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On the validity of the Rapini-Papoular surface anchoring energy form in nematic liquid crystals

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Résumé. — Dans des travaux récents, on a prétendu que la forme simple de Rapini-Papoular pour l'énergie d'ancrage des cristaux liquides nématiques n'est plus valable pour les grandes déformations. Nous montrons que, si l'on prend en compte l'effet flexoélectrique, les données expérimentales réanalysées restent en accord avec le modèle de Rapini-Papoular. L'effet flexoélectrique doit être considéré dans tous les cas pratiques où la longueur d'écran de Debye du matériau se compare (ou est supérieure) à la longueur d'extrapolation de l'ancrage. Près de la transition nématique-isotrope il faut aussi considérer l'énergie diélectrique associée à la polarisation d'ordre. Cet effet peut justifier la forme fonctionnelle proposée pour interpréter les données expérimentales couple de surface/angle de surface près de la transition nématique-isotrope.

Abstract. — Recent reports have claimed that the simple Rapini-Papoular form for the anchoring energy of nematic liquid crystals is not correct for large distortions. We show that, taking into account the dielectric energy associated with the flexoelectric effect, a reanalysis of the data is consistent with the Rapini-Papoular form. The consideration of flexoelectricity is necessary in most practical cases where the Debye screening length of the material compares to (or is larger than) the surface anchoring energy extrapolation length. Close to the nematic-isotropic transition, another dielectric effect, related to the order-electricity, must also be considered. This effect can justify the functional form proposed in order to interpret the experimental data giving the surface torque *vs.* tilt angle near the nematic isotropic transition.

1. Introduction.

The bulk texture distortions of nematic liquid crystals are described by a curvature elasticity, now well understood. On the other hand, close to boundaries, the nematic orientation also depends on the specific properties of the surfaces, so that the situation is more complicated. Most of the time, a given surface forces the nematic director $\mathbf{n}$ to orient, locally, parallel to an easy direction $\mathbf{n}_0$. To describe the surface distortions $\mathbf{n} - \mathbf{n}_0$ which can be induced by a volume one, it is necessary to know the surface anchoring energy F_s. In the simplest case of larger symmetry ($\mathbf{n}_0$ normal or parallel to the surface), people have tried to check the Rapini-Papoular (R-P) [1] form of the kind :

$$F_s = -\frac{1}{2} W \left(\mathbf{n} \cdot \mathbf{n}_0\right)^2,$$

where $W\left(\sim 10^{-2}\,\text{cgs}\right)$ is often renormalized in terms of the curvature elastic constant $k_{ii}\left(\sim 10^{-6}\,\text{cgs}\right)$, defining an extrapolation length $L = k_{ii}/W \sim 1\ \mu\text{m}$. Experimentalists have tried to measure L and to test the assumed angular dependence $\left(\mathbf{n} \cdot \mathbf{n}_0\right)^2$ for F_s. To study this angular dependence, one must impose a large curvature distortion close to the surface, i.e. a large variation of $\mathbf{n}$ on a distance comparable to L. One can find data in recent literature [2-7] which seem to demonstrate that the R-P form is not correct. In fact, for these highly distorted situations, the bulk nematic also presents a volume flexoelectric polarization proportional to the curvature [8]. This polarization induces space charges, and then an electric field, so that the volume distortion energy should also include a flexoelectric term [8]. This flexoelectric contribution was most of the time neglected, under the assumption that the flexo-induced space charges were completely screened by ionic conductivity [9]. In fact, the Debye screening length L_D for typical nematic materials can be comparable to (or larger than) L. This implies that, to interpret the data

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relative to large surface distortions experiments, one must add the flexoelectric energy to the curvature elastic term i.e. consider the nematic close to the surface as a dielectric medium, rather than as a conducting material. In this paper, reanalysing our previously published data and other authors' contributions [2-5] we show that, if the flexoelectric contribution is taken into account, the R-P form for the anchoring energy remains valid for large distortions. Finally, we show that close to the nematic-isotropic transition temperature (T_c), another kind of dielectric energy must be introduced, related to the electric surface polarization associated with order electricity [10]. The effect of this new term is to change the functional form of the anchoring energy.

2. Electric considerations.

Let us consider a nematic slab, limited by walls at $z = 0$ and $z = d$. In the hypothesis of uniform anchoring on the solid plates, all physical quantities depend only on the normal coordinate z. Maxwell's equation

$$\text{div } D = 4\,\pi\rho_I\,, \tag{1}$$

where ρ_I is the ion-density, becomes

$$\mathrm{d}\left(\varepsilon_{33}\,E_3 + 4\,\pi P_3\right)/\mathrm{d}z = 4\,\pi\rho_I\,. \tag{2}$$

In (2) P_3 is the z-component of the polarization due to flexoelectric and orderelectric effects, ε_{33} the z,z component of the dielectric tensor and E_3 the only non-vanishing component of the electric field (since rot $\mathbf{E} = 0$). As is well known, ρ_I appears when an electrical potential V modifies the equilibrium density N_i of the species i through a linearized Boltzmann factor, and is given by

$$\rho_I = -\,L_D^{-2}\,V\,, \tag{3}$$

where the Debye length L_D of the medium is defined as

$$L_D^{-2} = kT/4\,\pi \sum_i q_i^2 N_i\,, \tag{4}$$

where kT is the Boltzmann factor.

By taking into account (3) and $E_3 = -\,\mathrm{d}V/\mathrm{d}z$, equation (2) becomes

$$\mathrm{d}\left(-\,\varepsilon_{33}\,\mathrm{d}V/\mathrm{d}z + 4\,\pi P_3\right)/\mathrm{d}z = -\,L_D^{-2}\,V\,. \tag{5}$$

Equation (5) shows that if ε_{33} and P_3 vary on a distance smaller than L_D, the term $L_D^{-2}\,V$ is negligible with respect to the term on the left side of equation (5). In this case we can write, for the continuity, $D_3 = 0$, i.e. we can consider the nematic as a dielectric medium.

Let us now verify that the Debye length L_D can compare to L in usual nematic materials. L_D given by (4), can be expressed as $L_D^2 = D\tau$, where D is the diffusion coefficient for ions and τ the charge relaxation time. τ is observed as the maximum frequency at which one can induce electrohydrodynamical instabilities [11]. Depending on the material conductivity, τ ranges from 10^{-1} to 10^{-3} s. D is of the order of 10^{-5} to 10^{-6} cm^2/s. With these values, one can estimate L_D to range between 0.3 μm up to 10 μm. The anchoring extrapolation length L is known to range from 0.1 μm for strong anchoring up to a few μm for weak anchoring. One sees that L_D can be comparable to (or larger than) L. In what follows, we consider tilt angle variations on a distance comparable to L and $L_D > L$. In this hypothesis equation (5) shows that the liquid crystal should be considered as a dielectric rather than as a conductive medium. As far as the order electricity is concerned, the surface polarization related to the gradient of order parameter [10] appears inside a boundary layer of thickness comparable to the coherence length ξ. ξ is usually of the order of a few hundred Å, much smaller than L_D. Then the dielectric energy associated with order electricity must always be taken into account.

3. Surface torque induced by antagonistic anchoring.

Let us first consider the experimental situation of references [2, 3], where a hybrid aligned nematic wedge cell, of variable thickness d, is discussed. The measurements are made at $T \ll T_c$ $\left(T_c - T \sim 20\ \mathrm{K}\right)$. One plate gives a strong « homeotropic » anchoring ($\mathbf{n}_{01} \perp$ to the plate), the other one a weak « planar » anchoring ($\mathbf{n}_{02} /\!/$ to the plate). In the thinner part $\mathbf{n}$ is forced equal to $\mathbf{n}_{01}$. In the thicker part, one finds a splay-bend hybrid orientation. For $d \sim L$, one observes a transition between these two states, giving a weak birefringence. Optical observations give the optical path difference Δl as a function of d. This allows us to determine the orientation $\mathbf{n}_2$ on the planar plate as a function of the mechanically induced curvature, i.e. to test the anchoring torque for large distortions $\left(\mathbf{n}_2 \sim \mathbf{n}_{01} \perp \mathbf{n}_{02}\right)$. In the distorted region a flexoelectric polarization $\mathbf{P}_f$ is present, which gives rise to an electric field [8]:

$$E(\theta) = 2\,\pi\left\{\left(e_{11} + e_{33}\right)/\varepsilon_{33}\right\} \times \sin(2\,\theta)\,(\mathrm{d}\theta/\mathrm{d}z)\,, \tag{6}$$

where i) θ is the angle made by $\mathbf{n}$ with the z-axis, ii) the z-axis is normal to the bounding wall and $z = 0$ on the homeotropic plate, iii) e_{11} and e_{33} are the flexoelectric coefficients, and iv) $\varepsilon_{33} = \varepsilon_{\parallel}\cos^2\theta + \varepsilon_{\perp}\sin^2 0$, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants parallel to $\mathbf{n}$ and normal to it, respectively. The electric field (6) modifies the Frank elastic free energy introducing a term connected to the interaction between P_f and $E(\theta)$. The new free energy density in this case is found to be [8]:

$$F(\theta) = \frac{1}{2} k_{33}\, g(\theta)\, (\mathrm{d}\theta/\mathrm{d}z)^2, \qquad (7)$$

where $k_{33}\, g(\theta)$ is the « effective » elastic constant, and :

$$g(\theta) = 1 - k \sin^2\theta + \\ + \left(k_f/4\right) \sin^2(2\theta) \Big/ \left\{ 1 - \left(\varepsilon_a/\varepsilon_\parallel\right) \sin^2\theta \right\}.$$

Furthermore k_{33} is the bend elastic constant, k_{11} is the splay elastic constant, $k = 1 - \left(k_{11}/k_{33}\right)$ is the relative elastic anisotropy ; $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$ is the dielectric anisotropy, and $k_f = 4\pi \left(e_{11} + e_{33}\right)^2 / k_{33}\, \varepsilon_\parallel$ is the dimensionless measure of the flexoelectricity. $g(\theta)$ shows that the effect of the flexoelectricity is to change the elastic anisotropy.

By using equation (7) it is possible to determine the equilibrium configuration by operating in a standard way [2]. As the anchoring energy on the homeotropic plate is strong and that of the planar plate is weak, using the R-P form : $F_s = \frac{1}{2} W \cos^2\theta_2$, where $\theta_2 = \theta\,(z = d)$, we obtain by routine calculations

$$d/L = 2\tilde{I}\left(\theta_2\right) \sqrt{g\left(\theta_2\right)} \Big/ \sin\left(2\theta_2\right), \qquad (8)$$

where $L = k_{33}/W$ and

$$\tilde{I}(x) = \int_0^x \sqrt{g(\theta)}\, \mathrm{d}\theta\,. \qquad (9)$$

The optical path difference is then :

$$\Delta l = n_0\, d \left\{ \left[\tilde{I}\left(\theta_2\right)/\tilde{J}\left(\theta_2\right)\right] - 1 \right\}, \qquad (10)$$

where

$$J(x) = \int_0^x \left\{ g(\theta) / \left(1 - R \sin^2\theta\right) \right\}^{1/2} \mathrm{d}\theta\,, \qquad (11)$$

and $R = 1 - \left(n_0/n_e\right)^2$, n_0 and n_e being the ordinary and extraordinary refraction indices, respectively.

In figure 1, Δl as a function of d is reported for various values of k_f. The liquid crystal is MBBA. We take : $L = 3$ μm, $k = 0.25$ [12], $R = 0.23$ [12], $\varepsilon_a = -0.7$, $\varepsilon = 4.7$ [13]. We point out that Δl is very sensitive to k_f variations. $k_f = 0$ is the prediction of R-P without flexoelectricity. $k_f = 2$ corresponds to $\left|e_{11} + e_{33}\right| \sim 6.5 \times 10^{-4}$ cgs and $k_f = 4$ corresponds to $\left|e_{11} + e_{33}\right| \sim 9.5 \times 10^{-4}$ cgs. On the contrary Δl is practically independent of k, for k in the range (0-0.5). Figure 2 shows the experimental data obtained on two samples having critical thicknesses $L_1 = 1.8$ μm and $L_2 = 3$ μm. The continuous curves are obtained by equation (5), for $k = 0.25$, $R = 0.23$, $\varepsilon_a = -0.7$, $\varepsilon_\parallel = 4.7$ and the same $k_f = 3.5$ (MBBA). The agreement is good. $k_f = 3.5$ implies,

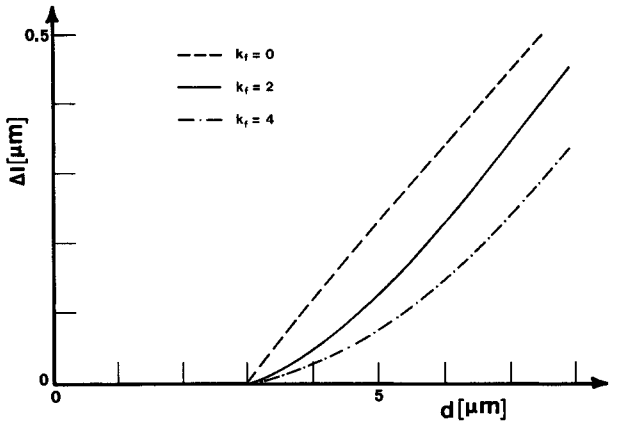

Fig. 1. — Optical path difference (Δl) *versus* thickness sample (d) in an hybrid cell with strong anchoring on the homeotropic wall. The curve with $k_f = 0$ corresponds to the Rapini-Papoular prediction, when the flexoelectricity is neglected.

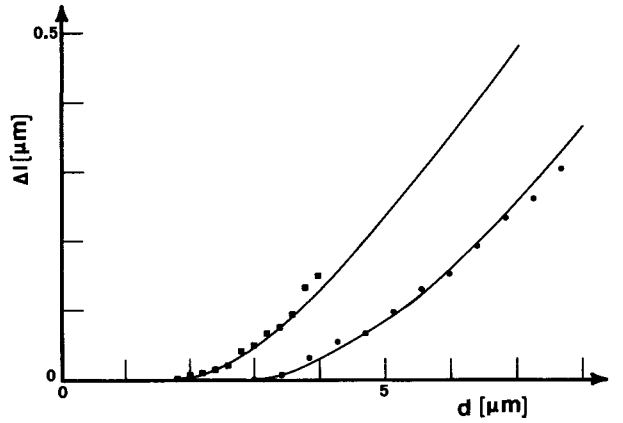

Fig. 2. — Best fit of experimental data for Δl *versus* d, with the flexoelectric model (see text).

with $k_{33} = 0.6 \times 10^{-6}$ dyne [12], the value $\left|e_{11} + e_{33}\right| = 8 \times 10^{-4}$ cgs, consistent with reference [14], for the same liquid crystal.

In our first analysis [2, 3], we had neglected the flexoelectric contribution, by assuming an infinitely large conductivity. We had found a surface torque for this experiment of the shape :

$$m_s\left(\theta_2\right) = m_2 \sin\left(2\theta_2\right) + m_6 \sin\left(6\theta_2\right), \qquad (12)$$

with $m_6/m_2 = 0.14$.

We can now understand the experimental appearance of the third harmonic for $2\theta_2$, by expanding the terms appearing in the boundary condition (8) in powers of $k_f/4 < 1$ (assuming for the sake of simplicity $\varepsilon_a = k = 0$). Equation (9) becomes :

$$2(L/d)\,\theta_2 = \sin\left(2\theta_2\right) - \left(k_f L/8d\right) \times \\ \times \left\{ 2\theta_2 \sin^2\left(2\theta_2\right) + \theta_2 - (1/4) \sin\left(4\theta_2\right) \right\}.$$

The zeroth order solution in k_f is :

$$\theta_2 = (d/2L) \sin(2\theta_2),$$

which finally gives a surface torque m_s of the shape :

$$m_s(\theta_2) = \{1 - (5/32) k_f\} \sin(2\theta_2) + + (k_f L/32 d) \sin(4\theta_2) + (k_f/32) \sin(6\theta_2).$$

Of these three terms, the first and the last are related to the surface, and the second to the volume (because of the presence of d). Far above the surface transition, the volume term can be neglected. The apparent surface torque contains the R-P term plus a third harmonic, as has been found experimentally. The relative coefficient of this last term can be estimated. With $k_f \sim 3$, the relative coefficient is 0.17 instead of the experimental one 0.14. This agreement is good when considering the approximations made. We can conclude that the introduction of the flexoelectric term in the free energy density makes the data of references [2, 3] consistent with the R-P form. Obviously other interpretations of the experimental data are possible. Anyway the flexoelectric term must be taken into account if $L < L_D$. A discussion about the order electric term is reported in section V.

4. Surface torque induced by an external field.

Let us now consider the case of reference [4], where one observes the distortion of a homeotropic nematic cell in between two plates with weak anchoring. The application of a transverse magnetic field **H** induces the « Freedericksz » transition, and creates a birefringence. The authors report on a large (20 %) decrease of the associated optical phase shift compared to that calculated from the R-P law for the anchoring energy. As we do not know the original detailed data, we cannot make an exact fitting to explain this decrease by the onset of flexoelectricity in the elastic free energy. We can just make an order of magnitude estimate.

In the limit of magnetic field H near to the threshold one H_t, the phase shift $\alpha = 2\pi \Delta l/\lambda$ is given by [15]

$$\alpha = 2\pi n_0 (d/\lambda) [R/(1-k)] \times \times [1 - (H_t/H)], \quad (13)$$

where $k = k - k_f$ is the effective elastic anisotropy, λ the wavelength of the laser beam and H_t is given by the well known relationship [1] :

$$\pi (L/d) (H_t/H_c) = \mathrm{ctg}\left\{\frac{1}{2}\pi (H_t/H_c)\right\}$$

with

$$H_c = (\pi/d) (k_{33}/\chi_a)^{1/2}.$$

The experiment of reference [4] was performed at 39.5 °C. By assuming, at this temperature, that : $n_0 = 1.5507$, $n_e = 1.7352$, $\chi_a = 0.967 \times 10^{-7}$ cgs, $k_{11} = 5.2 \times 10^{-7}$ dynes, $k_{33} = 5.7 \times 10^{-7}$ dynes [4], we obtain : $H_c = 26.3$ kG. Furthermore by taking into account the experimental value of $H_t = 19.9$ kG the anchoring energy is found to be $W \sim 1.16 \times 10^{-2}$ erg/cm^2.

From equation (13) we deduce

$$(d\alpha/dH)_{H=H_t} = 2\pi n_0 (d/\lambda) [R/(1-\tilde{k})] \times \times (1/H_t). \quad (14)$$

The experimental value of $(d\alpha/dH)_{H=H_t}$ is 0.375 rad/kG, which gives $\tilde{k} = -0.28$, and hence $k_f = 0.37$. To this k_f corresponds, with the above mentioned values for the elastic constants, $|e_{11} + e_{33}| \sim 3 \times 10^{-4}$ ues.

This relatively low value for the flexoelectric constant of MBBA could be simply explained, since the experiment has been made at 39.5 °C, i.e. very close to the nematic-isotropic transition temperature T_c, in the 45 °C range (note that T_c is very sensitive to the presence of impurities ; unfortunately its exact value is not reported in Ref. [4]). To explain their data, the authors have used an anchoring energy of the form :

$$F_s(\theta_s) = C_2 \sin^2\theta_s - C_4 \sin^4\theta_s \quad (15)$$

where θ_s is the surface tilt angle.

As we have previously shown [3], such an expansion is not useful, because it is built with non-orthogonal functions. It is then difficult to make a comparison between their evaluated constants and the flexoelectric contribution. Nevertheless, we can show that the apparent surface torque must contain a third harmonic term, as in the previous case.

Expanding the boundary condition for this symmetric magnetic problem, for small k_f, we find for the surface torque the expression :

$$m_s(\theta_s) = [1 - (3/32) k_f] \sin(2\theta_s) + + (k_f/32) \sin(6\theta_s). \quad (16)$$

The third order term should have a relative coefficient of the order of 1.3×10^{-2} for the previously estimated $k_f \sim 0.4$, i.e. it is very small.

Consequently equation (16) cannot fit the experimental data reported in reference [4], for $H > H_c$, if the anchoring energy has the R-P form. It follows that equation (15) has a physical meaning, i.e. it is not only a fitting function, as we will show in next section.

A last experiment can be quoted, which suggests that the R-P form is not correct [5]. It describes a planar-homeotropic transition under AC electric field of the nematic 5CB, close to the nematic-

isotropic transition. In fact this experiment also shows a saturation of the surface energy for large angle, analogous to the previous case.

5. Influence of order-electricity on the anchoring energy.

In a previous paper [10] we have shown that to a spatial variation of the scalar order parameter S is connected an electric polarization $\mathbf{P}_0$, called order-polarization, given by

$$\mathbf{P}_0 = r_1 (\mathbf{n} \,.\, \mathbf{grad}\, S)\, \mathbf{n} + r_2\, \mathbf{grad}\, S\,. \qquad (17)$$

The coefficients r_1 and r_2 are of the order of $e_{11} + e_{33}$, and for $S \to 0$, $r_1 \to e_{11} + e_{33}$ and $r_2 \to -\,(1/3)\left(e_{11} + e_{33}\right)$. In our unidimensional problem, $S = S(z)$, and it changes only near the limiting walls over a distance b of the order of some hundred of Å.

It follows that P_0 is different from zero only for $z \in (0, b)$ and $z \in (d-b, d)$. As we have already pointed out, $b \ll L_D$. Consequently in the boundary layers the nematic must be considered as a dielectric medium. The electric field related to P_0 is

$$E_0(z) = -\,4\,\pi P_{03}/\varepsilon_{33}\,. \qquad (18)$$

The free energy density connected to (17) and (18) is $f_E = -\frac{1}{2}\mathbf{E}_0\,\mathbf{P}_0$, i.e.

$$f_E(\theta, \mathrm{d}S/\mathrm{d}z) = \left(2\,\pi/\varepsilon_{33}\right)\left(r_1 \cos^2\theta + r_2\right)^2 \times \times\, (\mathrm{d}S/\mathrm{d}z)^2 \qquad (19)$$

$f_E(\theta, \mathrm{d}S/\mathrm{d}z)$ is different from zero only in $(0, b)$ and $(d-b, d)$; hence it can be considered as a surface contribution. By taking into account that $\theta(z)$ changes over a distance of the order of the extrapolation distance L, we can consider $\theta(z)$ as a constant, in the above mentioned boundary layers, equal to $\theta(0)$ or $\theta(d)$.

The « surface anchoring energy » introduced by (19) is

$$f_s\left(\theta_s\right) = \int_0^d f_E(\theta, \mathrm{d}S/\mathrm{d}z)\,\mathrm{d}z \simeq \simeq 2\,b\,f_E\left\{\theta_s,\ (\mathrm{d}S/\mathrm{d}z)_s\right\} \qquad (20)$$

where

$$(\mathrm{d}S/\mathrm{d}z)_s \simeq \left(S_v - S_s\right)/b\,, \qquad (21)$$

S_v being the bulk order parameter. Equation (20) is obtained by assuming the limiting walls to be characterized by the same physical properties and hence $S(0) = S(d) = S_s$, $\theta(0) = \theta(d) = \theta_s$ and

$$(\mathrm{d}S/\mathrm{d}z)_0 = -\,(\mathrm{d}S/\mathrm{d}z)_d = (\mathrm{d}S/\mathrm{d}z)_s.$$

We observe that S_s depends on the surface treatment, whereas S_v and b depend only on the nematic properties and on the temperature.

In the present section we do not consider the dielectric energy analysed in section 3, since, as has been shown, it only changes the elastic anisotropy of the nematic, and its contribution to (20) is negligible.

By using equations (19) and (21), (20) becomes

$$f_s\left(\theta_s\right) \simeq \left(2\,\pi/\varepsilon_{33}\right)\left(r_1 \cos^2\theta_s + r_2\right)^2 \times \times \left(S_v - S_s\right)^2/b\,. \qquad (22)$$

Equation (22) shows that $f_s\left(\theta_s\right)$ has no longer the symmetry of the R-P form, since it could induce a minimum energy direction oblique to the surface.

Very far from T_c, S_s is not very different from S_v [16], and the contribution (22) to the surface anchoring energy is negligible. In fact, if

$$\left|\, S_v - S_s \,\right| \sim 5 \times 10^{-2} \quad [16]$$

$$b \sim 200\ \text{Å} \qquad \left|\, e_{11} + e_{33} \,\right| \sim 5 \times 10^{-4}\ \text{ues},$$

$\varepsilon_\parallel$ and $\varepsilon_\perp \sim 5$ (MBBA), we obtain that $f_s\left(\theta_s\right)$ is of the order of magnitude of $10^{-5}\ \mathrm{erg/cm^2}$. On the contrary, near to T_c, $\left|\, S_v - S_s \,\right| \sim 0.3$ [16] and hence $f_s\left(\theta_s\right)$ is found to be of the order of $10^{-2}\ \mathrm{erg/cm^2}$. We observe that $f_s\left(\theta_s\right)$, given by equation (22) is independent of the easy axis of the substrate-nematic interaction ; it depends on the nematic properties as well as the substrate characteristics. The effective anchoring energy G_s is the sum of the term F_s proposed by R-P, and of $f_s\left(\theta_s\right)$ and is found to be :

$$G_s\left(\theta_s\right) = F_s + f_s\left(\theta_s\right) = -\,U_2 \cos^2\theta_s + U_4 \cos^4\theta_s + \text{const.} \qquad (23)$$

for the experimental situation of reference [4], where the easy axis is normal to the limiting wall. In (29) $U_2 = (W/2) + \left(2\,U_4/3\right) > 0$ and

$$U_4 = 2\,\pi\left(e_{11} + e_{33}\right)^2\left(S_v - S_s\right)^2/(\varepsilon b)\,,$$

where $\varepsilon_\parallel \sim \varepsilon_\perp = \varepsilon$. With the above mentioned material parameters $U_4 \sim 1.3 \times 10^{-2}\ \mathrm{erg/cm^2}$, in agreement with references [4, 5]. The excellent agreement between U_4 and the C_4 coefficient of references [4, 5] is, probably, fortuitous, but the order of magnitude is correct. Furthermore we observe that $U_4 > 0$ and $U_2 > 0$, as shown by equation (28), where $r_1 > 0$ and $r_2 < 0$ [10], in agreement with [4, 5].

Finally we observe that the contribution to the surface anchoring energy coming from order polarization could also explain the pronounced pre- and post-transitional effects of the total surface tension of p-azoxyanisole and p-anisaldazine observed by Krishnaswamy *et al.* [17]. In fact, according to the

surface treatment and liquid crystal type, $S_s \gtrless S_v$; consequently $(S_v - S_s)^2/b$ can reach its maximum for $T < T_c$ or $T > T_c$. Of course we do not know the effective value of the surface gradient of the order parameter in reference [17], necessary to estimate the influence of order electricity on the total surface tension. We can however point out that its behaviour as a function of temperature could be easily understood taking into account the contribution given by equation (22).

6. Conclusions.

The anchoring energy of nematic liquid crystals at a solid interface has been proposed by Rapini and Papoular in the form $F_s = -\frac{1}{2} W(\mathbf{n} \cdot \mathbf{n}_0)^2$, where $\mathbf{n}_0$ is the easy direction, usually along a symmetry direction. Many reports, referring to experiments performed very far from T_c, have claimed that the R-P form is not valid. All these analyses, neglecting the flexoelectric contribution to the free energy, were based on the assumption that the conductivity of the material was large enough, so that the flexoelectric charges were completely screened by free ions dissolved in the material. In this paper we have shown that, in many cases where a departure from the R-P form was claimed, the introduction of the flexoelectric energy, in a surface layer comparable with the surface extrapolation length L, makes the data consistent with the R-P form. This is probably due to the fact that, in most materials, the Debye screening length L_D compares to (or is larger than) the surface extrapolation length L. It would be interesting to test this conductivity effect by doping a nematic material to go continuously from the dielectric situation $L_D > L$ to the conductive situation $L_D < L$. At present, we do not know why the R-P form is so good. We have no definite arguments to support it. It would be interesting to check if the R-P form remains correct when $\mathbf{n}_0$ is no longer a symmetry axis of the geometrical interface.

Other reports, referring to experiments performed near T_c show that the R-P form is not in agreement with the experimental data. In these cases to introduce the flexoelectric contribution in the free energy does not allow to interprete the experimental observations. But for $T \sim T_c$ the order parameter can precipitately change near the bounding walls. Hence, it is necessary to take into account another dielectric contribution to the free energy density, which is equivalent to a surface energy. This term comes from order-electricity ; it changes the functional form of the anchoring energy, introducing a term proportional to $\cos^4 \theta_s$, in agreement with recent reports [4, 5]. Also the corresponding coefficient has the correct order of magnitude.

Finally in Faetti's experiment [19], another distortion geometry was considered in order to determine the form of F_s. The $\mathbf{n}$ curvature close to the surface is now a pure twist induced by a magnetic field. The R-P form seems to be correct for large deviations $\mathbf{n} - \mathbf{n}_0$ up to $\pi/4$. This result is consistent with our new point of view : by symmetry, the twist cannot induce any flexo-electric or order-electric polarization.

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