\phi, \phi_z) = \frac{1}{2} K_{33}(1 - k \sin^2 \phi) \phi_z^2 + G(\phi)$$

where K_{33} is the bend elastic constant, $k = 1 - (K_{11}/K_{33})$ the elastic anisotropy and $G(\phi)$ the free energy density connected with the external fields. Consequently $\partial A / \partial \phi_z = K_{33} \times (1 - k \sin^2 \phi) \phi_z$ and then

$$\left(\frac{\partial A}{\partial \phi_z}\right)_b = K_{33}(1 - k \sin^2 \phi_b) \phi_z(b).$$

In a general problem with different anchoring energy on the bounding walls we have $\phi_1 \neq \phi_2$ and furthermore $\phi_z(1) \neq \phi_z(2)$. Moreover the arbitrary variations η_1 and η_2 can be different. From these observations it follows that in equation (11) all terms are necessary.

In order to determine the exact boundary conditions for Mada's theory we observe that, A being a quadratic function of ϕ_z [2], equation (9) is an ordinary second-order differential equation. Then the solution is of the kind $\phi = \phi(C_1, C_2; z)$, where the C_b are integration constants determined by the (unknown) boundary conditions. If $C_b = \phi_b$ (pretilt angles) we have that the function minimizing the generalized functional (8) is $\phi = \phi(\phi_1, \phi_2; z)$. This form of ϕ represents a family of curves with two parameters. When $\phi = \phi(\phi_1, \phi_2; z)$ is the solution of the proposed problem, a function infinitesimally close to it is $\phi' = \phi'(\phi'_1, \phi'_2; z)$, where $\phi'_b = \phi_b + \alpha_b$, with $\alpha_b \ll \phi_b$. Consequently it is possible to write :

$$\phi' = \phi + \left(\frac{\partial \phi}{\partial \phi_b}\right)_{\alpha_b=0} \alpha_b + O(\alpha_b^2) \quad (12)$$

and then for the variation $\eta(z)$ we get

$$\eta(z) = \phi' - \phi = \left(\frac{\partial \phi}{\partial \phi_b}\right)_{\alpha_b=0} \alpha_b = \left(\frac{\partial \phi}{\partial \phi_b}\right)_{\alpha_b=0} \eta_b \quad (13)$$

because, obviously, $\alpha_b = \eta_b$.

Equation (13) gives, by employing elementary theorems,

$$\eta_z(b) = \left(\frac{\partial \phi_z}{\partial \phi_a}\right)_b \eta_a. \quad (14)$$

By substituting (14) into (11) and taking into account the fact that the η_b are linearly independent, we obtain the boundary conditions for the functional (8) as :

$$\begin{aligned} -\left(\frac{\partial A}{\partial \phi_z}\right)_1 + \frac{\partial \bar{A}_1}{\partial \phi_1} + \left(\frac{\partial \bar{A}_1}{\partial \phi_z} \frac{\partial \phi_z}{\partial \phi_1}\right)_1 + \left(\frac{\partial \bar{A}_2}{\partial \phi_z} \frac{\partial \phi_z}{\partial \phi_1}\right)_2 &= 0 \\ \left(\frac{\partial A}{\partial \phi_z}\right)_2 + \frac{\partial \bar{A}_2}{\partial \phi_2} + \left(\frac{\partial \bar{A}_2}{\partial \phi_z} \frac{\partial \phi_z}{\partial \phi_2}\right)_2 + \left(\frac{\partial \bar{A}_1}{\partial \phi_z} \frac{\partial \phi_z}{\partial \phi_2}\right)_1 &= 0. \end{aligned} \quad (15)$$

Then the proposed theory predicts that the boundary conditions for $z = -d/2$, for example, also contain a term related to the surface energy on the boundary at $z = d/2$.

This fact implies that the orientating action of the walls is not local, but global, contrary to the experimental results [9] on thick NLC samples, as we have pointed out in section 1.

It is possible to deduce the correct boundary conditions (15) following another procedure. In fact if $\phi = \phi(\phi_1, \phi_2; z)$ is the solution of equation (9), with undetermined ϕ_b , substitution into (8) yields $F = F(\phi_1, \phi_2)$. Thus F is an ordinary function of the tilt angles on the boundaries. By imposing $\partial F / \partial \phi_b = 0$, which are the necessary conditions for extrema, we obtain

$$\frac{\partial F}{\partial \phi_b} = \frac{\partial}{\partial \phi_b} \int_{-d/2}^{d/2} \Lambda(\phi, \phi_z) dz + \frac{\partial}{\partial \phi_b} \bar{\Lambda}_1(\phi, \phi_z) + \frac{\partial}{\partial \phi_b} \bar{\Lambda}_2(\phi, \phi_z), \quad (16)$$

where, obviously, $\phi_z = \phi_z(\phi_1, \phi_2; z)$. But, by hypothesis, ϕ is a solution of equation (9). Then the first term on the right side of (16) is $(-1)^b (\partial \Lambda / \partial \phi_z)^b$. Then it is easy to show that equation (16) gives equation (15).

In particular, when the wall 2 is at $z \rightarrow \infty$ (and then $\phi_z \rightarrow 0$ for $z \rightarrow \infty$), or there is a strong anchoring on it, the first equation of the system (15) becomes :

$$-\left(\frac{\partial \Lambda}{\partial \phi_z}\right)_1 + \left(\frac{\partial \bar{\Lambda}_1}{\partial \phi}\right)_1 + \left(\frac{\partial \bar{\Lambda}_1}{\partial \phi_z} \frac{\partial \phi_z}{\partial \phi_1}\right)_1 = 0.$$

Then it is possible to rewrite the above as :

$$-\left(\frac{\partial \Lambda}{\partial \phi_z}\right)_1 + \left(\frac{\partial \bar{\Lambda}_1}{\partial \phi}\right)_1 - \left[\left(\frac{\partial \bar{\Lambda}_1}{\partial \phi_z}\right)_z\right]_1 + \left[\left(\frac{\partial \bar{\Lambda}_1}{\partial \phi_z} \frac{\partial \phi_z}{\partial \phi_1}\right)_z\right]_1 = 0. \quad (17)$$

This equation differs from that proposed by Mada by the last term, which is generally different from zero.

From this observation it follows that the boundary conditions given in Mada's paper for the homeotropic or planar configuration (Eqs. (20) and (21) of Ref. [6]) are incorrect. Then it is very curious that in references [6, 8-11] an excellent agreement between theory and experiment has been claimed.

4. δF in the unidimensional case.

As pointed out in section 2, Mada gives the following boundary conditions :

$$\begin{aligned} \left(\frac{\partial \bar{\Lambda}}{\partial \phi_z}\right)_z - \frac{\partial \bar{\Lambda}}{\partial \phi} + \frac{\partial \Lambda}{\partial \phi_z} &= 0 & z = -d/2 \\ \left(\frac{\partial \bar{\Lambda}}{\partial \phi_z}\right)_z - \frac{\partial \bar{\Lambda}}{\partial \phi} - \frac{\partial \Lambda}{\partial \phi_z} &= 0 & z = d/2 \end{aligned} \quad (6')$$

for the previously examined unidimensional problem (Sect. 3).

In this situation equation (7) is :

$$\delta \bar{F} = \left[\left(\frac{\partial \bar{\Lambda}}{\partial \phi_z} \eta\right)_z\right]_2 + \left[\left(\frac{\partial \bar{\Lambda}}{\partial \phi_z} \eta\right)_z\right]_1. \quad (7')$$

Now we will show that this quantity is generally different from zero [16].

Let us consider a NLC cell submitted to a magnetic field. If the sample is initially in the homeotropic configuration ($\mathbf{n} \parallel \mathbf{z}$) and the field is normal to the undistorted $\mathbf{n}$ ($\mathbf{H} \parallel \mathbf{x}$) for $H > H_{th}$ we have the well known Freedericksz transition [2].

In this case the free energy density $\Lambda(\phi, \phi_z)$ of equation (8) yields

$$\Lambda(\phi, \phi_z) = \frac{1}{2} K(\phi_z^2 - \lambda^{-2} \sin^2 \phi) \quad (18)$$

in the one constant approximation (assumed for the sake of simplicity, but this hypothesis is not necessary).

In equation (18) K is the (common) elastic constant and λ is the magnetic coherence length [2].

Furthermore the easy axis $\mathbf{d}$ being parallel to z (homeotropic alignment), we have in equation (3) $d_i = \delta_{3i}$ and $\partial_i = \delta_{3i} \frac{d}{dz}$.

Consequently $d_i d_j \partial_i n_j = -\sin \phi \phi_z$ and $d_j \partial_i n_j = \delta_{i3} \sin \phi \phi_z$.

By substituting these terms in (2) and (3) and by putting $\bar{K} = (\bar{K}_1 + \bar{K}_2)/2$, we obtain

$$\bar{\Lambda}_b(\phi, \phi_z) = \frac{1}{2} \Delta \pi_b \sin^2 \phi_b + \frac{1}{4} \bar{K}(b) \sin^2 2 \phi_b \phi_z^2(b). \quad (19)$$

We limit ourselves to a symmetric problem, i.e. $\Delta \pi_1 = \Delta \pi_2$, $\bar{K}(1) = \bar{K}(2)$ which implies $\phi_1 = \phi_2 = \psi$ (in this case Eqs. (6') are identical).

As is well known, equation (9), with $\Lambda(\phi, \phi_z)$ given by (18), after trivial integration [2] yields

$$\phi_z^2 = \Lambda^{-2}(\sin^2 \phi_{mx} - \sin^2 \phi) \quad (20)$$

where $\phi_{mx} = \phi(0)$. Equation (20) is valid for any boundary conditions, and depends only on the bulk free energy density. All the information on anchoring energy is contained in ϕ_{mx} and also, in ϕ .

By substituting (19) into (7') we obtain

$$\begin{aligned} \delta F = \frac{1}{2} \bar{K} \{ & [2 \sin 4 \phi_2 \phi_z^2(2) + \sin 2 \phi_2 \phi_{zz}(2)] \eta_2 + \\ & + [2 \sin 4 \phi_1 \phi_z^2(1) + \sin 2 \phi_1 \phi_{zz}(1)] \eta_1 + \\ & + \sin^2 2 \phi_2 \phi_z(2) \eta_z(2) + \sin^2 2 \phi_1 \phi_z(1) \eta_z(1) \} . \end{aligned} \quad (7'')$$

Now, by taking into account the fact that the problem is symmetric with respect to $z = 0$ we have : $\phi_1 = \phi_2 = \psi$, $\phi_z(1) = -\phi_z(2) = \lambda^{-1}(\sin^2 \phi_{mx} - \sin^2 \psi)^{1/2}$ and $\phi_{zz}(1) = \phi_{zz}(2) = -(1/2) \lambda^{-2} \sin 2 \psi$.

Consequently equation (7'') becomes

$$\begin{aligned} \delta F = \frac{1}{2} \bar{K} \lambda^{-1} \{ & \lambda^{-1} [2 \sin 4 \psi (\sin^2 \phi_{mx} - \sin^2 \psi) - \frac{1}{2} \sin^2 2 \psi] (\eta_1 + \eta_2) + \\ & + \sin^2 2 \psi (\sin^2 \phi_{mx} - \sin^2 \psi)^{1/2} [\eta_z(1) - \eta_z(2)] \} . \end{aligned} \quad (21)$$

In equation (1) ϕ_{mx} and ψ are connected by means of the boundary conditions (6'). By substituting in (6') equation (19) we deduce :

$$\frac{\bar{K}}{2} \sin 4 \psi \phi_z^2 + \frac{\bar{K}}{2} \sin 2 \psi \phi_{zz} - \frac{\Delta \pi}{2 \bar{K}} \sin 2 \psi + \phi_z = 0$$

and then, for the previous relations, after a routine calculation, we obtain

$$\begin{aligned} \lambda^{-1}(\sin^2 \phi_{mx} - \sin^2 \psi)^{1/2} = & \frac{K}{\bar{K} \sin 4 \psi} \times \\ & \times \left\{ -1 + \sqrt{1 + \left(\frac{\bar{K}}{K}\right)^2 \sin 2 \psi \sin 4 \psi \left(2 \lambda^{-2} \sin^2 2 \psi + \frac{\Delta \pi}{\bar{K}}\right)} \right\} . \end{aligned} \quad (22)$$

For $H \rightarrow H_{th}$ it yields $\phi_{mx} \rightarrow \psi \rightarrow 0$ and $\lambda \rightarrow \lambda_{th}$. In this limit equation (22) gives

$$\lambda^{-1}(\phi_{mx}^2 - \psi^2)^{1/2} \simeq \frac{1}{L} \psi + O(\psi^2) \quad (23)$$

where $L = K/\Delta\pi$ is the de Gennes-Kléman extrapolation distance [17]. By substituting (23) in (21) we obtain, finally

$$\delta F = -\bar{K}\lambda^{-1}(\eta_1 + \eta_2)\psi^2 + O(\psi^3) \quad (24)$$

where η_1 and η_2 are arbitrary. Equation (24) shows that $\delta F \neq 0$. Hence equations (6') are not sufficient to give an extremum for the functional (8), as we have already pointed out.

5. Electric Freedericksz threshold vs. sample thickness.

As is well known if the anchoring energy is finite, the Freedericksz threshold is thickness dependent. Mada affirms that his theory can explain a non-monotonic behaviour of the critical field vs. the sample thickness. In this section we will show that the agreement with experiment is connected with the wrong boundary conditions employed by him.

Let us consider a symmetric homeotropic sample, as in section 4, submitted to an electric field E parallel to the z -axis. If the dielectric anisotropy $\varepsilon_a = \varepsilon_{||} - \varepsilon_{\perp}$ is negative we have an electric Freedericksz transition when $E > E_{th}$ [2].

In the hypothesis of small $|\varepsilon_a/\varepsilon_{||}|$ equation (9) still yields equation (20) where, now, λ is the electric coherence length.

By (20) we deduce, in the one constant approximation,

$$\int_{\phi_1}^{\phi_{mx}} (\sin^2 \phi_{mx} - \sin^2 \phi)^{-1/2} d\phi = d/2 \lambda \quad (25)$$

which is a relation between ϕ_1 , ϕ_{mx} and λ . Furthermore (20) gives also

$$\int_{\phi_1}^{\phi(z)} (\sin^2 \phi_{mx} - \sin^2 \phi)^{-1/2} d\phi = (z + d/2)/\lambda, \quad (26)$$

from which it is possible to evaluate the function $\phi(z)$. In this case the boundary conditions (15) result in

$$\begin{aligned} & - (2/\lambda) (\sin^2 \phi_{mx} - \sin^2 \phi_1)^{1/2} + (1/L) \sin 2\phi_1 + (\bar{K}/2 K \lambda^2) \times \\ & \times \left\{ 2 \sin 4\phi_1 (\sin^2 \phi_{mx} - \sin^2 \phi_1) + \sin^2 2\phi_1 \left(\sin 2\phi_{mx} \frac{\partial \phi_{mx}}{\partial \phi_1} - \sin 2\phi_1 \right) \right\} = 0 \end{aligned} \quad (27)$$

because ϕ_{mx} and ϕ_1 are connected by means of equation (25).

Near the threshold field ($E \rightarrow E_{th}$), $\phi_{mx} \rightarrow \phi_1 \rightarrow 0$ and then equation (27) becomes

$$- (1/\lambda) (\phi_{mx}^2 - \phi_1^2)^{1/2} + (1/L) \phi_1 + 2(\bar{K}/K \lambda^2) \phi_1 \left[\phi_{mx}^2 - \phi_1^2 + \phi_1 \left(\phi_{mx} \frac{\partial \phi_{mx}}{\partial \phi_1} - \phi_1 \right) \right] = 0. \quad (28)$$

Furthermore in this limit equation (25) gives $\phi_1 = \phi_{mx} \cos(d/2 \lambda)$; from this we deduce $\partial \phi_{mx} / \partial \phi_1 = \sec(d/2 \lambda)$, which is finite, in the weak anchoring hypothesis. Consequently in equation (28) the two first terms are $O(\phi_{mx})$, while the two last terms are $O(\phi_{mx}^3)$. It follows

that

$$\phi_1 = (L/\lambda) [1 + (L/\lambda)^2]^{-1/2} \phi_{mx} + O(\phi_{mx}^2). \quad (29)$$

By substituting equation (29) into (25) we derive the threshold field (in the limit $\phi_{mx} \rightarrow 0$) as :

$$\frac{\pi}{2} - \operatorname{tg}^{-1} \frac{L}{\lambda_{th}} = \frac{d}{2 \lambda_{th}} \quad (30)$$

which is the Rapini-Papoular relation [17].

Equation (30) shows that the threshold field is a monotonic function of the sample thickness d , contrary to the result of reference [11]. We point out that the one constant approximation is not a restrictive hypothesis (see Eq. (11) of Ref. [11]).

6. Pretilt angle vs. temperature.

We analyse the behaviour of the pretilt angle vs. temperature, at the NLC-air interface.

As in the experiment of Chiarelli [8] we suppose that the easy axis on the free surface is parallel to the z -axis and, furthermore, that a magnetic field H is applied parallel to the x -axis [6]. Moreover we consider the NLC sample to be very thick, i.e. we suppose that for a given magnetic field H the magnetic coherence length is much smaller than the sample thickness. Under these conditions, it is possible to consider the sample as a semi-infinite medium.

If the origin is placed on the free surface and the z -axis is positive in the air we have $\phi \rightarrow \pi/2$ for $z \rightarrow -\infty$. Now in (20) $\sin \phi_{mx} = 1$, and then

$$\phi_z = -\lambda^{-1} \cos \phi. \quad (31)$$

The boundary conditions (15) for this case become

$$-2\lambda \cos \phi_1 + (\lambda^2 \Delta\pi/K) \sin 2\phi_1 - (\bar{K}/2K) \sin^3 2\phi_1 + (\bar{K}/K) \cos^2 \phi_1 \sin 4\phi_1 = 0. \quad (32)$$

This equation is important in order to study the behaviour of ϕ_1 vs. the temperature.

Taking into account that $\bar{K}$ and K are elastic constants, Mada [6] supposes $\bar{K}/K$ to be temperature-independent. Furthermore as $\lambda = H^{-1} \sqrt{K/\chi_a}$, $K \propto S^2$ and $\chi_a \propto S$ we obtain $\lambda \propto S^{1/2}$. If $K \simeq 10^{-6}$ dyn, $\chi_a \simeq 10^{-7}$ cgs, $\Delta\pi \simeq 10^{-2}$ erg/cm² [5] and $H \simeq 10^4$ G we deduce that the first term in (32) is not negligible [6].

On the contrary if $\Delta\pi$ is greater than 10^{-1} erg/cm² [5] it is possible to drop the first term and the boundary condition (32) gives

$$\lambda^2 \frac{\Delta\pi}{K} = 2 \cos^2 \phi_1 (3 \sin^2 \phi_1 - 1). \quad (33)$$

Because the first term is positive, it follows that $\phi_1 > 35^\circ$, which is not in agreement with the experimental data [8]. Furthermore, $\lambda^2/\bar{K} \propto S^{-1}$ and if $\Delta\pi \propto S$ [7], we deduce that ϕ_1 is temperature-independent, contrary to the conclusion of reference [6]. Moreover we point out that the experiment of Chiarelli [8] confirms that ϕ_1 is not affected by magnetic field variation, while equation (33) gives a relation between ϕ_1 and H .

7. Conclusion.

We have analysed the theory proposed by Mada to study the NLC-surface interaction. By considering the first variation of the total free energy we have shown that the Mada's boundary conditions are not correct, and therefore that some of the conclusions of this author must be reconsidered. Moreover, we have developed a variational method to give the right boundary

conditions when the surface interaction free energy depends both on the tilt angle and on its derivative.

We have also analysed the Freedericksz transition vs. sample thickness and the pretilt angle vs. temperature, already considered by Mada.

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Appendix 1.

The first variation of F , given by equation (4), in δn_i and $\delta(\partial_j n_i)$ is

$$\delta F = \iiint_V \left\{ \frac{\partial A}{\partial n_i} \delta n_i + \frac{\partial A}{\partial(\partial_j n_i)} \delta(\partial_j n_i) \right\} dV + \oint_S \left\{ \frac{\partial \bar{A}}{\partial n_i} \delta n_i + \frac{\partial \bar{A}}{\partial(\partial_j n_i)} \delta(\partial_j n_i) \right\} d\sigma. \quad (\text{A.1})$$

In the hypothesis of pure reorientation the operator δ commutes with the operators of differentiation, and then the relation $\delta(\partial_j n_i) = \partial_j(\delta n_i)$ holds $\forall P \in V$, limited by S . Under these conditions it is possible to write

$$\frac{\partial A}{\partial(\partial_j n_i)} \partial_j(\delta n_i) = \partial_j \left\{ \frac{\partial A}{\partial(\partial_j n_i)} \delta n_i \right\} - \delta n_i \partial_j \left\{ \frac{\partial A}{\partial(\partial_j n_i)} \right\} \quad (\text{A.2})$$

and an analogous relation for $[\partial \bar{A} / \partial(\partial_j n_i)] \partial_j(\delta n_i)$.

By substituting (A.2) in (A.1) and by applying Gauss' theorem we obtain

$$\begin{aligned} \delta F = & \iiint_V \left\{ \frac{\partial A}{\partial n_i} - \partial_j \frac{\partial A}{\partial(\partial_j n_i)} \right\} \delta n_i dV + \\ & + \oint_S \left\{ \frac{\partial A}{\partial(\partial_j n_i)} \nu_j + \frac{\partial \bar{A}}{\partial n_i} - \partial_j \frac{\partial \bar{A}}{\partial(\partial_j n_i)} \right\} \delta n_i d\sigma + \oint_S \partial_j \left\{ \frac{\partial \bar{A}}{\partial(\partial_j n_i)} \delta n_i \right\} d\sigma. \end{aligned} \quad (\text{A.3})$$

In the strong anchoring hypothesis $\delta n_i \equiv 0$, $\forall P \in S$, and then from equation (A.3) it is possible to deduce the Euler-Lagrange equations (5).

In the opposite case of weak anchoring energy the δn_i ($\forall P \in S$) are arbitrary functions, as is well known from the variational calculus. In this situation, if n_i are solutions of equation (5) with the boundary conditions (6), equation (A.3) gives

$$\delta F = \oint_S \partial_j \left\{ \frac{\partial \bar{A}}{\partial(\partial_j n_i)} \delta n_i \right\} d\sigma = \oint_S \text{div } \mathbf{u} d\sigma \quad (\text{A.4})$$

where $u_j = [\partial \bar{A} / \partial(\partial_j n_i)] \delta n_i$. Equation (A.4) is generally different from zero, as it is possible to show with a simple example. In fact, if S is a sphere of radius R , with the centre at the origin of the Cartesian reference frame, and $\mathbf{u}$ is the vector position, we have that $\text{div } \mathbf{u} = 3$ and then

$$\oint_S \text{div } \mathbf{u} d\sigma = 12 \pi R^2 \neq 0.$$

In order to show that (A.4) is not zero in a general case it is sufficient to suppose that $u_j \in C^2$, i.e. let u_j and its derivatives be continuous functions. In this case it is possible to apply the theo-

rem of the average to equation (A.4), which yields

$$\delta F = (\operatorname{div} \mathbf{u})_{\mathbf{p}_0 \in S} S.$$

Consequently if $\delta F = 0$, $\forall \delta n_i$, there always exists a point $\mathbf{P}^* \in S$ such that

$$(\operatorname{div} \mathbf{u})_{\mathbf{P}^* \in S} = 0. \quad (\text{A.5})$$

But if the δn_i are the solutions of the system

$$\frac{\partial \bar{\Lambda}}{\partial (\partial_j n_i)} \delta n_i = x_j$$

equation (A.5) gives an absurd result. Then the conclusion $\delta F = 0$, $\forall \delta n_i$, is not correct and the boundary conditions (6) are not sufficient to give an extremum for the functional (4).

In section 4, we give an other demonstration of this fact with a unidimensional problem.

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