PHYSICAL REVIEW E VOLUME 56, NUMBER 5 NOVEMBER 1997

Pseudomolecular models for nematic liquid crystals

G. Barbero* and L. R. Evangelista
Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, Paraná, Brazil

(Received 17 July 1996)

The limits of the pseudomolecular approach to evaluate the elastic properties of nematic liquid crystals are critically analyzed. We discuss the importance of the uniformly convergent series entering into this description. If these series are not uniformly convergent, the elastic constants evaluated in this manner are meaningless. A special kind of mixing of Maier-Saupe and Nehring-Saupe interaction laws is analyzed. We show that the splay-bend elastic constant has a nonmonotonic behavior with respect to the mixing factor. This result indicates that the subsurface deformations, if any, are not only due to the splay-bend term. [S1063-651X(97)07111-0]

PACS number(s): 61.30.Gd, 61.30.Cz

It is well known that, in the harmonic approximation, the elastic free-energy density of a nematic liquid crystal (NLC) is given by the Frank expression [1]. The bulk elastic properties are described by the K_{11}, K_{22}, K_{33}, and K_{24} elastic constants. They are phenomenological parameters, introduced by taking into account of the symmetry of the nematic phase [2]. The manner to introduce these elastic constants is to expand the elastic energy density f in terms of the first spatial derivatives of the nematic director $n_{i,j}=\partial n_i/\partial x_j$. Hence, starting from $f=f(n_i,n_{i,j})$ in second order one obtains

$$f=f_0+L_{ij}n_{i,j}+\tfrac{1}{2}K_{ijkl}n_{i,j}n_{k,l}, \qquad (1)$$

where f_0 is the elastic energy density of the undeformed state. The elastic tensors of elements L_{ij} and K_{ijkl} are decomposed in terms of the elements of symmetry of the nematic phase [2].

The first attempts to connect the elastic constant to the intermolecular interaction responsible for the nematic phase have been done by Nehring and Saupe [3] by means of a simple phenomenological model, and the basic simplifying hipotheses are presented in the following.

Let $e(\vec{a},\vec{a}\,';\vec{r})$ be the intermolecular interaction between the molecules whose orientations are $\vec{a}$ and $\vec{a}\,'$, placed in $\vec{R}$ and in $\vec{R}\,'=\vec{R}+\vec{r}$. The interaction energy is supposed to be different from zero for $R_i\leqslant r\leqslant R_o$, where the lower cutoff R_i is of the order of the molecular dimensions, and the upper cutoff R_o can be chosen by comparing $e(\vec{a},\vec{a}\,',R_o)$ with the thermal agitation energy k_BT, where k_B is the Boltzmann constant and T the absolute temperature. However, R_o is of the order of a few molecular dimensions, and the model is expected to be rather insensible to R_o. Thus, at the end of the calculation, the limit $R_o\rightarrow\infty$ can be performed. Nehring and Saupe assume furthermore perfect nematic order. Hence $\vec{a}$ coincides with $\vec{n}$. In this framework the interaction energy between two small volume elements $d\tau$ and $d\tau'$ in $\vec{R}$ and $\vec{R}\,'$ is

$$d^2U(\vec{n},\vec{n}\,';\vec{r})=e(\vec{n},\vec{n}\,';\vec{r})dN\ dN'. \qquad (2)$$

In Eq. (2), $dN=\rho(\vec{R})d\tau$ and $dN'=\rho(\vec{R}\,')d\tau'$ are the number of molecules contained in $d\tau$ and $d\tau'$, respectively and $e(\vec{n},\vec{n}\,';\vec{r})$ the molecular interaction energy introduced above, in the perfect nematic order approximation. By supposing a constant density, i.e., $\rho(\vec{R})=\rho(\vec{R}\,')=\rho$, Eq. (2) is reduced to

$$d^2U(\vec{n},\vec{n}\,';\vec{r})=g(\vec{n},\vec{n}\,';\vec{r})d\tau\ d\tau', \qquad (3)$$

where $g(\vec{n},\vec{n}\,';\vec{r})=\rho^2e(\vec{n},\vec{n}\,',\vec{r})$.

In the elastic approximation, $\vec{n}$ changes slowly with r. This means that in Eq. (3), $|\vec{n}\,'-\vec{n}|=|\delta\vec{n}|\ll 1$ over the interaction range of the molecular forces. Hence $g(\vec{n},\vec{n}\,';\vec{r})=g(\vec{n},\vec{n}+\delta\vec{n};\vec{r})$ can be expanded in a power series of $\delta\vec{n}$. At the second order in δn_i we obtain

$$g(\vec{n},\vec{n}\,';\vec{r})=g(\vec{n},\vec{n};\vec{r})+q_i\delta n_i+\tfrac{1}{2}q_{ij}\delta n_i\delta n_j+\cdots, \qquad (4)$$

where

$$q_i=\left(\frac{\partial g}{\partial n_i'}\right)_{\vec{n}\,'=\vec{n}} \quad \text{and} \quad q_{ij}=\left(\frac{\partial^2 g}{\partial n_i' n_j'}\right)_{\vec{n}\,'=\vec{n}} \qquad (5)$$

are defined in terms of the intermolecular interaction. The derivatives appearing in Eq. (5) are evaluated on the undeformed state. In Eq. (4), $g(\vec{n},\vec{n};\vec{r})$ is the interaction characterizing the homogeneous state, where $\vec{n}$ is position independent.

In order to obtain the elastic energy density, it is then necessary to expand $\delta n_i=\delta n_i(\vec{R},\vec{r})$ in power series of x_i, the Cartesian components of the vector representing the relative position of $\vec{n}\,'$ with respect to $\vec{n}$. We have, at the second order in x_i,

$$\delta n_i=n_{i,j}x_j+\tfrac{1}{2}n_{i,jk}x_jx_k+\cdots, \qquad (6)$$

where the derivatives are evaluated in $\vec{R}$. By substituting Eq. (6) into Eq. (4), and rearranging the terms, we obtain, at the second order in x_i,

---

*Permanent address: Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi 24, 10129 Turin, Italy.

© 1997 The American Physical Society

$$g(\vec{n},\vec{n}';\vec{r})=g(\vec{n},\vec{n};\vec{r})+q_i n_{i,k}x_k + \tfrac{1}{2}\,(q_i n_{i,kl}+q_{ij}n_{i,k}n_{j,l})x_k x_l . \tag{7}$$

In the mean-field approximation the total energy of the NLC is given by [4]

$$\mathscr{F}=\tfrac{1}{2}\int\int\int_{\tau}\int\int\int_{\tau'} g(\vec{n},\vec{n}';\vec{r})d\tau\, d\tau' . \tag{8}$$

The elastic energy density is then, as follows from Eq. (8),

$$f=\tfrac{1}{2}\int\int\int_{\tau'} g(\vec{n},\vec{n}';\vec{r})d\tau' . \tag{9}$$

Substitution of expansion (7) into Eq. (9) yields

$$f=f_0+L_{ik}n_{i,k}+L_{ikn}n_{i,kn}+L_{ijkn}n_{i,k}n_{j,n} , \tag{10}$$

where

$$f_0=\tfrac{1}{2}\int\int\int_{\tau'} g(\vec{n},\vec{n};\vec{r})d\tau' \tag{11}$$

is the elastic energy density of the undeformed state, whereas the elastic tensors of elements L_{ik}, L_{ikn}, and L_{ijkn} are given by

$$L_{ik}=\tfrac{1}{2}\int\int\int_{\tau'} q_i u_k r\, d\tau' ,$$

$$L_{ikn}=\tfrac{1}{4}\int\int\int_{\tau'} q_i u_k u_m r^2 d\tau' ,$$

$$L_{ijkn}=\frac{1}{4}\int\int\int_{\tau'} q_{ij} u_k u_m r^2 d\tau' , \tag{12}$$

with $\vec{u}=\vec{r}/r$, and hence $x_k=u_k r$. The term linear in the deformation tensor $n_{i,j}$ is expected to vanish in the bulk, where the ground state is the undeformed one. Only for cholesteric liquid crystals in the bulk does this tensor exist. However, for nematic liquid crystals a term of this kind may exist near the boundaries, where the symmetry is lower than in the bulk. Hence, according to the approach presented above, it is possible, at least in principle, to evaluate the elastic tensors of elements L_{ik}, L_{ikn}, and L_{ijkn} when the interparticle interaction is known.

However, even if everything seems to be done in a correct manner, it is necessary to pay attention to the obtained results, and in what manner they have been deduced. First of all, as it has been already stressed, when f is given by Eq. (10) there are mathematical problems to find the vectorial field $\vec{n}=\vec{n}(\vec{R})$ minimizing the total elastic energy [5]. In this case, in some situations, the average nematic orientation may present a sharp variation near the limiting walls [6]. Hence, in this case expression (4) does not work very well, and probably the second-order expansion is not enough. Moreover, whenever $g(\vec{n},\vec{n}',\vec{r})$ is a power law in r, according to which the intermolecular interaction decreases as $1/r^m$, expansion (7) diverges. In fact, in this special cases, as it follows from Eq. (5), q_i and q_{ij} decrease like $1/r^m$. Hence in expansion (7) the terms after the mth increase with r. Finally, we observe that the elastic tensors of elements L_{ik}, L_{ikn}, and L_{ijkn} are obtained by integrating term to term the power series (7). But, as is well known [7], this operation may be done only if the series is uniformly convergent. Now, the first expansion giving $g(\vec{n},\vec{n}',\vec{r})$ in terms of δn_i is supposed to be uniformly convergent. After that, expansion (6) is also assumed to be of the same kind. However, the substitution of Eq. (6) into Eq. (4) can give rise to a power series which is not uniformly convergent. Consequently, the final series (7) could be convergent in a nonuniform way. Hence only if one is able to demonstrate that it is uniformly convergent, the elastic tensors of elements L_{ik}, L_{ikn}, and L_{ijkn} are meaningful.

In the following we shall suppose that the approach presented above works well. In this framework we shall consider some classical intermolecular laws presented in the past to study the nematic liquid crystal. However, we are aware that the simple quasimicroscopic approach has several limits. Hence only the main results will be discussed.

A generic two-body interaction $g(\vec{n},\vec{n}',\vec{r})$ depends only on the three invariants $(\vec{n}\cdot\vec{n}')$, $(\vec{n}\cdot\vec{u})$, and $(\vec{n}'\cdot\vec{u})$, and on the modulus r of $\vec{r}$. Therefore [8],

$$g=g[(\vec{n}\cdot\vec{u}),(\vec{n}'\cdot\vec{u}),(\vec{n}\cdot\vec{n}'),r], \tag{13}$$

which can be expanded in Taylor's series as follows:

$$g=-\sum_{a\ b\ c} J_{a,b,c}(r)(\vec{n}\cdot\vec{u})^a(\vec{n}'\cdot\vec{u})^b(\vec{n}\cdot\vec{n}')^c, \tag{14}$$

where $J_{a,b,c}(r)>0$ and $\lim_{r\to\infty}J_{a,b,c}(r)=0$, because the intermolecular forces are assumed attractive and short range. If $a=b=0$, g does not depend on $\vec{u}$, but only on the relative orientation of $\vec{n}$ with respect to $\vec{n}'$. We call this kind of molecular interaction of the first kind. In the opposite case in which g depends also on $\vec{u}$, the intermolecular forces are of second kind. When g is of the first kind, its minimum value is reached for $\vec{n}\|\vec{n}'$. In the other case, the minimum energy of two interacting molecules depends on the relative position. In this second case, only in the bulk is the ground state the undeformed one [which corresponds to the minimum of f_0, given by Eq. (11)].

Following the approach proposed by Vertogen [9], and supposing the interaction volume of spherical shape, one obtains

$$K_{11}=\tfrac{1}{2}\sum_{a,b,c}\frac{J(a,b,c)}{(a+b+1)(a+b+3)}\left[\frac{3ab}{a+b-1}+c\right],$$

$$K_{22}=\tfrac{1}{2}\sum_{a,b,c}\frac{J(a,b,c)}{(a+b+1)(a+b+3)}\left[\frac{ab}{a+b-1}+c\right] \tag{15}$$

$$K_{33}=\tfrac{1}{2}\sum_{a,b,c}\frac{J(a,b,c)}{a+b+3}\left[\frac{ab}{a+b+1}+c\right],$$

$$K_{24}=-\tfrac{1}{4}\sum_{a,b,c}\frac{J(a,b,c)(b+c)}{(a+b+1)(a+b+3)},$$

for the bulk elastic constants, and

$$K_{13}=-\frac{1}{2}\sum_{a,b,c}\frac{J(a,b,c)\ b}{(a+b+1)(a+b+3)}, \tag{16}$$

for the splay-bend elastic constant [8]. In Eq. (16), $J(a,b,c)=4\pi\int_{R_i}^{R_o}J_{a,b,c}(r)r^4dr$. As discussed elsewhere, if the interaction energy is of the first kind, $K_{13}=0$, and f_0 does not depend on the $\vec{n}$ orientation even in a surface layer comparable with the range of the intermolecular forces. In the opposite case, where the interaction energy is of the second kind, K_{13} can be different from zero. In this case, f_0 gives rise to a kind of anisotropic surface energy [8]. In fact, special attention has been devoted to the influence of the K_{13} elastic term on the nematic orientation in the framework of the continuum approach [10–16]. The same problem has been anlyzed by means of a pseudomolecular model [6,17], by considering an intermolecular interaction which is a superposition of the Maier-Saupe $g_{\mathrm{MS}}=-C/r^6(\vec{n}\cdot\vec{n}')^2$ and Nehring-Saupe $g_{\mathrm{NS}}=-C/r^6[\vec{n}\cdot\vec{n}'-3(\vec{n}\cdot\vec{u})(\vec{n}'\cdot\vec{u})]^2$ interactions of the kind

$$g=\nu g_{\mathrm{MS}}+(1-\nu)g_{\mathrm{NS}}. \tag{17}$$

Very recently, Zumer [18], in a hexagonal lattice approximation studied the existence of subsurface deformations in the case in which g is of the kind

$$g(\epsilon)=-J(r)[(\vec{n}\cdot\vec{n}')-3\epsilon(\vec{n}\cdot\vec{u})(\vec{n}'\cdot\vec{u})]^2, \tag{18}$$

where

$$J(r)=\frac{C}{r^6}e^{-r/\lambda}. \tag{19}$$

In the above expressions, $C>0$. The exponential decreasing has been introduced in order to avoid problems with the uniform convergence of series (7). It describes a short-range interaction between the molecules. As is well known [2], only in this case is an elastic description, in which f is a local property, possible. Hence λ is supposed to be of a few molecular dimensions. Notice that expression (18), for what concerns the angular part, reduces to g_{MS} for $\epsilon=0$ and to g_{NS} when $\epsilon=1$. Then, the parameter ϵ plays the role of a mixing parameter. In this framework, in Ref. [18], the amplitude of the subsurface deformation vs ϵ is analyzed.

Here we want to notice that in the range $0\leqslant\epsilon\leqslant1$, K_{13} is not a monotonic function of ϵ. In fact, from Eq. (18) one sees that the coupling constants are

$$J_{a,b,c}(r)=J(r)[\delta_{a\,0}\delta_{b\,0}\delta_{c\,2}-6\epsilon\delta_{a\,1}\delta_{b\,1}\delta_{c\,1}+9\epsilon^2\delta_{a\,2}\delta_{b\,2}\delta_{c\,0}], \tag{20}$$

where δ_{ij} is Kronecker's delta. Consequently, the elastic constants given by Eqs. (15) and (16) result to be

$$K_{11}=K_{33}=\tfrac{1}{3}\,J[1-\tfrac{12}{5}\,\epsilon+\tfrac{54}{35}\,\epsilon^2],$$

$$K_{22}=\tfrac{1}{3}J[1-\tfrac{6}{5}\,\epsilon+\tfrac{18}{35}\,\epsilon^2], \tag{21}$$

$$K_{24}=-\tfrac{1}{6}\,J[1-\tfrac{6}{5}\,\epsilon+\tfrac{27}{35}\,\epsilon^2],\quad K_{13}=-J\frac{\epsilon}{5}[-1+\tfrac{9}{7}\,\epsilon],$$

where

$$J=4\pi C\int_{R_i}^{\infty}\frac{e^{-r/\lambda}}{r^2}dr=4\pi C\left[\frac{1}{R_i}e^{-R_i/\lambda}+\frac{1}{\lambda}\mathrm{Ei}\left(-\frac{R_i}{\lambda}\right)\right]. \tag{22}$$

In Eq. (22), $\mathrm{Ei}(R_i)$ is the exponential integral [7], and we have performed the limit $R_o\rightarrow\infty$, because the exponential is converging rapidly to zero.

From the relations reported above we deduce the following: (i) K_{11} is equal to K_{33} for all ϵ values. This result is expected since, for $g=g_{\mathrm{MS}}$ or $g=g_{\mathrm{NS}}$, the splay and bend elastic constants are always equal, in the framework of a pseudomolecular approach when the interaction volume is supposed to be of spherical shape. (ii) The bulk elastic constants are positive for $0\leqslant\epsilon\leqslant1$. No exotic effects, as the ones analyzed some years ago [19,20] are expected. (iii) The splay-bend elastic constant K_{13} vanishes for $\epsilon=0$ because the interaction reduces to one of the first kind. It also vanishes for $\epsilon=\frac{7}{9}\approx0.78$, which is a unexpected result. This means that for $\epsilon\approx0.78$ the subsurface deformation, if any, is connected with the homogeneous part of the elastic energy, but not to the K_{13} term [21].

In conclusion, we have shown that the pseudomolecular model has to be applied taking care of the convergence of the power series appearing in this approach. This follows from the fundamental hypothesis of the elastic theory, in which the molecular forces are assumed as being of ''contact'' [2]. The Maier-Saupe and Nehring-Saupe interaction laws are of this kind only if an appropriate cutoff is introduced. We also discussed the splay-bend elastic constant relevant to an intermolecular interaction represented by a mixing of the abovementioned interactions. We found that K_{13} is not a monotonic function of the mixing factor ϵ.

Many thanks are due to P. Galatola (Turin) for enlightening discussions. Financial support from CNPq (Brazil) is gratefully acknowledged.

---

[1] F. C. Frank, Discuss. Faraday Soc. **25**, 19 (1958).
[2] L. Landau and E. Lifschitz, *Théorie de l'Élasticité* (MIR, Moscow, 1967).
[3] J. Nehring and A. Saupe, J. Chem. Phys. **54**, 337 (1971); **56**, 5527 (1972).
[4] E. B. Priestley, P. J. Wojtowicz, and Ping Sheng, *Introduction to Liquid Crystals* (Plenum, New York, 1976), Chap. 4.
[5] C. Oldano and G. Barbero, Phys. Lett. A **110**, 213 (1985).
[6] G. Barbero, L. R. Evangelista, and S. Ponti, Phys. Rev. E **52**, 1265 (1995).

[7] I. S. Gradshtein and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1980).

[8] G. Barbero and R. Barberi, in *Physics of Liquid Crystalline Materials*, edited by I. C. Khoo and F. Simoni (Gordon and Breach, New York, 1993).

[9] G. Vertogen, Physica A **117**, 227 (1983).

[10] V. M. Pergamenshchik, Phys. Rev. E **48**, 1254 (1993).

[11] P. I. C. Teixeira, V. M. Pergamenshchik, and T. J. Slukin, Mol. Phys. **80**, 1339 (1993).

[12] S. Faetti, Phys. Rev. E **49**, 4192 (1994).

[13] S. Faetti, Phys. Rev. E **49**, 5332 (1994).

[14] S. Ponti, Phys. Lett. A **200**, 165 (1995).

[15] S. Stallinga and G. Vertogen, Phys. Rev. E **53**, 1692 (1996).

[16] S. Stallinga, J. A. M. M. van Haaren, and J. M. A. van den Erenbeemd, Phys. Rev. E **53**, 1701 (1996).

[17] P. Galatola, C. Oldano, M. Rajteri, and G. Barbero, Phys. Lett. A **210**, 101 (1996).

[18] S. Zumer (unpublished).

[19] G. Gompper and M. Schick, Phys. Rev. E **48**, 1882 (1993).

[20] F. S. Schmid and M. Schick, Phys. Rev. Lett. **62**, 1647 (1989).

[21] M. Rajteri, G. Barbero, P. Galatola, C. Oldano, and S. Faetti, Phys. Rev. E **53**, 6093 (1996).