

Gradient flexoelectric effect and thickness dependence of anchoring energy

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We generalize a previous model that was proposed to interpret the thickness dependence of the anchoring energy relevant to the nematic-liquid-crystal–solid substrate interaction. We show that beside the dielectric coupling between the surface electric field and the nematic liquid crystal, the quadrupolar flexoelectric coupling plays an important role. Possible nonmonotonic trends of the anchoring energy strength versus the thickness of the sample are predicted to be due to this new coupling mechanism.

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Nematic liquid crystals (NLC's) are quadrupolar ferroelectric materials formed by rodlike molecules [1]. In the bulk their properties are completely characterized when the average molecular orientation $\mathbf{n} = \langle \mathbf{a} \rangle$ is known, and the fluctuation of the molecular orientation \mathbf{a} with respect to \mathbf{n} expressed by $S = \frac{3}{2}[\langle (\mathbf{n} \cdot \mathbf{a})^2 \rangle - \frac{1}{3}]$ is also known. In this formula, \mathbf{a} , the molecular orientation, coincides with the long axis of the rodlike molecule. \mathbf{n} is called the NLC director and S , the scalar order parameter [1]. By means of these two quantities it is possible to define a traceless tensor order parameter

$$Q_{ij} = \frac{3}{2}S[n_i n_j - \frac{1}{3}\delta_{ij}], \quad (1)$$

having quadrupolar structure [2]. If Q_{ij} is position independent the NLC state is called fundamental. In the event that Q_{ij} is position dependent, by operating as in the classical theory of elasticity, it is possible to write an “elastic” energy density quadratic in the spatial derivatives of Q_{ij} [3]. This is done in many textbooks.

As follows from (1), Q_{ij} can be position dependent when:

(a) S is constant, but $\mathbf{n} = \mathbf{n}(\mathbf{r})$. This situation is the simplest one, and it can be described in a simple elastic manner, since \mathbf{n} changes over macroscopic length [4].

(b) \mathbf{n} is constant, but $S = S(\mathbf{r})$. This situation is more difficult to analyze because S changes over a quasimicroscopic length ξ , called the NLC coherence length [3]. Furthermore, S variations are associated with order-electric polarization, giving rise to complicated dielectric energy terms [5].

The NLC director \mathbf{n} may be oriented by means of an external magnetic or electric field [1], or by means of a surface treatment of the solid substrates limiting the NLC sample [6]. In the first case anisotropic properties of the NLC material, like the diamagnetic or dielectric tensor, are used. In the second case the orienting properties of the solid substrate on the NLC are used. In fact, it is known that a NLC in contact with a surface, in the absence of bulk constraints, is oriented in a well-defined manner [6]. This orientation is characterized by an “easy axis,” indicated by $\boldsymbol{\pi}$. Hence in the absence of bulk torque the surface director \mathbf{n}_S coincides with $\boldsymbol{\pi}$. When a bulk distortion is present, \mathbf{n}_S may deviate from $\boldsymbol{\pi}$. In this case the anchoring is called “weak.” The surface energy

f_S gives an idea about the restoring torque, which it is necessary to overcome to induce a surface deformation.

The surface energy f_S originates from two fundamental interactions: the first one is the NLC-NLC interaction; the second one is the NLC-substrate interaction. As discussed in [7] this surface energy is delocalized over a few molecular lengths near the limiting surface. It can be considered as a surface property, independent of the bulk of the NLC. Its experimental determination is possible, e.g., by means of the analysis of the threshold field inducing a deformation in a uniform NLC sample [8].

Recent experiments have shown that the surface energy, in some situations, strongly depends on the thickness of the sample [9–11]. Barbero and Durand, by invoking a selective ion adsorption, have shown that the thickness dependence of the surface energy may be due to the electrostatic contribution of the adsorbed ions to the total energy of the NLC sample [12]. By using a self-consistent method they have extended the Langmuir law valid for neutral particle adsorption [13] to charged particles [14]. The theory proposed by Barbero and Durand [12] has been tested by Valenti *et al.* [15], and it has been found to be in relatively good agreement with the experimental results. More recently, similar experimental investigation has been performed by Barbero *et al.* [16]. They found that the agreement is good only for a small thickness of the sample, whereas for thick samples the agreement is poor.

In this paper we will generalize the model of Ref. [12], and show that a new important electric term has to be considered in it. First, we recall the main physical idea of the model of Ref. [12]. A solid substrate is characterized by an easy direction $\boldsymbol{\pi}$ and an anchoring strength w . For a small deviation of \mathbf{n}_S from $\boldsymbol{\pi}$, the surface energy may be written in the form

$$f_S = -\frac{1}{2}w(\mathbf{n}_S \cdot \boldsymbol{\pi})^2, \quad (2)$$

proposed by Rapini and Papoular long ago [17].

When the solid substrate is in contact with the NLC the selective ion adsorption takes place. For instance, the positive ions are attracted by the solid surface, whereas the negative ions are repelled. In this situation a double layer, in the sense of Debye and Hückel [18], of thickness of the order of the Debye screening length λ_D , exists near

the bounding surfaces. By denoting with σ the electric charge density adsorbed on the surface, the electric field near the surface is approximatively given by (continuous charge approximation)

$$E(z) = (\sigma / \epsilon \epsilon_0) \exp(-z / \lambda_D). \quad (3)$$

In (3), ϵ is the average relative dielectric constant of the NLC, ϵ_0 is the dielectric constant of the vacuum, and z is the distance of the considered point from the solid surface. The electric field is normal to the surface by symmetry.

Since the NLC is an anisotropic material having $\epsilon_{\parallel} \neq \epsilon_{\perp}$, where \parallel and \perp refer to \mathbf{n} , the dielectric anisotropy $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$ is generally different from zero. The field given by (3) has therefore an orienting effect on the NLC. The related dielectric energy density is

$$F_{el} = -\frac{1}{2} \epsilon_a \epsilon_0 (\mathbf{n} \cdot \mathbf{E})^2 = -\frac{1}{2} \epsilon_a \epsilon_0 E^2(z) \cos^2 \theta, \quad (4)$$

where $\theta = \cos^{-1}(\mathbf{n} \cdot \mathbf{k})$, with \mathbf{k} the unit vector parallel to the z axis, is the NLC tilt angle. The dielectric energy per unit area is obtained by integrating (4) from 0 to ∞ . By taking into account (3) simple calculations give

$$f_{el} = \int_0^{\infty} F_{el} dz = -\frac{1}{4} \epsilon_0 \epsilon_a \left[\frac{\sigma}{\epsilon \epsilon_0} \right]^2 \lambda_D \cos^2 \theta, \quad (5)$$

with the hypothesis that θ is position independent.

The effective surface energy is obtained by adding (2) and (5). It is important to stress that w is thickness independent. On the contrary, f_{el} is thickness dependent because, as shown in [14], the surface density of adsorbed charges depends on the volume on the NLC sample.

All previous discussion follows directly from the model of Ref. [12]. However, we want to underline that there is another term connected with a field of the kind given by (3), which was not considered in Ref. [12]. In fact, as is well known from the electrostatic theory [19], a medium having an electrical quadrupole density q_{ij} in a nonuniform field \mathbf{E} has an electric (potential) energy density given by

$$F_q = -q_{ij} E_{i,j}, \quad (6)$$

where $E_{i,j} = \partial E_i / \partial x_j$ are the spatial gradients of the electric field. In (6) we use the Einstein convention on the repeated indices. NLC's are quadrupolar ferroelectric materials having an electrical quadrupole density q_{ij} proportional to the tensor order parameter

$$q_{ij} = -\bar{e} Q_{ij}, \quad (7)$$

where \bar{e} is the quadrupole density. Consequently the energy term (6) for NLC materials is written as

$$F_q = \bar{e} Q_{ij} E_{i,j}. \quad (8)$$

In the simplest case in which the electric field is of the kind $\mathbf{E} = E(z) \mathbf{k}$, where $E(z)$ is given by (3), F_q can be rewritten as

$$F_q = e (\cos^2 \theta - \frac{1}{3}) \frac{dE}{dz}, \quad (9)$$

where $e = (3/2) S \bar{e}$ is the total flexoelectric coefficient [20,21]. This flexoeffect in the nonhomogeneous electric

field has been called the "gradient flexoelectric effect" [22]. The dielectric energy, having quadrupolar origin, per unit surface is obtained by integrating (9) from 0 to infinity. By supposing, as before, the NLC orientation to be position independent, from (9) one obtains

$$\begin{aligned} f_q &= \int_0^{\infty} F_q dz = -e (\cos^2 \theta - \frac{1}{3}) \frac{\sigma}{\epsilon \epsilon_0} \\ &= -e \frac{\sigma}{\epsilon \epsilon_0} \cos^2 \theta + \text{const}, \end{aligned} \quad (10)$$

where the constant term is not important in our analysis, since it is independent of the NLC orientation.

The total energy per unit surface, playing the role of the effective anchoring energy, is given by

$$f_{\text{eff}} = f_s + f_{el} + f_q. \quad (11)$$

Let us consider now the case in which the easy axis is parallel to $\mathbf{k} \cdot \boldsymbol{\pi} \parallel \mathbf{k}$. This means that the surface tries to impose a homeotropic alignment. In this situation (11) is written as

$$f_{\text{eff}} = -\frac{1}{2} w_{\text{eff}} \cos^2 \theta, \quad (12)$$

where

$$w_{\text{eff}} = w + \frac{\sigma}{\epsilon \epsilon_0} \left[\frac{\epsilon_a}{2\epsilon} \lambda_D \sigma + 2e \right] \quad (13)$$

is the effective anchoring energy strength. It is important to stress that according to the sign of ϵ_a and e , w_{eff} may increase or decrease when the ion adsorption takes place. In the case in which $\epsilon_a < 0$ and the quadrupolar term is neglected, the ions' adsorption gives rise to a destabilizing term, independently of the sign of the adsorbed charges, since this term is quadratic in σ . On the contrary, when the quadrupolar term is taken into account, the sign of σ is important. Different situations are considered in the following.

(a) In the case in which $\epsilon_a < 0$, $e < 0$ [23] (e.g., MBBA [*N*-(*p*-methoxybenzylidene)-*p'*-butylaniline]), and $\sigma > 0$ the trend of w_{eff} vs σ is monotonically decreasing (see Fig. 1). The effective anchoring strength vanishes at a critical σ_c given by

$$\sigma_c = 2 \frac{\epsilon}{|\epsilon_a|} \frac{|e|}{\lambda_D} \left\{ -1 + \left[1 + \frac{\epsilon_0 |\epsilon_a|}{2|e|^2} \lambda_D w \right]^{1/2} \right\}. \quad (14)$$

For $\sigma < \sigma_c$ the easy axis is parallel to \mathbf{k} . For $\sigma > \sigma_c$ the easy axis is normal to \mathbf{k} (because $w_{\text{eff}} < 0$).

(b) In the case $\epsilon_a < 0$, $e > 0$ [24], and $\sigma > 0$, the trend of w_{eff} vs σ is not monotonic. It presents a maximum for

$$\sigma_M = 2 \frac{e}{\lambda_D} \frac{\epsilon}{|\epsilon_a|}. \quad (15)$$

For $\sigma < \sigma_M$ the stabilizing effect of the quadrupolar contribution dominates the destabilizing effect of the unusual dielectric coupling. For $\sigma > \sigma_M$ the dielectric energy gives the most important term. w_{eff} vanishes at a critical density

$$\sigma_c = 2 \frac{e}{\lambda_D} \frac{\epsilon}{|\epsilon_a|} \left\{ 1 + \left[1 + \frac{\epsilon_0 |\epsilon_a|}{2e^2} \lambda_D w \right] \right\}. \quad (16)$$

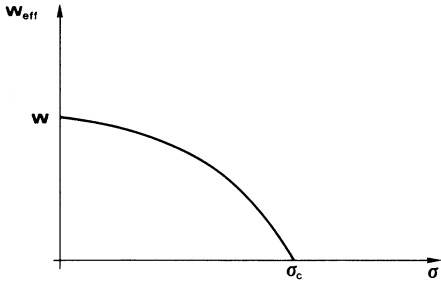


FIG. 1. w_{eff} vs σ for $\epsilon_a < 0$, $e < 0$, and $\sigma > 0$. The dielectric and quadrupolar terms destabilize the initial homeotropic orientation. Hence w_{eff} decreases when σ increases. The homeotropic orientation is unstable for $\sigma > \sigma_c$.

As before, for $\sigma < \sigma_c$ the easy axis is parallel to \mathbf{k} , and for $\sigma > \sigma_c$ it is perpendicular to it. The trend of w_{eff} vs σ is shown in Fig. 2.

(c) Let us consider now the case in which $\epsilon_a > 0$, $e < 0$ [24], and $\sigma > 0$. In this situation w_{eff} vs σ presents a minimum for

$$\sigma_m = 2 \frac{|e| \epsilon}{\lambda_D \epsilon_a} \quad (17)$$

The $w_{\text{eff}}(\sigma = \sigma_m)$ is given by

$$w_{\text{eff}}(\sigma = \sigma_m) = w - 2 \frac{|e|^2}{\lambda_D \epsilon \epsilon_a} \quad (18)$$

It is interesting to observe that, if

$$w_0 = 2 \frac{|e|^2}{\lambda_D \epsilon \epsilon_a} > w, \quad (19)$$

there is a double transition homeotropic \rightarrow planar \rightarrow homeotropic for the critical densities

$$\sigma_{1,2} = \sigma_m [1 \pm \sqrt{1 - w/w_0}]. \quad (20)$$

For $\sigma < \sigma_m$ the destabilizing effect of the quadrupolar term dominates the stabilizing effect of the usual dielectric interaction. It is vice versa for $\sigma > \sigma_m$. These cases are shown in Figs. 3(a) and 3(b).

(d) The case in which $\epsilon_a > 0$, $e > 0$ [24,25] [e.g., 5CB (*p*-pentyl-*p'*-cyanobiphenyl)], and $\sigma > 0$ shows a monotonic increase of w_{eff} vs σ , since both electric terms stabilize the initial orientation. This situation is shown in Fig. 4.

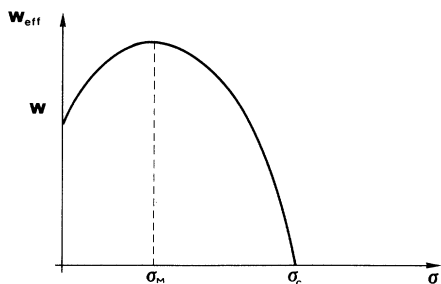


FIG. 2. w_{eff} vs σ for $\epsilon_a < 0$, $e > 0$, and $\sigma > 0$. The dielectric term destabilizes the initial homeotropic orientation, whereas the quadrupolar term stabilizes it. For $\sigma < \sigma_m$, the quadrupolar term dominates the dielectric one and hence $w_{\text{eff}} > w$. The homeotropic orientation is unstable for $\sigma > \sigma_c$.

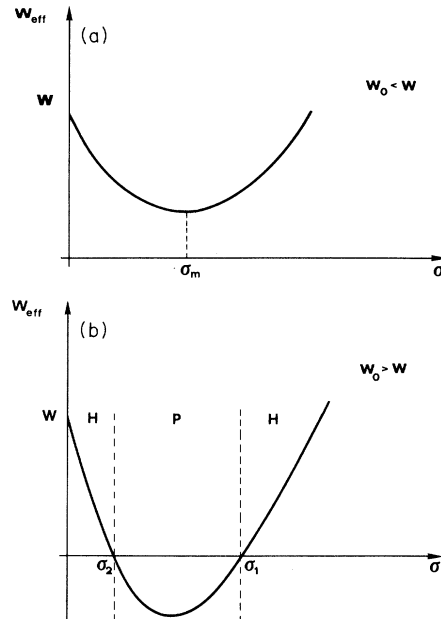


FIG. 3. w_{eff} vs σ for $\epsilon_a > 0$, $e < 0$, and $\sigma > 0$. In this situation the dielectric term stabilizes the homeotropic orientation, whereas the quadrupolar term destabilizes it. For large σ , w_{eff} is larger than w . (a) if $w_0 = 2e^2/(\lambda_D \epsilon \epsilon_a) < w$, the effective anchoring energy has a nonmonotonic trend vs σ , but the initial homeotropic easy direction remains stable. (b) If $w_0 > w$ the quadrupolar term dominates the dielectric one for $\sigma < \sigma_1$. In this situation a double surface transition H (homeotropic) \rightarrow P (planar) \rightarrow H (homeotropic) is predicted.

lize the initial orientation. This situation is shown in Fig. 4.

(e) The case, in which $\epsilon_a < 0$, $e < 0$, and $\sigma < 0$, is similar to case (b).

(f) The case in which $\epsilon_a < 0$, $e > 0$, and $\sigma < 0$ is similar to case (a).

(h) The case in which $\epsilon_a > 0$, $e > 0$, and $\sigma < 0$ is similar to case (c).

The case in which the easy direction is perpendicular to \mathbf{k} can be analyzed in the same way.

In a previous paper it was shown that the absorbed

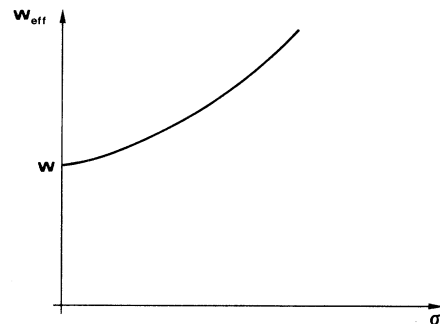


FIG. 4. w_{eff} vs σ for $\epsilon_a > 0$, $e > 0$, and $\sigma > 0$. The dielectric and quadrupolar terms stabilize the homeotropic orientation. Hence w_{eff} increases with σ .

charge σ depends on the thickness of the NLC as [14]

$$\sigma = \Sigma \frac{d}{d + 2\lambda_D}, \quad (21)$$

where Σ depends on the conductivity of the liquid crystals, on the adsorption energy, and on the number of free sites on the surface. We can deduce from (21) that the trends of w_{eff} vs σ discussed above can be interpreted as trends of w_{eff} vs the thickness of the NLC sample.

It is important to stress that the two terms of electric origin appearing in Eq. (11), i.e., f_{el} and f_q , have usually the same order of magnitude. In the case of 5CB analyzed by Blinov and Kabaenkov [9], one has $\epsilon_a \sim 13$, $\epsilon \sim 12$ [26], $\epsilon \sim 10^{-10}$ SI (Système International) units [24], $\sigma < \Sigma \sim 10^{-7}$ C/cm², and $\lambda_D \sim 0.6$ μm [27]. Consequently, $f_q/f_{\text{el}} = 4e\epsilon/(\epsilon_a\sigma\lambda_D) > \frac{1}{2}$, showing that the quadrupolar contribution to f_{eff} is of the same order of the ordinary dielectric contribution. In Fig. 5 the experimental data by Blinov and Kabaenkov [9] are shown. The continuous curve is obtained by means of Eqs. (13) and (21). The parameters of the best fit are $w_0 = -2.2 \times 10^{-3}$ J/m², $\Sigma = 5.9 \times 10^{-8}$ C/cm², and $e = 4.9 \times 10^{-11}$ SI units. The agreement is fairly good. In conclusion we stress the main points of our paper. We have shown that the flexoelectric contribution connected to the quadrupole interaction between the NLC and the electric-field gradient due to the selective ion adsorption has an important influence on the effective surface energy strength w_{eff} . The dependence of w_{eff} vs σ has been derived, and we predict that in some special cases it is possible to observe a double transition. The case in which σ is due to selective ion adsorption, and hence is thickness dependent, has also been considered. Of course, our

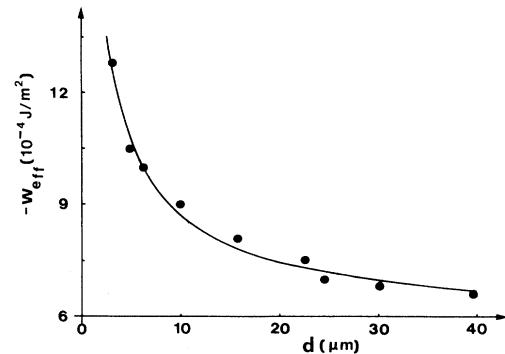


FIG. 5. Experimental data by Blinov and Kabaenkov [9] of w_{eff} vs d concerning 5CB in the initial planar alignment (points) and the theoretical curve obtained by means of the proposed model. The parameters of the best fit are: $w_0 = -2.2 \times 10^{-3}$ J/m² [9], $\Sigma = 5.9 \times 10^{-8}$ C/cm² [27], $e = 4.9 \times 10^{-11}$ SI units [24], $\epsilon_a = 13$, $\epsilon = 12$ [26], and $\lambda_D = 0.6$ μm [27].

model is able to also explain surface transitions observed in NLC's oriented by means of the Langmuir-Blodgett film, when the surface density of the film changes. To do this it is necessary to connect the adsorbed charges with the surface density of the film. An analysis in this direction is being studied and will be presented elsewhere. A homeotropic-planar transition has already been observed under these circumstances [10].

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