Elastic effects of long-range quadrupolar interactions in nematic liquid crystals

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We discuss the role of the quadrupolar interaction in nematic liquid crystal samples in the shape of a slab, limiting the study to planar deformations. Our analysis shows that this interaction gives rise to a bulk energy density that, in the elastic approximation, depends linearly on the second spatial derivative and quadratically on the first spatial derivative of the nematic orientation. We show that this bulk energy density can be separated in a surfacelike term, which gives rise just to a surface contribution, plus a term having the usual form. Both terms depend on the first derivative of the tilt angle and are proportional to the square of the electrical quadrupolar density. The bulk term, quadratic in the first derivative of the tilt angle, renormalizes the usual elastic energy density connected to the short-range forces. The bulk elastic constant of quadrupolar origin can be negative and one order of magnitude smaller than the effective elastic constants for typical nematic liquid crystals. According to our analysis this interaction is responsible for an elastic anisotropy proportional to the square of the electrical quadrupolar density, which depends on the nematic orientation. The surfacelike term is proportional to the first derivative of the tilt angle. It calls mind to the splay-bend elastic term, although the tilt angle dependence is more complicated. The relevant elastic constant is of the same order of magnitude as the bulk one, due to the same interaction. We evaluate also the energy density in the surface layers, where the quadrupolar interaction is restricted by the surface. In this case we show that the free energy contribution due to the surface layers is reduced to a classical anchoring energy. The solution of the variational problem by means of a simple version of the density functional theory is presented. [S1063-651X(98)11612-4]

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I. INTRODUCTION

The elastic behavior of nematic liquid crystals is described by the Frank elastic constants [1]. They are phenomenological parameters introduced by means of symmetry considerations [2]. From a molecular point of view it is possible to connect the elastic constants with the interparticles interaction, responsible for the nematic phase [3–5]. However, as has been emphasized by Evans and Sluckin [6], Sluckin [7], Osipov and Sluckin [8], and Osipov, Sluckin, and Cox [9] that special attention has to be devoted to the long-range interactions, and, in particular, to the quadrupole-quadrupole interaction. Since nematic liquid crystals are quadrupolar media, it seems important to us to analyze the characteristics of this type of interaction. The electrostatic quadrupole-quadrupole interaction energy decays as R^{-5}, where R is the intermolecular distance. This slow decay of the quadrupolar interaction makes the quadrupolar free energy density intrinsically nonlocal. In particular, it has been shown [10] that this free energy density cannot be reduced to the Frank elastic form in the general three-dimensional case. In this case, a more complex nonlocal approach should be used to take into account the quadrupolar interaction. The literature on the macroscopic behavior of nematic liquid crystals is usually devoted to the study of planar director distortions in a nematic slab. In such a case, the director field lies everywhere in a plane orthogonal to the slab plane and depends only on the distance from the surfaces of the slab. In this paper, we will show that, in the special case of planar director distortions, the quadrupolar free energy density can be reduced to an elastic form. For this reason we limit our analysis to a nematic sample of slab shape, with perfect nematic order. The nematic deformation is assumed to be planar and one dimensional and the director is fully described by the tilt angle formed by it with the geometrical normal to the walls of the sample. In this framework we show that the quadrupolar interaction gives rise, in the elastic approximation, to an energy density that can be separated in a bulk and in a surface contribution. The bulk contribution is proportional to the square of the first spatial derivative of the tilt angle. It is characterized by an elastic constant that depends on the nematic orientation, proportional to the square of the nematic quadrupolar density. The surface contribution contains two terms. One is connected to a surfacelike term linear in the first spatial derivative of the tilt angle. Due to this dependence, it reminds the splay-bend elastic term introduced long ago by Nehring and Saupe [3] and discussed recently by several authors [11–16]. The other term comes from the quadrupolar interaction restricted by the surface, localized in a surface layer the thickness of which is of the order of the molecular dimension. It depends only on the surface nematic orientation, and it can be considered as an intrinsic anchoring energy.

Our paper is organized as follows. In Sec. II the energy density due to the quadrupolar interaction is deduced. In that section it is shown that it is a nonlocal quantity. This means that its value does not depend only on the state of the system in a point, but on the state of the system in an appropriate range. The reduction of the nonlocal problem to a local one is discussed in Sec. III. There the bulk elastic constant, the maximum elastic anisotropy and the value of the surfacelike elastic constant connected to the quadrupolar interaction are

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calculated. The evaluation of the energy density due to the quadrupolar interaction in the framework of the electrostatics theory is reported in Sec. IV. In Sec. V the problem is approached by means of a simple version of the density functional theory [17,18]. The integral equation governing the distorted nematic profile in the bulk is obtained, and the limit of dimensionless molecules is discussed. In this way we are able to partially recover the main results deduced in Sec. III. The energy density of quadrupolar origin in the surface layers is considered in Sec. VI. In this section it is shown that in the surface layers the energy contribution connected with the homogeneous part of the energy density balances exactly the elastic energy term linear in the spatial derivative of the tilt angle. This result is in agreement with the prediction of a recently proposed general theory [19].

II. QUADRUPOLAR INTERACTION

The nematic liquid crystal is assumed to be perfectly oriented (the nematic order parameter $S=1$ [1]). Its molecules are assumed to be, in a first approximation, of spherical shape and the nematic order is assumed to be only due to the attractive long-range dispersion forces. The radius of the sphere is $r_0/2$.

In the following we shall evaluate the interaction energy due to the quadrupole-quadrupole interaction. To do this we assume that (1) the nematic molecules are hard spheres of radius $r_0/2$ and the single particle density is everywhere uniform $[\rho(r_1)=N=const]$; (2) the quadrupole is in the center of the sphere; (3) the two-particle density $\rho(r_1,r_2)$ is assumed to be given by $\rho(r_1,r_2)=\rho(r_1)h(|\mathbf{r}_1-\mathbf{r}_2|/r_0)$, where $h(X)=0$ for $X<1$ and $h(X)=1$ for $X>1$; (4) the impenetrability of the molecules is taken into account by means of another interaction (of contact) responsible for the Frank elastic constants of the nematic liquid crystal.

Since we assume perfect nematic order, the molecular major axis **a** coincides with the nematic director **n**. Hence, the molecular quadrupolar tensor is $q_{ij}=q[n_in_j-(1/3)\delta_{ij}]$, where q is the molecular quadrupole. The bulk density of quadrupolar tensor is

$$\mathcal{Q}_{ij}=Nq_{ij}=e(n_in_j-\tfrac{1}{3}\delta_{ij}). \tag{1}$$

The quantity $e=Nq$ is the quadrupolar density. Its value, for typical nematic liquid crystals, is of the order of the flexoelectric coefficient [20].

The electrical interaction between the quadrupoles $q_{ij}=q_{ij}(\mathbf{r})$ and $q'_{ij}=q_{ij}(\mathbf{r}')$ located in $\mathbf{r}$ and in $\mathbf{r}'$, the relative position of which is $\mathbf{R}=\mathbf{r}'-\mathbf{r}$, is given by [21]

$$g=\tfrac{1}{12}kq_{ij}\frac{\partial^2}{\partial x_i\partial x_j}\left\{\frac{(x_m-x'_m)q'_{mn}(x_n-x'_n)}{R^5}\right\}, \tag{2}$$

where k depends on the system of units used. By substituting the molecular quadrupolar tensor q_{ij} into Eq. (2) the quadrupolar interaction between two nematic molecules in $\mathbf{r}$ and in $\mathbf{r}'$, the directors of which are $\mathbf{n}=\mathbf{n}(\mathbf{r})$ and $\mathbf{n}'=\mathbf{n}(\mathbf{r}')$ respectively, is given by [22]

$$g(\mathbf{n},\mathbf{n}',\mathbf{R})=\frac{kq^2}{12R^5}\{1+2(\mathbf{n}\cdot\mathbf{n}')^2-20(\mathbf{n}\cdot\mathbf{u})(\mathbf{n}'\cdot\mathbf{u})(\mathbf{n}\cdot\mathbf{n}')-5[(\mathbf{n}\cdot\mathbf{u})^2+(\mathbf{n}'\cdot\mathbf{u})^2]+35(\mathbf{n}\cdot\mathbf{u})^2(\mathbf{n}'\cdot\mathbf{u})^2\}. \tag{3}$$

In our analysis the centers of the spherical molecules of radius $r_0/2$, indicated by $\mathbf{r}$ and $\mathbf{r}'$, are assumed to lie in a slab limited by two plane surfaces at $z=\pm d/2$ of a Cartesian reference frame. Then, the actual thickness of the nematic layer is $D=d+r_0$. However, from now on, we will refer to d as the thickness of the nematic layer. This parameter corresponds to the thickness of the distribution of quadrupoles. The problem is assumed to be planar and one dimensional. This means that $\mathbf{n}$ is everywhere parallel to a plane that we assume to be the (x,z) plane, and depends only on the z coordinate. Hence $\mathbf{n}=\mathbf{n}(z)=[\sin\theta(z),0,\cos\theta(z)]$, where $\theta=\cos^{-1}(\mathbf{n}\cdot\mathbf{z})$ is the tilt angle.

In this framework the interaction energy between the quadrupole in $\mathbf{r}=(0,0,z)$ and the one in $\mathbf{r}'=(x',y',z')$, for which $\mathbf{R}=(x',y',z'-z)$ can be easily evaluated by Eq. (3). It depends on the tilt angles of the interacting quadrupoles $\theta=\theta(z)$ and $\theta'=\theta(z')$ and on their relative position $\mathbf{R}$: $g=g(\theta,\theta';x',y',z'-z)$. In the mean field approximation the energy density due to the quadrupolar interaction energy g is given by

$$f_q(\mathbf{r})=\frac{1}{2}\int_\tau N^2g(\mathbf{n},\mathbf{n}',\mathbf{R})d\tau', \tag{4}$$

where N is the molecular density, which in our analysis we assume to be position independent [23]. Due to assumption (3), the integration volume τ in Eq. (4) is the whole sample volume except for a sphere of radius r_0 around $\mathbf{r}$. In our planar and one-dimensional problem Eq. (4) reads

$$f_q(z)=\frac{1}{2}\int_\tau N^2g(\theta,\theta';x',y',z'-z)dx'dy'dz'. \tag{5}$$

It is useful for further considerations to define the quantity

$$G(\theta,\theta';z'-z)=\frac{1}{2}\int_\Sigma N^2g(\theta,\theta';x',y',z'-z)dx'dy'. \tag{6}$$

It represents the contribution to the energy density in z due to a layer of thickness dz' at a distance $z'-z$. To evaluate $G(\theta,\theta';z'-z)$ we use a polar reference frame in the (x',y') plane. Let ρ and ϕ be the polar coordinates of a point in the (x',y') plane. A simple analysis shows that for $|z'-z|>r_0$, $0\leq\rho<\infty$, and for $|z'-z|\leq r_0$, $\sqrt{r_0^2-(z'-z)^2}\leq\rho<\infty$. In the first case Σ is the whole (x',y') plane, whereas in the second case Σ is the part of the (x',y') plane outside the circle of radius $\rho_m=\sqrt{r_0^2-(z'-z)^2}$. In terms of $G(\theta,\theta';z'-z)$ the energy density given by Eq. (5) reads

$$f_q(z)=\int_{-d/2}^{d/2}G(\theta,\theta';z'-z)dz'. \tag{7}$$

A simple calculation shows that

$$G(\theta,\theta';z'-z)=0, \quad \text{for} \quad |z'-z|\geqslant r_0, \tag{8}$$

and

$$G(\theta,\theta';z'-z)=\mathcal{H}(z'-z)T(\theta,\theta') \quad \text{for} \quad |z'-z|\leqslant r_0, \tag{9}$$

where the kernel $\mathcal{H}(z'-z)=\mathcal{H}(z-z')$ and the function $T(\theta,\theta')=T(\theta',\theta)$ are defined by

$$\mathcal{H}(z'-z)=\frac{\pi k e^2}{96 r_0^3}\left[1-6\left(\frac{z'-z}{r_0}\right)^2+5\left(\frac{z'-z}{r_0}\right)^4\right], \tag{10}$$

and

$$T(\theta,\theta')=3+19\cos^2\theta\cos^2\theta'-7(\cos^2\theta+\cos^2\theta') -4\sin(2\theta)\sin(2\theta'). \tag{11}$$

Equation (8) means that a compact layer of quadrupoles of thickness dz' does not produce any electrical effect outside of the layer itself.

The total energy, per unit surface, of quadrupolar origin is given by

$$F_q=\int_{-d/2}^{d/2} f_q(z)dz. \tag{12}$$

We separate the nematic liquid crystal sample of slab shape in three regions: the bulk, defined by $-d/2+r_0\leqslant z\leqslant d/2-r_0$, and two surface layers, where $d/2-r_0\leqslant|z|\leqslant d/2$, and we decompose F_q as follows:

$$F_q=\int_{-d/2}^{-d/2+r_0} f_{qi}(z)dz+\int_{-d/2+r_0}^{d/2-r_0} f_{qb}(z)dz + \int_{d/2-r_0}^{d/2} f_{qi}(z)dz. \tag{13}$$

$f_{qi}(z)$ and $f_{qb}(z)$ are the bulk energy densities due to the quadrupolar interaction in the surface layers and in the bulk, respectively. Following a standard procedure, it is convenient to rewrite Eq. (13) as

$$F_q=\int_{-d/2}^{-d/2+r_0}[f_{qi}(z)-f_{qb}(z)]dz+\int_{-d/2}^{d/2} f_{qb}(z)dz + \int_{d/2-r_0}^{d/2}[f_{qi}(z)-f_{qb}(z)]dz, \tag{14}$$

i.e., as the sum of a bulk contribution plus two surface contributions, which are connected with the presence of the surface layers where the energy density is different from the bulk one. Setting $\Delta f_q(z)=f_{qi}(z)-f_{qb}(z)$ and

$$F_s^{(-)}=\int_{-d/2}^{-d/2+r_0}\Delta f_q(z)dz,$$

$$F_s^{(+)}=\int_{d/2-r_0}^{d/2}\Delta f_q(z)dz,$$

$$F_{\text{bulk}}=\int_{-d/2}^{d/2} f_{qb}(z)dz, \tag{15}$$

Eq. (14) can be rewritten as

$$F_q=F_s^{(-)}+F_{\text{bulk}}+F_s^{(+)}. \tag{16}$$

We shall consider in the following the energy of the bulk and of the surface layers separately.

In the bulk the energy density is given by Eq. (7) that, by taking into account Eqs. (8),(9), can be rewritten as

$$f_{qb}(z)=\int_{z-r_0}^{z+r_0}\mathcal{H}(z'-z)T(\theta,\theta')dz'. \tag{17}$$

Equation (17) gives the energy density due to the quadrupolar interaction. If there are other interactions, the total energy density in the bulk is obtained, in a first approximation, by adding all the contributions. It is important to note that the energy density given by Eq. (17) is *nonlocal*, because it depends on all the values of θ in the range $(z-r_0,z+r_0)$. To go further we have two possibilities. The first is to reduce f_{qb} to a local form by means of some limit operation. The second is to face the problem taking into account the nonlocality underlined above. In Sec. III we will reduce f_{qb} to a local form, in the elastic approximation, whereas in Sec. V the nonlocal analysis is presented.

In our analysis we assume that, beside the quadrupolar interaction, there is also a short-range interaction giving rise to an elastic energy density that for our planar and one-dimensional problem reads

$$f_e=\tfrac{1}{2}(K_{11}\sin^2\theta+K_{33}\cos^2\theta)\left(\frac{d\theta}{dz}\right)^2 =\tfrac{1}{2}K_{33}(1-\Delta\sin^2\theta)\left(\frac{d\theta}{dz}\right)^2, \tag{18}$$

where $\Delta=(K_{33}-K_{11})/K_{33}$ is the elastic anisotropy. In the one constant approximation $K_{11}=K_{33}=K$ and $\Delta=0$. In this framework the Frank elastic energy density is given by

$$f_e=\tfrac{1}{2}K\left(\frac{d\theta}{dz}\right)^2, \tag{19}$$

which will be used in the following.

III. ENERGY DENSITY OF QUADRUPOLAR ORIGIN IN THE BULK: DIRECT CALCULATION

In this section we are interested in the calculation of the bulk free energy F_{bulk} defined in Eq. (15). In the bulk, the energy density $f_{qb}(z)$ given by Eq. (17) depends only on the director angles in a very thin layer of molecular thickness $2r_0$. Then, if the director angle θ changes over a macroscopic length, the nonlocal energy density $f_{qb}(z)$ can be replaced by a local elastic expansion in the derivatives of θ at z. It is important to emphasize here that this elastic local description is only possible due to the planar character of the director distortion. Indeed, Eq. (17) is the direct consequence of the fact that two nematic layers of thickness dz and dz' having a uniform director orientation do not interact if $|z'$

$-z|>r_0$ [see Eq. (8)]. To reduce f_{qb} to a local quantity we put $\theta'=\theta+\delta\theta(z,z')$. Since $|z'-z|\leqslant r_0$, which is a molecular dimension, $|\delta\theta(z,z')|\ll 1$. Consequently $T(\theta,\theta')$ can be expanded in power series of $\delta\theta(z,z')$. We obtain

$$T(\theta,\theta')=T_0(\theta)+T_1(\theta)\delta\theta+\tfrac{1}{2}T_2(\theta)(\delta\theta)^2, \tag{20}$$

where, as it follows from Eq. (11),

$$T_0(\theta)=T(\theta,\theta)=(3-30\cos^2\theta+35\cos^4\theta), \tag{21}$$

$$T_1(\theta)=\left(\frac{\partial T}{\partial\theta'}\right)_{\theta'=\theta}=5\sin(2\theta)(3-7\cos^2\theta), \tag{22}$$

and

$$T_2(\theta)=\left(\frac{\partial^2 T}{\partial\theta'^2}\right)_{\theta'=\theta}=-2(7-65\cos^2\theta+70\cos^4\theta). \tag{23}$$

In the elastic approximation $\delta\theta(z,z')$ can be written as

$$\delta\theta(z,z')=\frac{d\theta}{dz}(z'-z)+\frac{1}{2}\frac{d^2\theta}{dz^2}(z'-z)^2. \tag{24}$$

By means of Eqs. (20),(24) we obtain for $T(\theta,\theta')$, when $z-r_0\leqslant z'\leqslant z+r_0$, the approximate expression

$$T(\theta,\theta')=T_0(\theta)+(z'-z)T_1(\theta)\frac{d\theta}{dz}+\tfrac{1}{2}(z'-z)^2\left[T_1(\theta)\frac{d^2\theta}{dz^2}+T_2(\theta)\left(\frac{d\theta}{dz}\right)^2\right]. \tag{25}$$

The bulk energy density of quadrupolar origin, in the elastic approximation, is obtained by substituting Eq. (25) into Eq. (17). Simple calculations give $f_{qb}=f_0+f_1+f_{13}+f_2$, where

$$f_0=T_0(\theta)\int_{z-r_0}^{z+r_0}\mathcal{H}(z'-z)dz' \tag{26}$$

is the homogeneous part of the energy density,

$$f_1=T_1(\theta)\frac{d\theta}{dz}\int_{z-r_0}^{z+r_0}(z'-z)\mathcal{H}(z'-z)dz' \tag{27}$$

is the bulk term linear in the first spatial derivative of the tilt angle,

$$f_{13}=\tfrac{1}{2}T_1(\theta)\frac{d^2\theta}{dz^2}\int_{z-r_0}^{z+r_0}(z'-z)^2\mathcal{H}(z'-z)dz' \tag{28}$$

is the bulk term linear in the second-order spatial derivative of the tilt angle, which reminds the splay-bend term [3], and finally

$$f_2=\tfrac{1}{2}T_2(\theta)\left(\frac{d\theta}{dz}\right)^2\int_{z-r_0}^{z+r_0}(z'-z)^2\mathcal{H}(z'-z)dz', \tag{29}$$

which calls to mind the usual Frank elastic term, since it is quadratic in $d\theta/dz$.

As follows from Eq. (10) which defines the kernel $\mathcal{H}(z'-z)$, in the bulk, we have

$$\int_{z-r_0}^{z+r_0}\mathcal{H}(z'-z)dz'=\int_{z-r_0}^{z+r_0}(z'-z)\mathcal{H}(z'-z)dz'=0, \tag{30}$$

and

$$\int_{z-r_0}^{z+r_0}(z'-z)^2\mathcal{H}(z'-z)dz'=-\frac{\pi ke^2}{315}. \tag{31}$$

Hence, in the bulk, $f_0=f_1=0$, whereas, by taking into account Eqs. (21)–(23), f_{13} and f_2 read

$$f_{13}=\frac{1}{2}\left(-\frac{\pi ke^2}{315}\right)5\sin(2\theta)(3-7\cos^2\theta)\frac{d^2\theta}{dz^2} \tag{32}$$

and

$$f_2=-\frac{1}{2}\left(-\frac{\pi ke^2}{315}\right)2(7-65\cos^2\theta+70\cos^4\theta)\left(\frac{d\theta}{dz}\right)^2. \tag{33}$$

The total bulk energy density is $f_{qb}=f_{13}+f_2$, that can be written in the form $f_{qb}=f_s+f_b$, where f_s and f_b are the surfacelike and bulk contributions given by

$$f_s=\frac{1}{2}\left(-\frac{\pi ke^2}{315}\right)\frac{d}{dz}\left[5\sin(2\theta)(3-7\cos^2\theta)\frac{d\theta}{dz}\right], \tag{34}$$

and

$$f_b=\frac{1}{2}\left(-\frac{\pi ke^2}{315}\right)[16-35\sin^2(2\theta)]\left(\frac{d\theta}{dz}\right)^2, \tag{35}$$

respectively.

Hence, the quadrupolar interaction gives rise to a bulk energy density that can be separated into surfacelike and bulk contributions. In the S.I. system of units, where $k=1/(4\pi\epsilon_0)$ Eqs. (34),(35) become

$$f_s=-\frac{e^2}{504\epsilon_0}\frac{d}{dz}\left[\sin(2\theta)(3-7\cos^2\theta)\frac{d\theta}{dz}\right], \tag{36}$$

$$f_b=-\frac{2e^2}{315\epsilon_0}\left(1-\frac{35}{16}\sin^2(2\theta)\right)\left(\frac{d\theta}{dz}\right)^2. \tag{37}$$

According to Eq. (16), the bulk contribution to the total energy F_q is obtained by integrating the bulk free energy density $f_{qb}=f_s+f_b$ over the whole interval $[-d/2,d/2]$. The first contribution, after integration, reduces to a surface energy density, which depends on $d\theta/dz$, of the kind

$$F_{sb}^{(-)}=\frac{e^2}{504\epsilon_0}\sin(2\theta)(3-7\cos^2\theta)\frac{d\theta}{dz}, \tag{38}$$

for $z=-d/2$, and to a similar contribution with opposite sign for $z=d/2$. The subscript sb means that this surface contribution to the surface energy density is, actually, a bulk term.

By comparing expression (38) with the K_{13}-elastic term [3], it is possible to define an ''effective'' K_{13}^e-elastic constant as follows:

$$K_{13}^e(\theta)=\frac{e^2}{252\epsilon_0}(3-7\cos^2\theta). \tag{39}$$

This splay-bend elastic constant is θ dependent. Its value is in the range

$$-e^2/63\epsilon_0 \leqslant K_{13}^e(\theta) \leqslant e^2/84\epsilon_0. \tag{40}$$

The bulk contribution, proportional to $(d\theta/dz)^2$, is given by Eq. (37). From this expression we deduce that the relevant elastic constant is θ dependent and given by

$$K_b(\theta)=-\frac{4e^2}{315\epsilon_0}\left(1-\frac{35}{16}\sin^2(2\theta)\right). \tag{41}$$

Its value is in the range

$$-4e^2/315\epsilon_0 \leqslant K_b(\theta) \leqslant 19e^2/315\epsilon_0. \tag{42}$$

Note that in Eq. (41) the quadrupolar elastic constant depends on the tilt angle via $\sin^2(2\theta)$. This angular dependence is similar to the one already discussed for the influence of the flexoelectric polarization on the elastic properties of nematic liquid crystals [24]. On the other hand, the usual elastic constant in the Frank expression, given by Eq. (18), depends on $\sin^2\theta$. This is a peculiarity of the quadrupolar interaction because the bulk energy density $f_{qb}=f_s+f_b$ does not follow from an expansion of the quadrupolar interaction energy of Eq. (3) in terms of $\partial n_i/\partial x_j$ and of $\partial^2 n_i/\partial x_j \partial x_k$, as usually done in the elastic theory. In fact this expansion does not converge, due to the R^{-5} of the quadrupolar interaction. A local expansion of the quadrupolar interaction is possible only for samples of slab shape.

For nematic orientations near to the homeotropic ($\theta \sim 0$) or planar ($\theta \sim \pi/2$) ones, $K_b(0)=K_b(\pi/2)=K_b(u)$ is negative and given by $K_b(u)=-4e^2/315\epsilon_0$. In the cgs-Gauss system of units $\epsilon_0=1/4\pi$, and hence $K_b(u)=(16\pi/315)e^2 \sim 0.16e^2$. Since for typical nematic liquid crystals $e^2 \sim K$, where K is the average Frank elastic constant, we can deduce that the quadrupolar contribution to the Frank elastic constant is rather small (nearly one order of magnitude smaller than the contribution due to the interactions of sterical origin).

We note that $K_b(\theta)$ is negative near to the homeotropic and planar orientation, and positive for a homogeneous orientation close to $\theta=\pi/4$, as follows from Eq. (37). In fact, as follows from Eq. (37), the quadrupolar interaction introduces a large elastic anisotropy given by $(e^2/36\epsilon_0)\sin^2(2\theta)$. It is similar to the one already discussed for the flexoelectric polarization [24]. From Eqs. (40) one has $-1 \lesssim K_{13}^e/K_b(u) \lesssim 1$. It follows that $K_{13}j$ is of the same order of magnitude of $K_b(u)$.

IV. ENERGY DENSITY OF QUADRUPOLAR ORIGIN IN THE BULK: ELECTROSTATICS APPROACH

The aim of this section is to reobtain Eqs. (36),(37) giving the surfacelike and bulk energy density due to the quadrupolar interaction by means of considerations based on the electrostatics theory. In this section we use always the S.I. system of units where $k=1/(4\pi\epsilon_0)$.

As is well known from elementary electrostatics, the electrostatic energy density in the bulk connected with a continuous distribution of quadrupoles is given by [21]

$$f_{qb}=-\tfrac{1}{12}\mathcal{Q}_{ij}\mathcal{E}_{ij}, \tag{43}$$

where $\mathcal{E}_{ij}=\partial E_i/\partial x_j$ are the spatial derivatives of the total field acting on the quadrupole. In our planar and one dimensional problem the elements of the quadrupolar tensor $\mathcal{Q}$ are given by Eq. (1) where $\mathbf{n}=[\sin\theta(z),0,\cos\theta(z)]$. Consequently,

$$\mathcal{Q}=e\begin{pmatrix} \sin^2\theta-\frac{1}{3} & 0 & \sin\theta\cos\theta \\ 0 & -\frac{1}{3} & 0 \\ \sin\theta\cos\theta & 0 & \cos^2\theta-\frac{1}{3} \end{pmatrix}. \tag{44}$$

This implies that $\mathcal{Q}_{yy}$ is position independent. Furthermore, since $\mathbf{E}$ is an electrostatic field, $\nabla\times\mathbf{E}=0$, and hence $\mathcal{E}_{ij}=\mathcal{E}_{ji}$.

According to the model used in Sec. III, the electric quadrupole is at the center of a sphere and, thus, the other quadrupoles are uniformly distributed out of a sphere of radius r_0. Consequently, the electric field acting on the quadrupole at the center of the sphere is only due to the uniform distribution outside the sphere. To evaluate $\mathcal{E}_{ij}$ we use the Clausius-Mossotti method [25]. According to this technique $\mathcal{E}_{ij}$ is given by

$$\mathcal{E}_{ij}=\mathcal{E}_{ij}^{(c)}-\mathcal{E}_{ij}^{(s)}, \tag{45}$$

where $\mathcal{E}_{ij}^{(c)}$ is due to the continuum distribution of quadrupoles (average field), and $\mathcal{E}_{ij}^{(s)}$ is due to the spherical quadrupole under consideration (spherical cavity field). To evaluate $\mathcal{E}_{ij}^{(c)}$ we have just to take into account that for a continuous quadrupolar material the electric displacement $\mathbf{D}^{(c)}$ is

$$D_i^{(c)}=\frac{1}{4\pi k}E_i^{(c)}-\frac{1}{6}\frac{\partial\mathcal{Q}_{ij}}{\partial x_j}, \tag{46}$$

if the medium is not polarizable and nonferroelectric. By assuming the nematic liquid crystal as a perfect insulator we have $\nabla\cdot\mathbf{D}^{(c)}=0$, that in our slab geometry reduces to $dD_z^{(c)}/dz=0$. Since in the problem under consideration $\mathcal{Q}_{ij}=\mathcal{Q}_{ij}(z)$ from Eqs. (46) we obtain

$$\mathcal{E}_{zz}^{(c)}=\frac{2\pi k}{3}\frac{d^2\mathcal{Q}_{zz}}{dz^2}. \tag{47}$$

Let us consider now the spatial gradients of the electric field $\mathbf{E}^{(s)}$, evaluated in the center of the sphere, created by the quadrupolar sphere. The electrical potential created in a point $\mathbf{r}$ by the sphere is

$$V^{(s)}(\mathbf{r})=\tfrac{1}{6}k\int_{\tau_0}\mathcal{Q}_{ij}(\mathbf{r}')\frac{\partial^2}{\partial x_i'\partial x_j'}\left(\frac{1}{R}\right)d\tau', \tag{48}$$

where τ_0 is the volume of the sphere, $\mathbf{r}'$ a generic point of the sphere where the quadrupolar tensor density is $\mathcal{Q}_{ij}(\mathbf{r}')$, $d\tau'$ is a volume element around $\mathbf{r}'$ and $\mathbf{R}=\mathbf{r}-\mathbf{r}'$. By means of simple calculations Eq. (48) can be rewritten as $V^{(s)}(\mathbf{r})=V_1(\mathbf{r})+V_2(\mathbf{r})+V_3(\mathbf{r})$, where

$$V_1(\mathbf{r})=\tfrac{1}{6}k\int_{\tau_0}\frac{\partial^2\mathcal{Q}_{ij}(\mathbf{r}')}{\partial x_i'\partial x_j'}\frac{1}{R}d\tau', \tag{49}$$

$$V_2(\mathbf{r})=\tfrac{1}{6}k\int_{\Sigma_0}N_i\mathcal{Q}_{ij}(\mathbf{r}')\frac{\partial}{\partial x_j'}\left(\frac{1}{R}\right)d\Sigma', \tag{50}$$

and

$$V_3(\mathbf{r})=\tfrac{1}{6}k\int_{\Sigma_0}-N_i\frac{\partial\mathcal{Q}_{ij}(\mathbf{r}')}{\partial x_j'}\frac{1}{R}d\Sigma'. \tag{51}$$

In Eqs. (50),(51) Σ_0 is the surface of the sphere and $\mathbf{N}$ the geometrical normal to the surface of the sphere, outward directed. As it is evident from Eq. (49), $V_1(\mathbf{r})$ is the electrical potential created in $\mathbf{r}$ by a bulk charge density given by

$$\rho(\mathbf{r}')=\frac{1}{6}\frac{\partial^2\mathcal{Q}_{ij}(\mathbf{r}')}{\partial x_i'\partial x_j'}. \tag{52}$$

On the other hand, from Eq. (50) we deduce that $V_2(\mathbf{r})$ is the electrical potential created in $\mathbf{r}$ by a surface distribution of dipoles, whose surface density is

$$P_j(\mathbf{r}')=\tfrac{1}{6}N_i\mathcal{Q}_{ij}(\mathbf{r}'). \tag{53}$$

Finally, Eq. (51) shows that $V_3(\mathbf{r})$ is the electrical potential created in $\mathbf{r}$ by a surface charge density given by

$$\sigma(\mathbf{r}')=-\tfrac{1}{6}N_i\frac{\partial\mathcal{Q}_{ij}(\mathbf{r}')}{\partial x_j'}. \tag{54}$$

In Eqs. (53),(54), $\mathbf{r}'$ is a point of Σ_0 where the geometrical normal is $\mathbf{N}$. Using a polar reference frame, with the z axis as polar axis, we have that for a point on Σ_0, $\mathbf{r}'=r_0\mathbf{N}$, where $\mathbf{N}=(\sin\Theta\cos\Phi,\sin\Theta\sin\Phi,\cos\Theta)$, Θ and Φ being the angular coordinates of a point on the sphere Σ_0. Furthermore, $d\Sigma'=r_0^2\sin\Theta d\Theta d\Phi=-r_0^2 d(\cos\Theta)d\Phi$.

The analysis presented above shows that a body of volume τ_0 limited by a surface Σ_0, whose density of quadrupolar tensor is $\mathcal{Q}_{ij}(\mathbf{r}')$, is equivalent to a bulk density of charges and to a surface distribution of dipoles and of charges [26]. Because $\mathcal{Q}_{ij}=\mathcal{Q}_{ij}(z)$ the general equations giving $\rho(\mathbf{r}')$ and $\sigma(\mathbf{r}')$ become

$$\rho(\mathbf{r}')=\frac{d^2\mathcal{Q}_{zz}(z')}{dz'^2}\quad\text{and}\quad\sigma(\mathbf{r}')=-N_i\frac{d\mathcal{Q}_{iz}(z')}{dz'}. \tag{55}$$

It follows that the electric field due to a sphere of quadrupolar material at an inner point $\mathbf{r}=(x,y,z)$ is given by $\mathbf{E}^{(s)}(\mathbf{r})=\mathbf{E}_1(\mathbf{r})+\mathbf{E}_2(\mathbf{r})+\mathbf{E}_3(\mathbf{r})$, where, as follows from the discussion reported above,

$$\mathbf{E}_1(\mathbf{r})=-k\int_{\tau_0}\rho(\mathbf{r}')\nabla\left(\frac{1}{R}\right)d\tau', \tag{56}$$

$$\mathbf{E}_2(\mathbf{r})=-k\int_{\Sigma_0}\frac{R^2\mathbf{P}(\mathbf{r}')-3[\mathbf{R}\cdot\mathbf{P}(\mathbf{r}')]\mathbf{R}}{R^5}d\Sigma', \tag{57}$$

and

$$\mathbf{E}_3(\mathbf{r})=-k\int_{\Sigma_0}\sigma(\mathbf{r}')\nabla\left(\frac{1}{R}\right)d\Sigma', \tag{58}$$

where $\rho(\mathbf{r}')$, $\mathbf{P}(\mathbf{r}')$, and $\sigma(\mathbf{r}')$ are given by Eqs. (52)–(54).

To evaluate f_{qb} given by Eq. (43), we have now to calculate $\mathcal{E}_{ij}^{(s)}$ in the center of the sphere. After that, by means of Eq. (45), it is possible to calculate $\mathcal{E}_{ij}$ acting on the sphere of quadrupolar material, in the limit of $r_0\to 0$. With this aim in mind, with the same approximation used above [see Eq. (24)], we expand $\mathcal{Q}_{ij}(z')$ in power series of z' up to the second order. Hence

$$\mathcal{Q}_{ij}(z')=\mathcal{A}_{ij}+\mathcal{B}_{ij}z'+\tfrac{1}{2}\mathcal{C}_{ij}z'^2, \tag{59}$$

where

$$\mathcal{A}_{ij}=\mathcal{Q}_{ij}(0),\quad \mathcal{B}_{ij}=\left\{\frac{d\mathcal{Q}_{ij}(z')}{dz'}\right\}_0,$$

$$\text{and}\quad \mathcal{C}_{ij}=\left\{\frac{d^2\mathcal{Q}_{ij}(z')}{dz'^2}\right\}_0. \tag{60}$$

The matrices $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ of elements $\mathcal{A}_{ij}$, $\mathcal{B}_{ij}$, and $\mathcal{C}_{ij}$ are, as follows from Eq. (44):

$$\mathcal{A}=e\begin{pmatrix}\sin^2\theta-\frac{1}{3} & 0 & \sin\theta\cos\theta\\ 0 & -\frac{1}{3} & 0\\ \sin\theta\cos\theta & 0 & \cos^2\theta-\frac{1}{3}\end{pmatrix},$$

$$\mathcal{B}=e\begin{pmatrix}\sin(2\theta) & 0 & \cos(2\theta)\\ 0 & 0 & 0\\ \cos(2\theta) & 0 & -\sin(2\theta)\end{pmatrix}\frac{d\theta}{dz}, \tag{61}$$

and

$$\mathcal{C}=2e\begin{pmatrix}\cos(2\theta) & 0 & -\sin(2\theta)\\ 0 & 0 & 0\\ -\sin(2\theta) & 0 & -\cos(2\theta)\end{pmatrix}\left(\frac{d\theta}{dz}\right)^2$$

$$+e\begin{pmatrix}\sin(2\theta) & 0 & \cos(2\theta)\\ 0 & 0 & 0\\ \cos(2\theta) & 0 & -\sin(2\theta)\end{pmatrix}\frac{d^2\theta}{dz^2}, \tag{62}$$

where all the quantities are evaluated in the center of the sphere.

Consequently $\rho(\mathbf{r}')$ and $\sigma(\mathbf{r}')$, given by Eqs. (55) are

$$\rho(\mathbf{r}')=\tfrac{1}{6}\mathcal{C}_{33}=\text{const},$$
$$\sigma(\mathbf{r}')=-\tfrac{1}{6}N_\alpha(\mathcal{B}_{\alpha z}+\mathcal{C}_{\alpha z}z'). \tag{63}$$

Let us consider now $\mathbf{E}_1(\mathbf{r})$ given by Eq. (56). Since $\rho(z')$ in the elastic approximation is position independent, as follows from Eq. (63), we have $\mathbf{E}_1(\mathbf{r})=(2\pi k/9)\mathcal{C}_{33}\mathbf{r}$. Hence,

$$\mathcal{E}_1(0)=\frac{2\pi k}{9}\mathcal{C}_{33}\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}. \tag{64}$$

To evaluate $\mathcal{E}_2(0)$ we have only to take into account that, by Eqs. (44),(53), it follows that

$$P_x(\mathbf{r}')=\tfrac{1}{6}[\mathcal{Q}_{xx}(z')\sin\Theta\cos\Phi+\mathcal{Q}_{xz}(z')\cos\Theta],$$
$$P_y(\mathbf{r}')=\tfrac{1}{6}\mathcal{Q}_{yy}\sin\Theta\sin\Phi,$$
$$P_z(\mathbf{r}')=\tfrac{1}{6}[\mathcal{Q}_{xz}(z')\sin\Theta\cos\Phi+\mathcal{Q}_{zz}(z')\cos\Theta], \tag{65}$$

where, on the surface of the sphere, $z'=r_0\cos\Theta$. Furthermore in Eq. (57) the vector $\mathbf{R}$ is given by $\mathbf{R}=(x-r_0\sin\Theta\cos\Phi, y-r_0\sin\Theta\sin\Phi, z-r_0\cos\Theta)$, as follows from the discussion reported above. By substituting Eqs. (65) with $\mathcal{Q}_{ij}(z')$ given by Eq. (59) into Eq. (57) after simple, but tedious calculations we obtain

$$\mathcal{E}_2(0)=\frac{8\pi k}{35}\begin{pmatrix}-3(\mathcal{C}_{11}+\mathcal{C}_{33})&0&\mathcal{C}_{13}\\0&-(\mathcal{C}_{11}+3\mathcal{C}_{33})&0\\\mathcal{C}_{13}&0&2(2\mathcal{C}_{11}+3\mathcal{C}_{33})\end{pmatrix}. \tag{66}$$

From Eq. (66) it follows that $\nabla\cdot\mathbf{E}_2=0$, as expected.

Let us consider, finally, the spatial derivatives of the field $\mathbf{E}_3$ given by Eq. (58), in the center of the sphere, when $\sigma(\mathbf{r}')$ is defined by Eq. (63). We have,

$$\mathcal{E}_3(0)=\frac{4\pi k}{15}\begin{pmatrix}2\mathcal{C}_{33}&0&-3\mathcal{C}_{13}\\0&2\mathcal{C}_{33}&0\\-3\mathcal{C}_{13}&0&-4\mathcal{C}_{33}\end{pmatrix}. \tag{67}$$

From Eq. (67) it follows again that $\nabla\cdot\mathbf{E}_3=0$.

To obtain the tensor $\mathcal{E}$ entering into Eq. (43), we have only to remember that in the elastic approximation, Eq. (47) reads

$$\mathcal{E}^{(c)}(0)=\frac{2\pi k}{3}\mathcal{C}_{33}\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix}. \tag{68}$$

By means of Eqs. (64),(66),(67) we evaluate the spatial derivatives of the electric field due to the sphere of quadrupolar material in its center. After that, using Eqs. (68) and (45) we obtain the tensor $\mathcal{E}$ of elements $\partial E_i/\partial x_j$. By substituting this result into Eq. (43) rewritten as $f_{qb}=-(1/12)\mathcal{A}_{ij}\mathcal{E}_{ij}$, and taking into account Eqs. (61),(62), we reobtain $f_{qb}=f_s+f_b$, where f_s and f_b are still given by Eqs. (36),(37).

We note that in this calculation the field created by the sphere of quadrupolar material plays a fundamental role. If one identifies the field acting on the quadrupole with the field due to the continuum distribution of quadrupoles, given by Eq. (47), one obtains different results. In particular, one obtains that the quadrupolar interaction is responsible for an elastic anisotropy, which is orientation dependent, but one is unable to show that its contribution to the Frank elastic constant can be negative.

V. NONLOCAL ANALYSIS

In the previous sections we have reduced the nonlocal quantity f_{qb} given by Eq. (17) to a bulk local quantity f_b plus a surfacelike contribution f_s, by means of a limit operation $r_0\to 0$. Now we want to analyze the problem taking into account explicitly the nonlocality of f_{qb}. As above we limit our analysis to the bulk, i.e., for $-d/2+r_0\leqslant z\leqslant d/2+r_0$.

The total energy, per unit surface area, of quadrupolar origin is given by

$$F_q=\int_{-d/2}^{d/2}f_q dz=\int_{-d/2}^{d/2}\int_{-d/2}^{d/2}G(\theta,\theta',z'-z)dz'dz, \tag{69}$$

as follows from Eq. (7). In our planar and one-dimensional problem the Frank elastic energy density, in the one constant approximation, is given by Eq. (19). Hence, the total energy per unit surface area is

$$F=\int_{-d/2}^{d/2}[f_e+f_q]dz$$
$$=\int_{-d/2}^{d/2}\left[\frac{1}{2}K\left(\frac{d\theta}{dz}\right)^2+\int_{-d/2}^{d/2}G(\theta,\theta',z'-z)dz'\right]. \tag{70}$$

Functional (70) is of the kind

$$F=\int_{-d/2}^{d/2}\left\{\mathcal{M}(d\theta/dz)+\int_{-d/2}^{d/2}\mathcal{N}[\theta(z),\theta(z');|z'-z|]dz'\right\}dz, \tag{71}$$

where $\mathcal{N}[\theta(z),\theta(z');|z'-z|]=\mathcal{N}[\theta(z'),\theta(z);|z'-z|]$. The function minimizing F given by Eq. (71) is solution of the integral-differential equation [27]

$$-\frac{d}{dz}\frac{d\mathcal{M}}{d(d\theta/dz)}+2\int_{-d/2}^{d/2}\frac{\partial\mathcal{N}}{\partial\theta(z)}dz'=0. \tag{72}$$

In our case, by taking into account Eqs. (19),(8),(9), in the bulk Eq. (72) reads

$$-K\frac{d^2\theta}{dz^2}+2\int_{z-r_0}^{z+r_0}\mathcal{H}(z'-z)\frac{\partial T(\theta,\theta')}{\partial\theta}dz'=0, \tag{73}$$

which is the equilibrium equation for the nonlocal problem under consideration. It is an integral-differential equation, the integral part of which is due to the nonlocal quadrupolar interaction. On the other hand, the differential part is due to the short-range interaction, responsible for the usual elastic energy density, which admits a local description. Let us assume now that r_0 is a very small quantity. This implies that the nematic molecules may be assumed practically dimensionless. Physically this means that we are interested in spatial variations of the observables entering into the problem occurring over lengths very large with respect to r_0. We call

$$R(\theta,\theta')=\frac{\partial T(\theta,\theta')}{\partial\theta}, \tag{74}$$

and, as we have already done in Sec. III, we assume that $|\delta\theta(z,z')|=|\theta'-\theta|\ll 1$, and furthermore that $\delta\theta(z,z')$ can be expanded in power series of $z'-z$, as shown in Eq. (24). In this framework $R(\theta,\theta')$ can be written as

$$R(\theta,\theta')=R_0(\theta)+(z'-z)R_1(\theta)\frac{d\theta}{dz}+\tfrac{1}{2}(z'-z)^2\left[R_1(\theta)\frac{d^2\theta}{dz^2}+R_2(\theta)\left(\frac{d\theta}{dz}\right)^2\right], \tag{75}$$

where, as follows from Eqs. (11),(74),

$$R_0(\theta)=R(\theta,\theta)=5\sin(2\theta)(3-7\cos^2\theta), \tag{76}$$

and

$$R_1(\theta)=\left(\frac{\partial R}{\partial\theta'}\right)_{\theta'=\theta}=35\sin^2(2\theta)-16,$$

$$R_2(\theta)=\left(\frac{\partial^2 R}{\partial\theta'^2}\right)_{\theta'=\theta}=35\sin(4\theta). \tag{77}$$

By substituting Eq. (75) into Eq. (73) and taking into account Eqs. (30),(31) we obtain

$$(K-\tfrac{16}{315}\pi ke^2)\frac{d^2\theta}{dz^2}+\frac{\pi}{9}ke^2\left[\sin^2(2\theta)\frac{d^2\theta}{dz^2}+\sin(4\theta)\left(\frac{d\theta}{dz}\right)^2\right]=0, \tag{78}$$

which is equivalent to

$$\tfrac{1}{2}\left[(K-\tfrac{16}{315}\pi ke^2)+\frac{\pi}{9}ke^2\sin^2(2\theta)\right]\left(\frac{d\theta}{dz}\right)^2=\text{const.} \tag{79}$$

This bulk equilibrium equation shows again that the quadrupolar interaction reduces the Frank elastic constant connected to short range interactions of $(16/315)\pi ke^2=4e^2/315\epsilon_0$. It gives rise, furthermore, to an elastic anisotropy that depends on the nematic orientation, the maximum value of which is $\pi ke^2/9=e^2/36\epsilon_0$. These results agree with those obtained in Sec. III. However, this bulk nonlocal analysis does not give any information about the surfacelike contribution, because it is based on the bulk integral-differential equilibrium equation [Eq. (73)], where surface contributions are absent.

VI. INTERFACIAL CONTRIBUTIONS TO THE SURFACE FREE ENERGY

In Sec. III, we have shown that the bulk free energy density in Eq. (17) can be separated into a bulk elastic term f_b and a surfacelike term f_s, which is equivalent to a surface energy density linear in $d\theta/dz$ [Eq. (38)]. Close to the interfaces in two thin interfacial layers of thickness r_0, the local free energy density is no longer given by $f_{qb}(z)$ of Eq. (17), as already underlined. Then, there is an excess of interfacial free energy that gives a further contribution to the surface free energy, which we have indicated above by $F_s^{(-)}$ and $F_s^{(+)}$. Here we are interested in calculating these specific interfacial contributions to the surface free energy. Let us consider, for instance, the upper interfacial layer of the nematic slab $(d/2-r_0<z<d/2)$ and indicate simply by F_s the quantity $F_s^{(+)}$. Using Eqs. (7)–(9), we find that the local free energy density in the interfacial layer is

$$f_{qi}(z)=\int_{z-r_0}^{d/2}\mathcal{H}(z'-z)T(\theta,\theta')dz'. \tag{80}$$

The excess of interfacial free energy density Δf_q, as discussed in Sec. II, is obtained by subtracting from $f_{qi}(z)$ the bulk free energy density $f_{qb}(z)$. We get from Eq. (17) and Eq. (80)

$$\Delta f_q(z)=-\int_{d/2}^{z+r_0}\mathcal{H}(z'-z)T(\theta,\theta')dz'. \tag{81}$$

By operating as in Sec. III, Δf_q can be written as $\Delta f_q(z)=\Delta f_0+\Delta f_1+\Delta f_{13}+\Delta f_2$, where

$$\Delta f_0=-T_0(\theta)\int_{d/2}^{z+r_0}\mathcal{H}(z'-z)dz', \tag{82}$$

$$\Delta f_1=-T_1(\theta)\frac{d\theta}{dz}\int_{d/2}^{z+r_0}(z'-z)\mathcal{H}(z'-z)dz', \tag{83}$$

$$\Delta f_{13}=-\tfrac{1}{2}T_1(\theta)\frac{d^2\theta}{dz^2}\int_{d/2}^{z+r_0}(z'-z)^2\mathcal{H}(z'-z)dz', \tag{84}$$

and

$$\Delta f_2=-\tfrac{1}{2}T_2(\theta)\left(\frac{d\theta}{dz}\right)^2\int_{d/2}^{z+r_0}(z'-z)^2\mathcal{H}(z'-z)dz'. \tag{85}$$

These are the direct equivalent of the bulk elastic terms in Eqs. (26)–(29). Note that, in contrast to the bulk case, Δf_0 and Δf_1 are now different from zero. According to the Gibbs theory of the interfacial phenomena, the surface free energy density F_s is obtained integrating Δf_q over the thin interfacial layer of thickness r_0 $(d/2-r_0<z<d/2)$. Δf_{13} and Δf_2 are of the same order of magnitude as the bulk terms f_{13} and f_2. Then, the integral over the thin interfacial layer of thickness r_0 vanishes in the limit $r_0\to 0$. Therefore, the surface free energy density due to the interfacial contributions is reduced to

$$F_s=F_0+F_1, \tag{86}$$

where

$$F_0=\int_{d/2-r_0}^{d/2}\Delta f_0 dz=-\int_{d/2-r_0}^{d/2}T_0(\theta)dz\int_{d/2}^{z+r_0}\mathcal{H}(z'-z)dz' \tag{87}$$

and

$$F_1=\int_{d/2-r_0}^{d/2}\Delta f_1 dz=-\int_{d/2-r_0}^{d/2}T_1(\theta)\frac{d\theta}{dz}dz \times\int_{d/2}^{z+r_0}(z'-z)\mathcal{H}(z'-z)dz', \tag{88}$$

where θ is a function of z. In the thin interfacial layer, we can approximate the $\theta(z)$ function with the truncated expansion

$$\theta(z)=\theta_s+\left(\frac{d\theta}{dz}\right)_{z=d/2}[z-(d/2)], \tag{89}$$

where θ_s is the value of function $\theta(z)$ at $z=d/2$. Correspondingly, functions $T_0(\theta)$ and $T_1(\theta)$ can be approximated by

$$T_0(\theta)=T_0(\theta_s)+\left(\frac{dT_0}{d\theta}\right)_{\theta=\theta_s}\left(\frac{d\theta}{dz}\right)_{z=d/2}[z-(d/2)],$$

$$\text{and}\quad T_1(\theta)=T_1(\theta_s). \tag{90}$$

It can be easily verified that higher expansion terms can be disregarded in Eqs. (89),(90) because they lead to surface energy contributions that vanish in the limit $r_0\to 0$. By substituting Eqs. (90) into Eq. (87), we finally obtain the expression of the surface free energy in terms of the surface director angle and its first derivative. We find $F_s=F_0^0+F_0^1+F_1^0$, where

$$F_0^0=-T_0(\theta_s)\int_{d/2-r_0}^{d/2}dz\int_{d/2}^{z+r_0}\mathcal{H}(z'-z)dz', \tag{91}$$

$$F_0^1=-\left(\frac{dT_0}{d\theta}\right)_{\theta=\theta_s}\left(\frac{d\theta}{dz}\right)_{z=d/2}\int_{d/2-r_0}^{d/2}[z-(d/2)]dz \times\int_{d/2}^{z+r_0}\mathcal{H}(z'-z)dz', \tag{92}$$

and

$$F_1^0=-T_1(\theta_s)\left(\frac{d\theta}{dz}\right)_{z=d/2}\int_{d/2-r_0}^{d/2}dz\int_{d/2}^{z+r_0}(z'-z) \times\mathcal{H}(z'-z)dz'. \tag{93}$$

F_0^0 in Eq. (91) represents the anchoring energy function that depends only on the surface director angle θ_s. F_0^1 in Eq. (92) is a linear elastic contribution coming from the homogeneous term in Eq. (87), whereas F_1^0 in Eq. (93) is another linear elastic term coming from F_1 in Eq. (88). Using the definition of $T_0(\theta)$ and $T_1(\theta)$ given in Eqs. (21),(22) we get $T_1(\theta)=(1/2)dT_0/d\theta$. Then, it is easy to show that $F_1^0=-F_0^1$, as recently predicted by means of general considerations based on the symmetry of the nematic phase [19]. Hence the only surviving contribution is the anchoring energy F_0^0. By taking into account for the definitions of functions $T_0(\theta)$ [Eq. (21)] and $\mathcal{H}(z'-z)$ [Eq. (10)], the integral in Eq. (91) leads to

$$F_s=F_0^0=\frac{ke^2\pi}{(24)^2r_0}(3-30\cos^2\theta_s+35\cos^4\theta_s). \tag{94}$$

This expression shows that the intrinsic anchoring energy of quadrupolar origin is characterized by an easy axis forming with the z axis the angle $\theta_s=\cos^{-1}\sqrt{3/7}$. The extrapolation length connected with this anchoring energy is of the order of $10^2\times r_0$. These results agree with those reported in Ref. [10].

In conclusion, the total surface energy due to the quadrupolar interaction is the sum of two contributions, which we have indicated by F_s and F_{sb}. The first one is a real interfacial term, having the form of a classical anchoring energy. It is given by Eq. (94). The second contribution is a surfacelike elastic term, which comes from the bulk energy density. It is given by Eq. (38).

VII. CONCLUSION

We have considered the influence of the quadrupolar interaction on the elastic properties of nematic liquid crystals. Due to the R^{-5} dependence of the quadrupolar interaction with respect to the distance of the interacting particles, a true elastic description is not possible. This means that in general the elastic constants depend on the size of the sample. An elastic description of this interaction is possible only for one-dimensional and planar deformations. In our paper we have considered nematic deformations of this kind in a sample of slab shape. Our analysis shows that the quadrupolar energy density is a nonlocal quantity, in the sense that it depends on the nematic deformation in a layer, not only at a point. The reduction of this nonlocal energy density to a local one has been performed by means of a power expansion in terms of the spatial derivatives of the tilt angle.

Our results show that in the bulk the quadrupolar energy density can be separated in a bulk and in a surfacelike contribution. The bulk contribution is characterized by an elastic constant $K_b(\theta)$ that depends on the nematic orientation. It is negative for nematic orientations close to the homeotropic or planar orientations, and positive for $\theta\sim\pi/4$. Its maximum

value is of the order of $K/10$, where K is the detectable Frank elastic constant. The angular dependence of the bulk quadrupolar elastic constant is different from the usual elastic constant. This difference is connected with the circumstance that the elastic expression of the quadrupolar interaction obtained in our paper is not simply a reduction of a three-dimensional expression. In fact such a general expression does not even exist. This different angular dependence takes into account a kind of compensation of the deformation ''in plane.'' It is similar to the one discussed for the influence of the flexoelectric effect on the elastic properties of nematic liquid crystals. The elastic constant of the surfacelike elastic term is of the same order of magnitude of the quadrupolar bulk elastic constant. We have also shown that the total surface energy due to the quadrupolar interaction contains two terms. The first term, having an elastic origin, is connected with a surfacelike term, coming from the bulk energy density. This contribution depends on the surface nematic tilt angle and on its gradient. The other term is due to the bulk interaction restricted by the surface, localized in a surface layer of molecular dimensions. It depends only on the surface nematic orientation and is characterized by a tilted easy axis and by an extrapolation length of the order of $10^2 \times r_0$, where r_0 is of the order of the molecular dimension.

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