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Elastic constants in a pseudomolecular approach for a mixed Maier-Saupe and Nehring-Saupe interaction law

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A pseudomolecular approach is employed to calculate the elastic constants of a nematic liquid crystal by assuming an interaction volume of ellipsoidal shape. We consider a special kind of mixed Maier-Saupe and Nehring-Saupe interaction law characterized by a mixing factor ϵ. To $\epsilon=0$ corresponds the Maier-Saupe law, whereas to the case $\epsilon=1$ corresponds the induced dipole-induced dipole interaction law. The dependence of the elastic constants on the eccentricity of the molecular volume shape and on the mixing factor is investigated by means of a numerical analysis. We show that, for particular values of the eccentricity, the K_{11} (splay) and K_{33} (bend) elastic constants become negative for some values of the mixing factor. Moreover, the nonmonotonic behavior of the splay-bend elastic constant with respect to the mixing factor, already reported in a spherical approximation for the interaction volume, is also observed. This result reinforces the indication that the subsurface deformations, if any, are not only due to the splay-bend term. [S1063-651X(98)00509-1]

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I. INTRODUCTION

The pseudomolecular approach to calculate the bulk elastic constants in nematic liquid crystals (NLC) is an approximate technique to determine the macroscopic properties of the system from the intermolecular interaction giving rise to the nematic phase [1]. The basic assumptions of the approach can be summarized as follows [2–4].

Let $U(\vec{a},\vec{a}\,',\vec{r})$ be the intermolecular interaction energy between the molecules placed in $\vec{R}$ and $\vec{R}\,'$, such that $\vec{r}=\vec{R}\,'-\vec{R}$, and whose long molecular axes are, respectively, denoted by $\vec{a}$ and $\vec{a}\,'$. This interaction energy is supposed to be different from zero in a region defined by $R_0\leqslant R\leqslant R_N$, where the lower cutoff, R_0, is of the order of the molecular dimension whereas the upper cutoff, R_N, defines the maximum dimension of the interaction volume. It is determined by comparing the $U(\vec{a},\vec{a}\,',\vec{r}_N)$ with the thermal energy K_BT, where K_B is the Boltzmann constant and T is the absolute temperature. Anyway, R_N is of the order of a few molecular dimensions, and the model is expected to be insensible to R_N, in such a way that, at the end of the calculation, the limit $R_N\to\infty$ could be performed. Furthermore, one assumes perfect nematic order. This means that the scalar order parameter of the nematic phase $S=1$, which is equivalent to assuming that the orientational entropy of the system is zero. In this hypothesis $\vec{a}\equiv\vec{n}$. The interaction energy between two small volume elements dv and dv', containing $dN=\rho(\vec{R})dv$ and $dN'=\rho(\vec{R}\,')dv'$ molecules, respectively, in $\vec{R}$ and $\vec{R}\,'$ is given by

$$\begin{aligned} d^2\mathcal{U}(\vec{n},\vec{n}\,',\vec{r}) &= U(\vec{n},\vec{n}\,',\vec{r})\rho(\vec{R})dv\,\rho(\vec{R}\,')dv' \\ &= g(\vec{n},\vec{n}\,',\vec{r})dv\,dv', \end{aligned} \tag{1}$$

where $\rho(\vec{R})=\rho(\vec{R}\,')=\rho$ is the density which will be supposed constant. Hence $g(\vec{n},\vec{n}\,',\vec{r})=\rho^2U(\vec{n},\vec{n}\,',\vec{r})$.

In the elastic approximation, it is supposed that $\vec{n}$ changes slowly with $\vec{R}$. Consequently we have $|\vec{n}-\vec{n}\,'|=|\delta\vec{n}|\ll 1$. Therefore it is possible to expand $g(\vec{n},\vec{n}+\delta\vec{n},\vec{r})$ in power series of $\delta\vec{n}$. It is assumed also that this series has uniform convergence, which is not always the case. In fact, this is indicative that the pseudomolecular method has severe limitations in its applicability when this condition is not fulfilled [4]. In the second order one obtains

$$g(\vec{n},\vec{n}\,',\vec{r})=g(\vec{n},\vec{n},\vec{r})+q_i\delta n_i+\frac{1}{2}q_{ij}\delta n_i\delta n_j+\cdots, \tag{2}$$

where

$$q_i=\left(\frac{\partial g}{\partial n_i'}\right)_{\vec{n}\,'=\vec{n}} \quad\text{and}\quad q_{ij}=\left(\frac{\partial^2 g}{\partial n_i'\partial n_j'}\right)_{\vec{n}\,'=\vec{n}}, \tag{3}$$

where the derivatives are evaluated on the reference state and the summation convention is assumed henceforth.

To obtain the elastic energy density it is necessary to expand $\delta n_i=\delta n_i(\vec{R},\vec{R}\,')$ in power series of x_i, which are the Cartesian components of the $\vec{r}$. In the second order one obtains

$$\delta n_i=n_{i,j}x_j+\frac{1}{2}n_{i,jk}x_jx_k+\cdots, \tag{4}$$

with the derivatives evaluated in $\vec{R}$. Substitution of Eq. (4) into Eq. (3) yields

$$\begin{aligned} g(\vec{n},\vec{n}\,',\vec{r}) &= g(\vec{n},\vec{n},\vec{r})+q_in_{i,k}x_k \\ &\quad +\frac{1}{2}(q_in_{i,kl}+q_{ij}n_{i,k}n_{j,l})x_kx_l. \end{aligned} \tag{5}$$

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Finally, the last assumption of the method is the mean field approximation, which implies a definition of the total energy of the NLC sample as

$$F=\frac{1}{2}\int_{v}\int_{v'}g(\vec{n},\vec{n}',\vec{r})\,dv\,dv'=\int_{v}f\,dv, \tag{6}$$

where the elastic energy density is given by

$$f=\frac{1}{2}\int_{v'}g(\vec{n},\vec{n}',\vec{r})\,dv'. \tag{7}$$

After the substitution of Eq. (5) into Eq. (7) one obtains

$$f=f_0+L_{ik}n_{i,k}+N_{ijk}n_{i,jk}+M_{ijkm}n_{i,k}n_{j,m}, \tag{8}$$

where we have introduced the elastic tensors

$$L_{ik}=\frac{1}{2}\int_{v'}q_iu_kr\,dv', \tag{9}$$

$$N_{ijk}=\frac{1}{4}\int_{v'}q_iu_ju_kr^2\,dv', \tag{10}$$

and

$$M_{ijkm}=\frac{1}{4}\int_{v'}q_{ij}u_ku_mr^2\,dv'. \tag{11}$$

Furthermore, the uniform part of the elastic energy density, i.e., the elastic energy density of the reference state, is given by

$$f_0=\frac{1}{2}\int_{v'}g(\vec{n},\vec{n},\vec{r})\,dv'. \tag{12}$$

In the above expressions, $\vec{u}=\vec{r}/r$, and hence $x_k=u_kr$. The integrations are performed over the interaction volume. For simplicity, in this kind of calculation it is usual to consider a spherical volume. However, the molecules are rodlike and R_0 is not well defined. For this reason it is also convenient to consider another kind of interaction volume such as, for instance, the ellipsoidal one [5].

II. ELASTIC CONSTANTS AND INTERACTION LAW

In this paper we will consider an interaction volume of ellipsoidal shape, i.e., we suppose that $g(\vec{n},\vec{n}',\vec{r})$ is different from zero in the region limited by two similar ellipsoids, whose inner part coincides with the molecular volume, and the outer part is defined by the long-range part of the intermolecular interaction. For simplicity, the two ellipsoids are supposed to be similar, having the same eccentricity. They are also supposed to be ellipsoids of revolution around $\vec{n}$. If the semiaxes are indicated by a and b, the eccentricity is defined as

$$e=1-(a_o/b_o)^2=1-(a/b)^2, \tag{13}$$

where the subscript o indicates the inner (molecular) volume and a,b refer to the outer volume. One observes that the dimensions of the outer part do not play a crucial role in the elastic constants we are calculating. In a reference frame in which the equation of the ellipsoid is given by

$$\frac{x^2+y^2}{a^2}+\frac{z^2}{b^2}=1, \tag{14}$$

the director $\vec{n}$ coincides with the long molecular axis. In spherical coordinates,

$$x=r\sin\theta\cos\phi,\quad y=r\sin\theta\sin\phi,\quad\text{and}\quad z=r\cos\theta, \tag{15}$$

and with the help of Eq. (13), we can rewrite Eq. (14) in the form

$$r_0(\theta)=R_0=\frac{a_o}{\sqrt{1-e\,\cos^2\theta}}\quad\text{and}\quad r_N(\theta)=R_N=\frac{a}{\sqrt{1-e\,\cos^2\theta}}, \tag{16}$$

respectively, for the inner and outer ellipsoids.

Let us focus our attention now on the interaction law. Among the intermolecular interaction energies giving rise to the NLC phase, the simplest one is the Maier-Saupe law [6] written as

$$g_{\rm MS}=\rho^2U_{\rm MS}=-\frac{C_{\rm MS}}{r^6}(\vec{a}\cdot\vec{a}')^2=-\frac{C_{\rm MS}}{r^6}(\vec{n}\cdot\vec{n}')^2, \tag{17}$$

where $C_{\rm MS}=\rho^2C$ is a positive constant, and we are assuming perfect nematic order. For this kind of interaction, a detailed analysis of surface and bulk elastic properties has been performed in a pseudomolecular approach for the ellipsoidal approximation [5]. Another intermolecular interaction takes into account the fact that the molecules forming NLC phases are polarizable. Therefore the induced dipoles play a role in the stability of the NLC phase. This fact is expressed in terms of the Nehring-Saupe interaction [1], which, in the hypotheses we are considering, is written as

$$g_{\rm NS}=\rho^2U_{\rm NS}=-\frac{C_{\rm NS}}{r^6}[\vec{n}\cdot\vec{n}'-3(\vec{u}\cdot\vec{u}')(\vec{u}\cdot\vec{n})]^2, \tag{18}$$

with $C_{\rm NS}=\rho^2\langle p^2(t)\rangle/2$ a positive constant and $p(t)$ the dipolar moment of the molecules. For this interaction, the pseudomolecular approach has been applied for an interaction volume of spherical shape to determine the bulk [2,3] and surface elastic properties [7]. Now, we will consider an intermolecular interaction in the mixed form [8,9]

$$g(\vec{n},\vec{n}',\vec{r})=-\frac{C}{r^6}e^{-r/\lambda}[\vec{n}\cdot\vec{n}'-3\epsilon(\vec{n}\cdot\vec{u})(\vec{n}'\cdot\vec{u})]^2, \tag{19}$$

where we have introduced a mixing parameter ϵ such that for $\epsilon=0$, $g=g_{\rm MS}$ whereas for $\epsilon=1$, $g=g_{\rm NS}$. In Eq. (19) we have also introduced a screening length λ to take into account the short-range intermolecular forces. Note that for $\lambda\to\infty$ the law is a long-range one. However, a theory of elasticity may be formulated only for intermolecular forces of short interaction range. This means that the interaction is relevant in a region very small with respect to the scale over which the spatial variation of the macroscopic order takes place. Consequently, λ is expected to be of the order of a few molecular sizes. For a material whose intermolecular energy has a quadrupolar symmetry λ plays a crucial role. It is possible to show that for $\lambda\rightarrow\infty$ all the elastic constants vanish, whereas for the case of finite λ, $K_{11}=K_{33}$ is negative [13]. However, for the interaction law (19) the results are not affected in a significant manner by changing the values of λ, as we will discuss later.

In order to calculate the elastic constants, let us evaluate q_i and q_{ij}, as given by Eq. (3). We easily obtain

$$q_i=-2J(r)[1-3\epsilon(\vec{n}\cdot\vec{u})^2][n_i-3\epsilon u_i(\vec{n}\cdot\vec{u})], \tag{20}$$

$$q_{ij}=-2J(r)[n_i-3\epsilon u_i(\vec{n}\cdot\vec{u})][n_j-3\epsilon u_j(\vec{n}\cdot\vec{u})],$$

where

$$J(r)=\frac{C}{r^6}e^{-r/\lambda}. \tag{21}$$

It is easy to show that the term in Eq. (8) connected to the second-rank tensor given by Eq. (9) does not contribute to the elastic energy density, as expected, because it is connected to the linear term in the deformation tensor, and, in the bulk, the ground state is the undeformed one. One expects that this tensor exists in the bulk only for cholesteric liquid crystals. For what concerns the third-rank tensor we have

$$N_{ijk}=\frac{1}{4}\int_{v'}r^2J(r)[1-3\epsilon(\vec{n}\cdot\vec{u})^2]$$

$$\times[n_i-3\epsilon u_i(\vec{n}\cdot\vec{u})]u_ju_kdv'=n_iB_{jk}+A_{ijk}, \tag{22}$$

where

$$B_{jk}=-\frac{1}{2}\int_{v'}r^2J(r)[1-3\epsilon(\vec{n}\cdot\vec{u})^2]u_ju_kdv, \tag{23}$$

and

$$A_{ijk}=\frac{3}{2}\epsilon\int_{v'}r^2J(r)[1-3\epsilon(\vec{n}\cdot\vec{u})^2](\vec{n}\cdot\vec{u})u_iu_ju_kdv'. \tag{24}$$

Finally, the fourth-rank tensor is rewritten as

$$M_{ijkm}=-\frac{1}{2}\int_{v'}r^2J(r)[n_i-3\epsilon u_i(\vec{n}\cdot\vec{u})]$$

$$\times[n_j-3\epsilon u_j(\vec{n}\cdot\vec{u})]u_ku_mdv'. \tag{25}$$

Consequently, the elastic energy density given by Eq. (8) is conveniently rewritten in the form

$$f=A_{ijk}n_{i,jk}+B_{jk}n_in_{i,jk}+M_{ijkm}n_{i,k}n_{j,m}. \tag{26}$$

Before evaluating the integrations over the interaction volume, it is convenient to decompose the tensors **A**, **B**, and **M** in terms of the unit tensor $\boldsymbol{\delta}$ and $\vec{n}$, which are the elements of symmetry characterizing the NLC phase. We have

$$A_{ijk}=A_1n_in_jn_k+A_2(n_i\delta_{jk}+n_j\delta_{ik}+n_k\delta_{ij}), \tag{27}$$

$$B_{ij}=B_1n_in_j+B_2\delta_{ij}, \tag{28}$$

and

$$M_{ijkm}=M_{kmij}=M_1n_in_jn_kn_m$$

$$+M_3(\delta_{km}\delta_{ij}+\delta_{ki}\delta_{mj}+\delta_{kj}\delta_{mi})$$

$$+M_2(n_kn_m\delta_{ij}+n_kn_i\delta_{mj}+n_kn_j\delta_{mi}$$

$$+n_mn_j\delta_{ki}+n_mn_i\delta_{kj}). \tag{29}$$

From Eq. (27) one easily deduces that

$$A_1=\frac{1}{2}(5n_in_kn_jA_{ijk}-3n_iA_{ijj}),$$

$$A_2=\frac{1}{2}(n_iA_{ijj}-n_in_kn_jA_{ijk}), \tag{30}$$

whereas from Eq. (28), by operating in the same way, one obtains

$$B_1=\frac{1}{2}(3n_in_jB_{ij}-B_{ii}),$$

$$B_2=\frac{1}{2}(B_{ii}-n_in_jB_{ij}). \tag{31}$$

Finally, from Eq. (29) we obtain

$$M_2=\frac{1}{8}(6n_in_jM_{ijkk}-5n_kn_mn_in_jM_{ijkm}-M_{kkii}),$$

$$M_3=\frac{1}{8}(n_kn_mn_in_jM_{ijkm}+M_{iikk}-2n_in_jM_{ijkk}). \tag{32}$$

In order to write the elastic energy density one has to calculate the terms

$$A_{ijk}n_{i,jk}=-3A_2(\mathrm{div}\ \vec{n})^2-A_2(\vec{n}\cdot\mathrm{curl}\,\vec{n})^2$$

$$-(A_1+A_2)(\vec{n}\times\mathrm{curl}\ \vec{n})^2$$

$$+A_2\mathrm{div}(\vec{n}\ \mathrm{div}\ \vec{n}+\vec{n}\times\mathrm{curl}\ \vec{n})+2A_2\mathrm{div}(\vec{n}\ \mathrm{div}\ \vec{n}),$$

$$B_{km}n_in_{i,km}=-B_2(\mathrm{div}\ \vec{n})^2-B_2(\vec{n}\cdot\mathrm{curl}\ \vec{n})2$$

$$-(B_1+B_2)(\vec{n}\times\mathrm{curl}\ \vec{n})^2$$

$$+B_2\mathrm{div}(\vec{n}\ \mathrm{div}\ \vec{n}+\vec{n}\times\mathrm{curl}\ \vec{n}), \tag{33}$$

$$M_{kmij}n_{i,k}n_{j,m}=3M_3(\mathrm{div}\ \vec{n})^2-M_3(\vec{n}\cdot\mathrm{curl}\ \vec{n})2$$

$$-(M_2+M_3)(\vec{n}\times\mathrm{curl}\ \vec{n})^2$$

$$-2M_3\mathrm{div}(\vec{n}\ \mathrm{div}\ \vec{n}+\vec{n}\times\mathrm{curl}\ \vec{n}),$$

To rewrite the elastic energy density given by Eq. (26) we add the expressions appearing in Eq. (33) to obtain

$$f=\frac{1}{2}[K_{11}(\mathrm{div}\,\vec{n})^2+K_{22}(\vec{n}\cdot\mathrm{curl}\,\vec{n})2$$
$$+K_{33}(\vec{n}\times\mathrm{curl}\,\vec{n})^2+K_{13}\mathrm{div}(\vec{n}\,\mathrm{div}\,\vec{n})$$
$$-(K_{22}+K_{24})\mathrm{div}(\vec{n}\,\mathrm{div}\,\vec{n}+\vec{n}\times\mathrm{curl}\,\vec{n})], \quad (34)$$

where

$$K_{11}=2(-3A_2-2B_2+3M_3),$$
$$K_{22}=2(-A_2-B_2+M_3),$$
$$K_{33}=2(-A_1-A_2-B_1-B_2+M_2+M_3), \quad (35)$$
$$K_{13}=2A_2 \text{ and } K_{22}+K_{24}=-(A_2+B_2-2M_3).$$

This completes the tool to calculate the elastic constants in the pseudomolecular approach we are considering. It is now sufficient to perform the integrations indicated in Eqs. (22)–(25) over the interaction volume of ellipsoidal shape.

III. NUMERICAL RESULTS

Let us now present the results of the numerical calculations employed to study the dependence of the elastic constants on the eccentricity and on the mixing factor ϵ. To perform the integrations to evaluate the elements of the elastic tensors in Eqs. (22)–(25) we choose the z axis of the coordinate system along $\vec{n}$. In spherical coordinates this implies to $\vec{n}\cdot\vec{u}=\cos\theta$ and

$$u_1=\sin\theta\cos\phi, \quad u_2=\sin\theta\sin\phi, \quad u_3=\cos\theta. \quad (36)$$

The following integral is relevant:

$$I(e,\theta)=\int_{r_0(\theta)}^{r_N(\theta)}J(r)r^4dr$$
$$=-C\int_{r_0(\theta)}^{r_N(\theta)}\frac{e^{-r/\lambda}}{r^2}dr$$
$$=-\frac{e^{-r_0(\theta)/\lambda}}{r_0(\theta)}+\frac{e^{-r_N(\theta)/\lambda}}{r_N(\theta)}$$
$$-\frac{1}{\lambda}\left[\mathrm{Ei}\left(\frac{-r_0(\theta)}{\lambda}\right)-\mathrm{Ei}\left(\frac{-r_N(\theta)}{\lambda}\right)\right], \quad (37)$$

where Ei(x) is the exponential integral [10]. The remaining integrations can be numerically performed and have the general form

$$B_{jk}=-\frac{C}{2}\int_0^{2\pi}\int_0^{\pi}I(e,\theta)[1-3\epsilon\cos^2\theta]u_ju_kd\theta d\phi, \quad (38)$$

$$A_{ijk}=\frac{3C}{2}\epsilon\int_0^{2\pi}\int_0^{\pi}I(e,\theta)[1-3\epsilon\cos^2\theta]\cos\theta u_iu_ju_kd\theta d\phi, \quad (39)$$

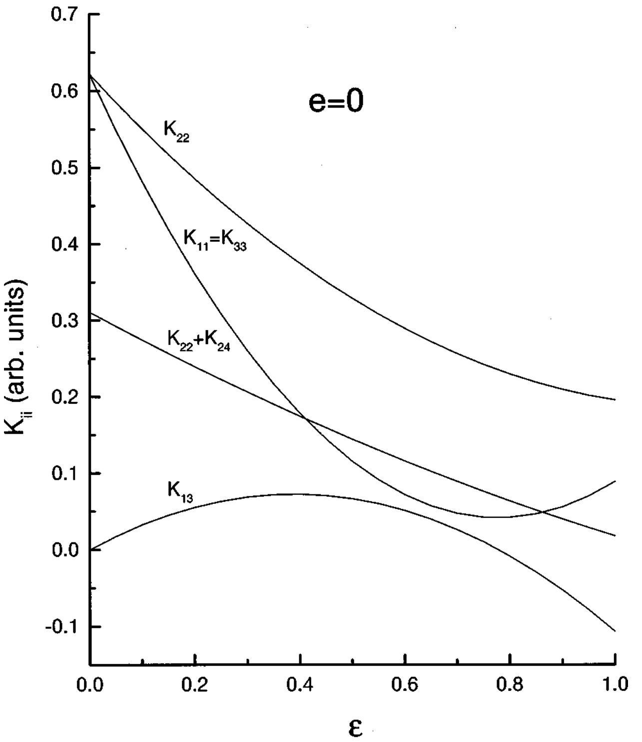

FIG. 1. Elastic constants of a nematic liquid crystal vs the mixing parameter ϵ for $e=0$ (spherical approximation). The splay-bend elastic constant $K_{13}=0$ for $\epsilon=7/9$.

and

$$M_{ijkm}=-\frac{C}{2}\int_0^{2\pi}\int_0^{\pi}I(e,\theta)[n_i-3\epsilon\cos\theta u_i]$$
$$\times[n_j-3\epsilon\cos\theta u_j]u_ku_md\theta d\phi. \quad (40)$$

From the above expressions it is possible to calculate the coefficients A_1, A_2, B_1, B_2, M_2, and M_3. Consequently, from the expressions (35) we obtain the trend of the elastic constants in the general form $K_{ij}(e,\epsilon)$ in units of the positive constant C.

In Fig. 1 the behavior of K_{11}, K_{22} and K_{33}, K_{13} and $K_{22}+K_{24}$ is shown as a function of the mixing factor ϵ for the case $e=0$ (spherical approximation). Several features of this figure deserve some comments. First of all, we observe that when $\epsilon=0$, which corresponds to the Maier-Saupe law, in the spherical approximation for the interaction volume, $K_{11}=K_{22}=K_{33}$ and $K_{13}=0$, as expected. On the other hand, for $e=0$ but for $\epsilon=1$, which corresponds to the Nehring-Saupe interaction law in the spherical approximation, we obtain the well-known result that $K_{11}=K_{33}<K_{22}$. Furthermore, for this kind of interaction law $K_{13}\neq 0$ [3]. Notice that the trend of K_{13} as a function of e is nonmonotonic. In fact, K_{13} starts from zero (for $\epsilon=0$, i.e., Maier-Saupe interaction law) and becomes zero again for $\epsilon=7/9$ [4].

However, for $e\neq 0$ the three bulk elastic constants can become distinct. One should consider that for typical rodlike NLC molecules, $e\approx 0.9$–0.95 [11]. However the effective molecular eccentricity is different from the geometrical one. This is probably due to the presence of a hard core in which the origin of the intermolecular interaction is localized. Ac-

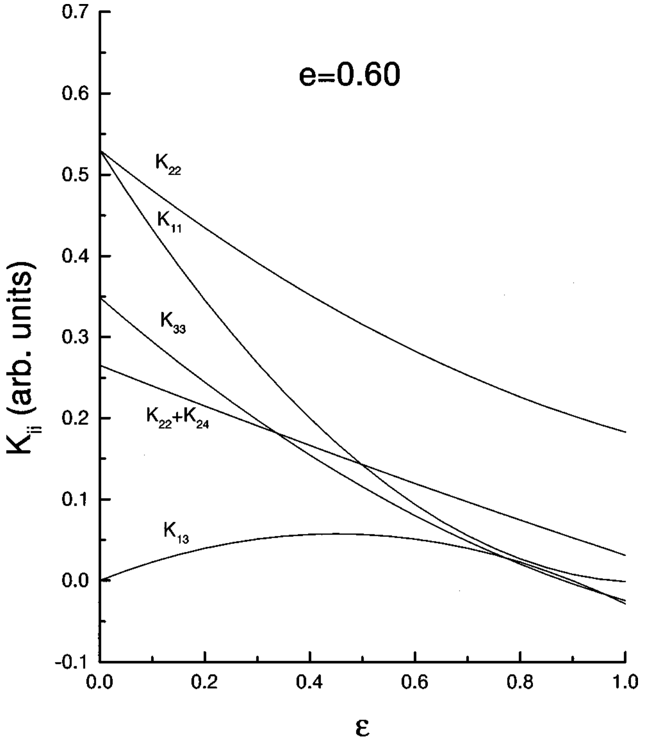

FIG. 2. The same as in Fig. 1 but for $e=0.60$. The bulk elastic constants of splay K_{11} and bend K_{33} become negative for $e\approx 0.9$. The nonmonotonic behavior of K_{13} is still present for this representative eccentricity.

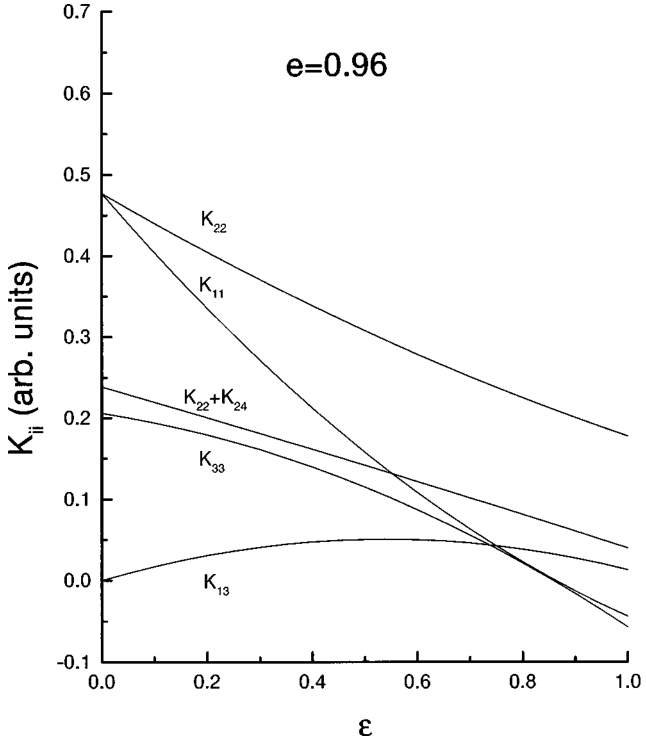

FIG. 3. The same as in Fig. 1 for $e=0.96$. This value of the eccentricity corresponds to a relation $b=5a$ between the major and the minor axes of the ellipsoid representing the molecular volume. The bulk elastic constants K_{11} and K_{33} can become negative as in the preceding case of Fig. 2.

cording to this point of view the soft tails [11] of the nematic molecules do not contribute to the interactions giving rise to the mesophase. Further, in the following analysis one considers as representative eccentricities for the calculations, namely, $e=0.60$ (Fig. 2), which is closer to these real systems, and $e=0.96$ (Fig. 3), which corresponds to a relation $b=5a$, i.e., a very long molecule.

In Fig. 2 we observe again a known limit: when $\epsilon=0$ we observe that $K_{11}=K_{22}>K_{33}$ [5]. There are, however, three new features arising with the variation of ϵ: K_{13} again presents a nonmonotonic behavior and becomes negative for $\epsilon\approx 0.9$. Note that, in this case, for $\epsilon=1$, i.e., the Nehring-Saupe interaction, K_{13} is still negative. The more drastic behavior, however, regards the bulk elastic constants K_{11} and K_{33} which become negative for similar values of ϵ. Since the elastic energy density has to be a positive definite quadratic form, this fact implies that for some particular values of the eccentricity (which is responsible for the ''geometrical anisotropy'') and of the mixing factor (which is, as stressed before, responsible for the anisotropic part of the intermolecular interaction energy) the nematic phase is not favored. Then, the molecules, for an interaction law of this kind, have no tendency to align along a common direction, as is required to form the NLC phase. This situation has been found in this context when the considered intermolecular interaction law is the quadrupolar one [13]. Finally, one observes that for a ''balanced'' mixing of the two interaction laws, like, for instance, for $\epsilon=0.5$, the three bulk elastic constants are different. This is a welcome result since from the experimental point of view the common situation is the one in which $K_{ii}, i=1,2,3$ are distinct [12].

In Fig. 3 we again observe that the two bulk elastic constants become negative for $\epsilon\approx 0.9$. However, the K_{13} is never negative for very long molecules. In all these figures the trend of $K_{22}+K_{24}$ is the expected one: it is an approximated linearly decreasing function of ϵ.

Another significant situation is depicted in Fig. 4 which exhibits the trend of the elastic constants vs the eccentricity of the interaction volume, i.e., it corresponds to the case of Nehring-Saupe interaction in the ellipsoidal approximation. We still have that when $e=0$ the well-known results for the spherical approximation are recovered [3]. But two elastic constants K_{11} and K_{33} become negative. This result indicates that the increasing in the anisotropy of the molecular volume works as a destabilizing effect for the nematic phase when the interaction is of the induced dipole-induced dipole type.

The general behavior we have presented above refers to the case $\lambda\simeq a_0$, where a_0 is a typical molecular dimension [see Eq. (13)]. But the global picture is not drastically affected by changing λ. Let us analyze, in particular, the limit $\lambda\rightarrow\infty$. The behavior of the elastic constants with respect to ϵ is basically the same as the one for λ finite in the case depicted in Fig. 1 (i.e., the spherical approximation). For the case of the Nehring-Saupe law $(\epsilon=1)$, depicted in Fig. 4, there are no qualitative changes in the behavior of the elastic constants and the bulk constants K_{11} and K_{33} still become negative, but now for $e\simeq 0.7$. For $e=0.96$, in reference to Fig. 3, these two bulk constants become negative for $\epsilon\simeq 0.8$ but also K_{13} becomes negative. The most significant changes refer to the case $e=0.6$. While in the case of Fig. 2 K_{11} and K_{33} become negative, in the limit of $\lambda\rightarrow\infty$ they are

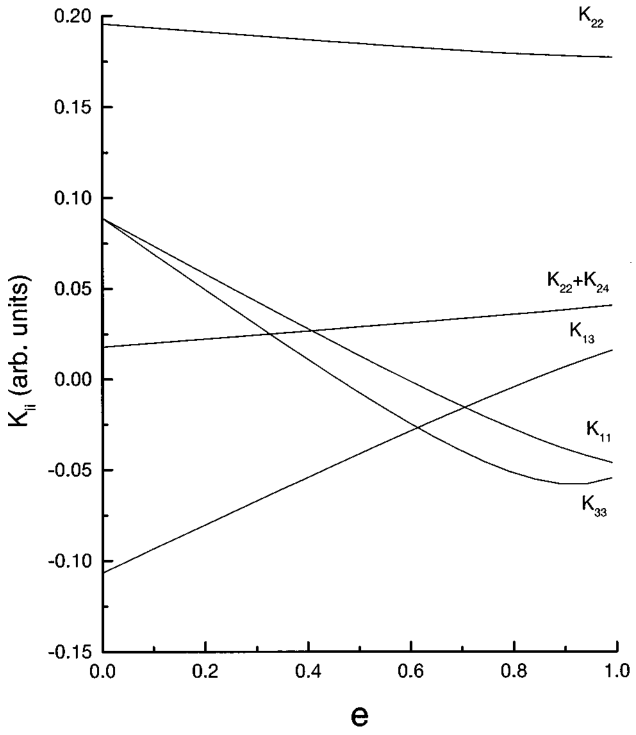

FIG. 4. Elastic constants of a NLC vs the eccentricity e for $\epsilon = 1.0$ (Nehring-Saupe interaction law). Note that also for this situation the bulk elastic constants of splay and bend become negative.

always positive for any value of ϵ. Only K_{13} becomes negative for $e \simeq 0.8$. Finally, let us stress that K_{22} and $K_{22}+K_{24}$ are not significantly changed in this limit. These results indicate that for this kind of interaction law, differently from the case of quadrupolar interaction [13], the screening of the potential represented by λ finite is not crucial. This is not surprising since the interaction law we are analyzing decays as r^{-6}.

IV. CONCLUDING REMARKS

We have shown that new features arise in the behavior of the elastic constants of a NLC when an anisotropic interaction volume is introduced. The calculations were performed by considering a special kind of mixed interaction law with a parameter ϵ accounting for the anisotropic part of the interaction law. Therefore this kind of analysis deals with two origins for the anisotropy of the system: one coming from the natural anisotropic molecular form and the other one from the anisotropy in the interaction. The analysis reveals the possibility that for the bulk (1) the elastic constants can become negative and in this sense the nematic phase is not favored; (2) it is possible to obtain the theoretical result that the elastic constants can be different for a representative value of the molecular anisotropy, which is close to the experimental situation.

For what concerns the behavior of the splay-bend elastic constant, K_{13}, one observes again that for some value of ϵ this elastic constant can be zero. Then, the origin of the subsurface deformation, if any, must be sought in another source. It is not due only to the presence of this term. As stressed before, this result was already obtained in the spherical approximation, but here it is reinforced for the ellipsoidal approximation.

The calculations were numerically performed and, as expected, the limit $R_N \to \infty$ can be performed at the end of the calculations. The outer dimension of the interaction volume does not affect the central results.

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