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The Structure of the Distortion Free-Energy Density in Nematics: Second-Order Elasticity and Surface Terms (*).

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Summary. — By means of a phenomenological approach, we demonstrate that the mixed splay-bend elastic constant K_{13} in the free energy density of nematic liquid crystals must be considered zero, unless the bulk contributions of the squares of the distortion second-order derivatives are taken into account, together with the squares of the first-order derivatives times the second-order derivatives, and with the fourth powers of the first-order derivatives. Such contributions just reduce to one in the presence of—and close to—a threshold. Furthermore, the saddle-splay K_{24} -term instead is shown always to play an essential role, as the bulk first-order elasticity, in determining the distortion free energy of nematics with weak anchoring subjected to spatial deformations. Finally, the new surfacelike elastic constants are shown to have a nilpotent character: thus they behave as well as K_{24} from the point of view of the variational calculus.

PACS 61.30 – Liquid crystals.

PACS 68.10.Cr – Surface energy (surface tension, interface tension, angle of contact, etc.).

1. – Introduction.

By discussing the Oseen-Frank formulation [1] of the free energy density in nematic liquid crystals (NLC), involving three «bulk» elastic constants, *i.e.* splay (K_{11}), twist (K_{22}) and bend (K_{33}), Nehring and Saupe [2, 3] considered two «surface» elastic constants, the so-called mixed splay-bend (K_{13}) and saddle-splay (K_{24}) [4, 5]. The surface character of K_{13} and K_{24} depends on the fact that both are divergence terms, thus affecting the properties of either NLC cells or domains subjected to weak anchoring [6].

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But, as is well known, the K_{13} -term leads to some paradoxes [7], being a function of the director components n_i and of all their spatial first-order derivatives [8] $n_{i,j} = \partial_j n_i = \partial n_i / \partial x_j$. This means that, the surface contribution being dependent on both n_i and $n_{i,j}$, the Euler-Lagrange equations, which are second-order equations in the ordinary elastic theory, have continuous solutions that do not minimize the total free energy [7]. On the contrary, it has been shown that the K_{24} -term in a convenient geometry [9] can be expressed only as a function of n_i , allowing one to solve the variational problem of finding the director profile, which governs the physical properties of the NLC.

In sect. 2 we demonstrate, by means of a phenomenological approach, that the elastic constant K_{13} must be considered zero in NLC, unless the squares of second-order derivatives $n_{i,jk}$ are taken into account in the free energy density, together with the squares of the first-order derivatives $n_{i,j}$ times the second-order derivatives, and with the fourth powers of the first-order derivatives. In the presence of a threshold, such new terms are shown in sect. 3 to reduce just to one, close to the threshold itself. Furthermore, in sect. 4 no paradoxes are shown to arise from the contemporary presence of both K_{13} and bulk second-order elastic constants. Moreover, we will prove that the saddle-splay, coming out from the same square source of the bulk elasticity, always provides the variational problem to be well posed. Also the surfacelike elastic constants, arising from the new squares of second-order terms, have a nilpotent character, thus behaving as well as K_{24} .

2. – Phenomenological analysis.

The free energy density of NCL was by Nehring and Saupe written as

$$(1) \quad f = \frac{1}{2} \{ K'_{11} (\text{div } \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + K'_{33} (\mathbf{n} \times \text{rot } \mathbf{n})^2 \} + \\ + K_{13} \text{div } (\mathbf{n} \text{ div } \mathbf{n}) - (K_{22} + K_{24}) \text{div } (\mathbf{n} \text{ div } \mathbf{n} + \mathbf{n} \times \text{rot } \mathbf{n}),$$

where $K'_{11} = K_{11} - 2K_{13}$, $K'_{33} = K_{33} + 2K_{13}$ are the effective splay- and bend-elastic constants respectively, rescaled by K_{13} [2, 10]. The analysis of Nehring and Saupe implies that the saddle-splay constant is connected, for symmetry reasons, to Frank-splay elastic constant and to the twist elastic constant by $2K_{24} = K_{11} - K_{22}$.

We note that the existence itself in the free energy density (1) of linear terms in second-order derivatives, like the one relevant to K_{13} , was already questioned but not analysed [11]. Our aim is to show that, if the K_{13} -term is considered, also other terms square in the second-order derivatives of the director, $n_{i,jk} n_{l,mp}$, must be taken into account, together with the squares of the first derivatives times the second derivatives, $n_{i,j} n_{k,l} n_{m,pq}$, and with the fourth powers of the first-order derivatives, $n_{i,j} n_{k,l} n_{m,p} n_{q,r}$.

In fact, the local free energy density can be expressed as a function of the deformation sources [2, 12-14]: $f = f(n_{i,j}; n_{i,jk}; \dots)$. We assume as deformation sources the director first- and second-order derivatives, $n_{i,j}$ and $n_{i,jk}$. Hence, the virtual variation of the free energy density close to an equilibrium configuration writes, by considering the dependence of f just up to the virtual variations of the second-order derivatives

$$(2) \quad \delta f = \lambda_{ij} \delta n_{i,j} + \mu_{ijk} \delta n_{i,jk},$$

where $\lambda_{ij} = \partial f / \partial n_{i,j}$, $\mu_{ijk} = \partial f / \partial n_{i,jk}$ and repeated indices are summed over. We note that the Ansatz assumed in eq. (2) is based on the hypothesis commonly accepted that contributions of the j -th order derivatives of the director are one order of magnitude smaller than the $(j-1)$ -th order derivatives.

The usual linear theory of elasticity of solids corresponds to considering in eq. (2) only the first-order derivatives, by neglecting higher-order terms. On the contrary, here just the terms of order higher than the second one are neglected.

With the aim of calculating the functional form of the free energy density f up to the fourth order with respect to $n_{i,j}$, the tensor fields λ_{ij} , μ_{ijk} are to be expanded in terms of the deformation sources, by taking into account only the actual deformation sources $n_{i,j}$ and $n_{i,jk}$. Hence the expansions turn out to be

$$(3) \quad \begin{cases} \lambda_{ij} = \lambda_{ij}^0 + A_{ijkl} n_{k,l} + B_{ijklm} n_{k,lm} + C_{ijkilm} n_{k,i} n_{m,p} + \\ \hspace{15em} + D_{ijkilmnpq} n_{k,lm} n_{p,q} + E_{ijkilmnpqr} n_{k,i} n_{m,p} n_{q,r}, \\ \mu_{ijk} = \mu_{ijk}^0 + M_{ijklm} n_{l,m} + N_{ijkilm} n_{l,mp} + O_{ijkilmnpq} n_{l,m} n_{p,q}, \end{cases}$$

where $\lambda_{ij}^0, \mu_{ijk}^0$ are tensor fields dependent only on the director components n_i and independent of $n_{i,j}$ and $n_{i,jk}$, as well as $(A_{ijkl}, B_{ijklm}, C_{ijklmp}, D_{ijklmpq}, E_{ijklmpqr})$ and $(M_{ijklm}, N_{ijklmp}, O_{ijklmpq})$.

By substituting eqs. (3) into eq. (2), we may see that just the λ_{ij}^0 -term is of the first order in the expression of the distortion free-energy density f , whereas (A_{ijkl}, μ_{ijkl}^0) give second-order terms, $(B_{ijklm}, C_{ijklmp}, M_{ijklm})$ third-order terms, and $(D_{ijklmpq}, E_{ijklmpqr}, O_{ijklmpqr})$ fourth-order terms, respectively.

Now the question could arise, why not to consider in the first equation of system (3) a term like $F_{ijklmp} n_{k, lmp}$, which in the above-mentioned hypothesis is in fact of the same order of the terms dependent on $D_{ijklmpq}$ and $E_{ijklmpqr}$? The criterion to be assumed is the following: λ_{ij} , μ_{ijk} are to be expanded only in terms of the deformation sources, as defined. In other words, eq. (2) is corrected if the hypothesis on the orders of magnitude of director derivatives is acceptable. Of course this fact is verified in the continuum description; but eq. (2) implies also that the virtual variations of the director derivatives of higher order than the second one must not appreciably influence any distortion, and then they always are to be considered equal to zero. By taking into account the general property of the mixed second-order derivatives in the set of the continuous functions:

$$(4) \quad \partial^2 f / \partial n_{i,j} \partial n_{k,lm} = \partial^2 f / \partial n_{k,lm} \partial n_{i,j},$$

the Maxwell thermodynamic relations are obtained, which provide the differential form, corresponding to the virtual variation δf , to be exact, thus ensuring the uniqueness of the integral f :

$$(4') \quad B_{ijklm} = M_{klmij}, \quad D_{ijklmpq} = O_{klmijpq}.$$

Moreover, simple considerations of symmetry [15] give

$$(5) \quad \left\{ \begin{array}{l} A_{ijkl} = A_{kl ij}, \\ C_{ijklmp} = C_{ijmpkl} = C_{kljmip}, \\ D_{ijklmpq} = D_{pqklmij}, \\ E_{ijklmpqr} = E_{kljmqpr} = E_{ijmqlr} = E_{ijklrmp} = E_{qrklmpij} = E_{mpkljqr}. \end{array} \right.$$

By substituting expansions (3) into eq. (2) according to Maxwell relations (4') and to symmetry properties (5), and afterwards integrating, the distortion free energy density reads

$$(6) \quad f = \lambda_{ij}^0 n_{i,j} + \mu_{ijk}^0 n_{i,jk} + \frac{1}{2} A_{ijkl} n_{i,j} n_{k,l} + B_{ijklm} n_{i,j} n_{k,lm} + \frac{1}{3} C_{ijklmp} n_{i,j} n_{k,l} n_{m,p} + \\ + \frac{1}{2} D_{ijklmpq} n_{i,j} n_{k,lm} n_{p,q} + \frac{1}{4} E_{ijklmpqr} n_{i,j} n_{k,l} n_{m,p} n_{q,r} + \frac{1}{2} N_{ijklmp} n_{i,jk} n_{l,mp}.$$

In order to calculate the form of all contributions due to each tensor field in eq. (6), let us consider the presence of all symmetry sources governing the NLC equilibrium configurations. As a matter of fact, common NLC are neither polar nor chiral: thus in eq. (6) the elastic coefficients of the tensor fields concerning the bulk terms odd either in the director \mathbf{n} or in the pseudoscalar $\mathbf{n} \cdot \text{rot } \mathbf{n}$ turn out to be zero, since they must be invariant for any transform of the type up-down and right-left. Hence, for usual NLC symmetry reasons determine the vanishing of the following tensor fields:

$$(7) \quad \lambda_{ij}^0 = 0, \quad B_{ijklm} = 0, \quad C_{ijklmp} = 0.$$

In fact, the most general expression of the tensor fields in eq. (6) is obtained as their complete expansions on the basis $(n_i, \delta_{ij}, \epsilon_{ijk})$, where δ_{ij} is Kronecker symmetric tensor, and ϵ_{ijk} is Levi-Civita antisymmetric pseudotensor [12-14, 16-18] (this procedure is usually referred to as Rivlin rule [19]).

According to Rivlin rule, the following relations are obtained in covariant form:

$$(8) \quad \begin{cases} f_\lambda = 0, \\ f_A = A_1 (\text{div } \mathbf{n})^2 + A_2 (\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + A_3 (\mathbf{n} \times \text{rot } \mathbf{n})^2 + A_4 \text{div } (\mathbf{n} \text{div } \mathbf{n} + \mathbf{n} \times \text{rot } \mathbf{n}), \\ f_\mu = \mu_1 (\text{div } \mathbf{n})^2 + \mu_2 (\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + \mu_3 (\mathbf{n} \times \text{rot } \mathbf{n})^2 + \\ + \mu_4 \text{div } (\mathbf{n} \text{div } \mathbf{n}) - \mu_2 \text{div } (\mathbf{n} \text{div } \mathbf{n} + \mathbf{n} \times \text{rot } \mathbf{n}), \end{cases}$$

where the index in the considered contribution to the distortion free energy density is relevant to the involved tensor field.

Notice that, if we considered just $n_{i,j}$ as deformation sources, thus eq. (6) should write with the previous criterion

$$(6') \quad f = \lambda_{ij}^0 n_{i,j} + \frac{1}{2} A_{ijkl} n_{i,j} n_{k,l}$$

and $K_{13} = 0$ would be rigorously achieved. This result is consistent with the assumptions posed in Oseen-Frank elastic theory. On the other hand, such a term is often disregarded [12-14, 20-22], but just for the reason that it has surface character (this opinion is referred to as «standard argument»). Instead, our point is that K_{13} is rigorously zero, but only in the frame of the usual first-order elastic theory. On the contrary, also in the usual first-order elasticity the other surfacelike term, relating to the saddle-splay elastic constant K_{24} , must be taken into account, since it arises not only from μ_{ijk}^0 , but from A_{ijkl} too.

Just, if any spatial deformation is absent, thus the saddle-splay distortion becomes identically zero, as is well known [4].

By considering the bulk terms in (8), we can see that the splay-, twist-, and bend-contributions first arise from both tensor field μ_{ijk}^0 , and A_{ijkl} . Note that by this phenomenological approach splay and bend are obtained not degenerate, as otherwise recognized by Longa *et al.* [23].

For what is concerning the terms coming from $(N_{ijklmp}, D_{ijklmpq} \text{ and } E_{ijklmpqr})$, we

TABLE I. – Contributions to the distortion free energy density of a nematic liquid crystal, due to the tensor field N_{ijklmp} .

1)	$n_{i,jj} n_{k,ki}$
2)	$n_{i,ij} n_{k,kj}$
3)	$n_{i,jk} n_{i,jk}$
4)	$n_{i,jk} n_{j,ik}$
5)	$n_{i,jj} n_{i,kk}$
6)	$n_i n_j n_{k,kl} n_{l,ij}$
7)	$n_i n_j n_{k,il} n_{k,ij}$
8)	$n_i n_j n_{k,ki} n_{l,lj}$
9)	$n_i n_j n_{k,il} n_{l,jk}$
10)	$n_i n_j n_{k,il} n_{k,jl}$
11)	$n_i n_j n_k n_l n_{m,ij} n_{m,kl}$

TABLE II. – Contribution to the distortion free energy density of a nematic liquid crystal, due to the tensor field $D_{ijklmpq}$. The terms marked by * are common to N_{ijklmp} .

1)	$n_i n_{j,i} n_{k,k} n_{j,ll}$
2)	$n_i n_{j,i} n_{k,k} n_{l,lj}$
3)	$n_i n_{j,i} n_{k,l} n_{k,jl}$
4)	$n_i n_{j,i} n_{k,l} n_{j,kl}$
5)	$n_i n_{j,i} n_{k,l} n_{l,jk}$
6)	$n_i n_{j,i} n_{k,j} n_{l,lk}$
7)	$n_i n_{j,i} n_{k,j} n_{k,ll}$
8)	$n_i n_{j,k} n_{k,j} n_{l,li}$
9)	$n_i n_{j,k} n_{l,l} n_{j,ki}$
10)	$n_i n_{j,j} n_{k,l} n_{l,ik}$
11)	$n_i n_{j,k} n_{k,l} n_{j,il}$
12)	$n_i n_{j,k} n_{k,l} n_{l,ij}$
13)	$n_i n_{j,j} n_{k,k} n_{l,li}$
14)	$n_i n_{j,k} n_{l,k} n_{l,ij}$
15)	$n_i n_{j,i} n_{j,k} n_{k,il}$ *
16)	$n_i n_{j,k} n_{j,k} n_{l,li}$ *
17)	$n_i n_{j,k} n_{j,l} n_{k,il}$ *
18)	$n_i n_{j,k} n_{j,i} n_{l,lk}$ *
19)	$n_i n_j n_k n_{l,l} n_{m,i} n_{m,jk}$
20)	$n_i n_j n_k n_{l,i} n_{m,k} n_{m,jl}$
21)	$n_i n_j n_k n_{l,i} n_{m,l} n_{m,jk}$
22)	$n_i n_j n_k n_{l,i} n_{l,k} n_{m,mj}$ *
23)	$n_i n_j n_k n_{l,i} n_{l,m} n_{m,jk}$ *

TABLE III. – Contribution to the distortion free energy density of a nematic liquid crystal, due to the tensor field $E_{ijklmpqr}$. The terms marked by * are common to $D_{ijklmpq}$, whereas the terms marked by ** are common to both N_{ijklmp} and $D_{ijklmpq}$.

1)	$n_{i,i} n_{j,j} n_{k,k} n_{l,l}$
2)	$n_{i,j} n_{j,i} n_{k,l} n_{l,k}$
3)	$n_{i,j} n_{j,i} n_{k,k} n_{l,l}$
4)	$n_{i,j} n_{j,k} n_{k,l} n_{l,i}$
5)	$n_{i,i} n_{j,k} n_{l,j} n_{k,l}$
6)	$n_{i,i} n_{j,j} n_{k,l} n_{k,l}$ *
7)	$n_{i,i} n_{j,k} n_{k,l} n_{j,l}$ *
8)	$n_{i,j} n_{j,k} n_{k,l} n_{i,l}$ *
9)	$n_{i,j} n_{k,i} n_{l,j} n_{k,l}$ *
10)	$n_{i,j} n_{j,i} n_{k,l} n_{k,l}$ *
11)	$n_{i,j} n_{k,j} n_{i,l} n_{k,l}$ **
12)	$n_{i,j} n_{i,j} n_{k,l} n_{k,l}$ **
13)	$n_i n_j n_{k,i} n_{l,m} n_{l,j} n_{k,m}$ *
14)	$n_i n_j n_{k,k} n_{l,m} n_{l,i} n_{m,j}$ *
15)	$n_i n_j n_{k,l} n_{m,i} n_{k,j} n_{l,m}$ *
16)	$n_i n_j n_{k,j} n_{k,i} n_{l,l} n_{m,m}$ *
17)	$n_i n_j n_{k,i} n_{k,j} n_{l,m} n_{l,m}$ *
18)	$n_i n_j n_{k,j} n_{k,i} n_{l,m} n_{m,l}$ *
19)	$n_i n_j n_{k,l} n_{k,m} n_{m,i} n_{l,j}$ **
20)	$n_i n_j n_{k,l} n_{k,l} n_{m,i} n_{m,j}$ **
21)	$n_i n_j n_k n_l n_{m,i} n_{m,j} n_{p,k} n_{p,l}$ **

observe that most of them give zero contribution to the distortion free energy density, due to the above-mentioned parity of \mathbf{n} and $\mathbf{n} \cdot \text{rot } \mathbf{n}$. In addition, some terms are found to be derived from both N_{ijklmp} and $D_{ijklmpq}$, or from both $D_{ijklmpq}$ and $E_{ijklmpqr}$, or from the three sources at the same time.

In table I the eleven contributions to f due to the tensor field N_{ijklmp} are reported, whereas table II shows the seventeen contributions due only to $D_{ijklmpq}$ and the six terms (marked by *) common to N_{ijklmp} . Besides, in table III the five contributions due only to $E_{ijklmpqr}$ are listed, together with the eleven terms (marked by *) common to $D_{ijklmpq}$, and the five terms (marked by **) common to both N_{ijklmp} and $D_{ijklmpq}$. Eventually, the number of independent elastic constants, arising from the new high-order tensor fields, is forty[2], due to the above-mentioned symmetry sources, provided the further explicit contributions of \mathbf{n} -derivatives of order higher than the second one are neglected, according to our criterion.

In appendix I the mechanism of the appearing of common terms in N_{ijklmp} , $D_{ijklmpq}$ and $E_{ijklmpqr}$ is analysed.

3. – Bulk second-order elasticity close to a threshold.

Let us stress the fact that in the ordinary first-order elastic theory only three bulk elastic constants completely describe the behaviour of common NLC, whereas

according to the second-order elastic theory other forty elastic constants are to be considered[24]. This means that in such a frame the quantitative approach to whatever elasticity problem becomes not realistic, except for the cases involving threshold phenomena.

In order to be convinced, let us consider for the sake of simplicity a planar deformation in NLC, for instance the one achieved in a cell with opposite boundary conditions (homeotropic at the one of the walls and homogeneous planar at the other one), the so-called hybrid aligned nematic (HAN) cell [25, 26]. A frame of reference $|x, z|$ is introduced, with the origin at the wall with homeotropic anchoring, x -axis parallel to such a wall, and z -axis normal to it. The local director \mathbf{n} is given by

$$(9) \quad \mathbf{n} = \mathbf{i} \sin \theta + \mathbf{k} \cos \theta,$$

where $\theta(z)$ is the tilt angle, that the director forms with respect to the z -axis. The new contributions to the free energy density are of the fourth order with respect to $n_{i,j}$, thus affecting also the bulk. In order to describe the arising of the possible threshold for mechanical instability in a HAN cell, due to the diminishing of the thickness d , it is convenient to express f as a function of θ : close to the threshold indeed the leading parameter is the amplitude θ_{\max} of the distortion.

Now, terms 2), 5) in table I and 13), 22) in table III read in covariant form, respectively,

$$(10) \quad \begin{cases} n_{i,j} n_{k,kj} = (\text{grad div } \mathbf{n})^2, \\ n_{i,jj} n_{i,kk} = (\nabla^2 \mathbf{n})^2, \\ n_{i,j} n_{i,j} n_{k,l} n_{k,l} = (\mathbf{n} \cdot \nabla^2 \mathbf{n})^2, \\ n_j n_k n_m n_p n_{i,j} n_{i,k} n_{l,m} n_{l,p} = (\mathbf{n} \times \text{rot } \mathbf{n})^4. \end{cases}$$

By taking into account eq. (9), the previous terms give simply

$$(11) \quad \begin{cases} (\text{grad div } \mathbf{n})^2 = \cos^2 \theta \dot{\theta}^4 + \sin 2\theta \dot{\theta}^2 \ddot{\theta} + \sin^2 \theta \ddot{\theta}^2, \\ (\nabla^2 \mathbf{n})^2 = \dot{\theta}^4 + \ddot{\theta}^2, \\ (\mathbf{n} \cdot \nabla^2 \mathbf{n})^2 = \dot{\theta}^4, \\ (\mathbf{n} \times \text{rot } \mathbf{n})^4 = \cos^4 \theta \dot{\theta}^4, \end{cases}$$

where $\dot{\theta} = d/dz$. All the other contributions are of the fourth order with respect to the deformation source $\dot{\theta}$.

Close to the threshold $\theta_{\max} \rightarrow 0$, therefore, the contributions of smallest order with respect to θ_{\max} are derived from the term $\ddot{\theta}^2$ in the second equation of system (11). Note that $\ddot{\theta}^2$ is of the second order with respect to θ_{\max} , whereas the other contributions vanish more rapidly, when θ_{\max} goes to zero. In conclusion, the additional bulk term in the free energy density can be simply written as

$$(8') \quad f_{\text{NDE}} = K^* (\nabla^2 \mathbf{n})^2 \simeq K^* \ddot{\theta}^2,$$

according to the present generalized elastic theory, K^* being the new bulk second-order elastic constant, the only one of the forty which survives close to the distortion threshold [26, 27].

Thus eq. (1), according to the usual first-order elastic theory, must be simply

written

$$(1') \quad f = \frac{1}{2} \{ K'_{11} (\operatorname{div} \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \operatorname{rot} \mathbf{n})^2 + K'_{33} (\mathbf{n} \times \operatorname{rot} \mathbf{n})^2 \} - (K_{22} + K_{24}) \operatorname{div} (\mathbf{n} \operatorname{div} \mathbf{n} + \mathbf{n} \times \operatorname{rot} \mathbf{n}),$$

whereas, according to the second-order elastic theory applied to the investigation of threshold phenomena, it must be read

$$(1'') \quad f = \frac{1}{2} \{ K'_{11} (\operatorname{div} \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \operatorname{rot} \mathbf{n})^2 + K'_{33} (\mathbf{n} \times \operatorname{rot} \mathbf{n})^2 \} + K_{13} \operatorname{div} (\mathbf{n} \operatorname{div} \mathbf{n}) - (K_{22} + K_{24}) \operatorname{div} (\mathbf{n} \operatorname{div} \mathbf{n} + \mathbf{n} \times \operatorname{rot} \mathbf{n}) + K^* (\nabla^2 \mathbf{n})^2.$$

4. – Surfcelike distortion free energy.

In the frame of the present second-order elastic theory, no paradox arises from the point of view of the variational calculus for the presence of K_{13} , derived by the tensor field μ_{ijk}^0 , since the bulk free energy density includes squares of second-order derivatives of the director \mathbf{n} [28], while the mixed splay-bend free energy is depending on $n_i, n_{i,j}$.

Furthermore, the saddle-splay coming from squares of first-order derivatives, the variational problem always is well posed. In the following subsect. 4'1 and 4'2 the previous sentences will be demonstrated, whereas in subsections 4'3 the new surfcelike elasticity of high order is shown to have the same behaviour as the saddle splay.

4'1. *Mixed splay-bend.* – Let us consider the distortion free energy F of a NLC-cell of volume V , limited by a surface S , where for the sake of simplicity no surface terms coming from squares of director derivatives are present (this is the case of a sample subjected only to planar deformations).

From eq. (1'') we can write, applying Gauss theorem to the surfcelike contribution,

$$(12) \quad F = \int_V f_b(n_i, n_{i,j}, n_{i,jk}) dV + \oint_S [f_a(n_i) + \mathbf{N} \cdot \mathbf{g}_{13}(n_i, n_{i,j})] dS,$$

where f_b is the bulk distortion free energy density, \mathbf{N} is the unit vector normal to the surface, and $f_a(n_i)$ takes into account the explicit anchoring [29]. The surface vector \mathbf{g} , is just coincident with $\mathbf{g}_{13} = K_{13} \mathbf{n} \operatorname{div} \mathbf{n}$, therefore it is solenoidal.

Equation (12) provides the virtual first variation of F close to an equilibrium configuration to be obtained as

$$(13) \quad \delta F = \int_V (\partial f_b / \partial n_i - \partial_j \partial f_b / \partial n_{i,j} + \partial_{jk}^2 \partial f_b / \partial n_{i,jk}) \delta n_i dV + \oint_S \{ [N_j (\partial f_b / \partial n_{i,j} - \partial_k \partial f_b / \partial n_{i,jk}) + \partial f_a / \partial n_i + \partial (\mathbf{N} \cdot \mathbf{g}_{13}) / \partial n_i] \delta n_i + [N_k \partial f_b / \partial n_{i,jk} + \partial (\mathbf{N} \cdot \mathbf{g}_{13}) / \partial n_{i,j}] \delta n_{i,j} \} dS.$$

The Euler-Lagrange (EL) equations are, in the generalized elastic theory, three fourth-order equations:

$$(14) \quad \partial f_b / \partial n_i - \partial_j \partial f_b / \partial n_{i,j} + \partial_{jk}^2 \partial f_b / \partial n_{i,jk} = \Lambda n_i,$$

where Λ is a Lagrangian multiplier, with three boundary conditions given by

$$(15) \quad N_j (\partial f_b / \partial n_{i,j} - \partial_k \partial f_b / \partial n_{i,jk}) + \partial f_a / \partial n_i + \partial (N \cdot \mathbf{g}_{13}) / \partial n_i = 0$$

and nine boundary conditions provided by

$$(16) \quad N_k \partial f_b / \partial n_{i,jk} + \partial (N \cdot \mathbf{g}_{13}) / \partial n_{i,j} = 0.$$

Thus, the difficulty in managing K_{13} pointed out in ref. [7] and widely discussed in ref. [29] in contrast with the opinion of Hinov [30], difficulty afterwards considered by Madhusudana [31], is definitively overcome.

Note that in the frame of the second-order elastic theory the explicit anchoring could also be expressed in the form $f_a(n_i, n_{i,j})$, as assumed by Mada [32]: this hypothesis would give just one more term into the boundary conditions (16).

4.2. Saddle-splay. – By assuming that $\mathbf{g}_{13} = 0$ (as in the case where in the NLC sample there is no splay at all), in the presence of a spatial distortion the surfacelike free energy density vector \mathbf{g}_s reduces to the saddle-splay term $\mathbf{g}_{24} = - (K_{22} + K_{24})(\mathbf{n} \operatorname{div} \mathbf{n} + \mathbf{n} \times \operatorname{rot} \mathbf{n})$, which is different from zero. For the sake of simplicity let us suppose the surfacelike high-order contribution f_{sNDE} to be zero.

We will demonstrate that also in the case of validity of eq. (6'), which explicitly reads as eq. (1'), *i.e.* also in the frame of the first-order elasticity, the saddle-splay never provides paradoxes. In fact, the distortion free energy F becomes now

$$(17) \quad F = \int_V f_b(n_i, n_{i,j}) dV + \oint_S [f_a(n_i) + N \cdot \mathbf{g}(n_i, n_{i,j})] dS,$$

and the virtual first variation of F is given by

$$(18) \quad \delta F = \int_V \{(\partial f_b / \partial n_i - \partial_j \partial f_b / \partial n_{i,j})\} \delta n_i dV + \\ + \oint_S \{[N_j \partial f_b / \partial n_{i,j} + \partial f_a / \partial n_i + \partial (N \cdot \mathbf{g}) / \partial n_i] \delta n_i + [\partial (N \cdot \mathbf{g}) / \partial n_{i,j}] \delta n_{i,j}\} dS.$$

Hence the EL equations read

$$(19) \quad \partial f_b / \partial n_i - \partial_j \partial f_b / \partial n_{i,j} = \Lambda n_i,$$

being generally three second-order equations, with just three boundary conditions:

$$(20) \quad N_j \partial (f_b + g_{k,k}) / \partial n_{i,j} + \partial f_a / \partial n_i = 0.$$

In fact, if eqs. (19) and (20) are satisfied, the virtual first variation δF reduces to

$$(21) \quad \delta F = \oint_S \{[-N_j \partial g_{k,k} / \partial n_{i,j} + \partial (g_j N_j) / \partial n_i] \delta n_i + [\partial (g_k N_k) / \partial n_{i,j}] \delta n_{i,j}\} dS,$$

but it is easy to demonstrate that the r.h.s. of eq. (21) always is identically zero. Let us consider the vector

$$(22) \quad U_m = [-\partial g_{k,k} / \partial n_{i,m} + \partial g_m / \partial n_i] \delta n_i + [\partial g_m / \partial n_{i,j}] \delta n_{i,j}.$$

By means of Gauss theorem, eq. (21) writes

$$(23) \quad \delta F = \int_V U_{m,m} dV,$$

but U_m is a solenoidal field, since starting from

$$(24) \quad g_m = -(K_{22} + K_{24})(n_m n_{k,k} - n_k n_{m,k})$$

we deduce

$$(25) \quad \begin{cases} \partial g_{i,i} / \partial n_{k,m} = -2(K_{22} + K_{24})(n_{i,i} \delta_{km} - n_{m,k}), \\ \partial g_m / \partial n_i = -(K_{22} + K_{24})(n_{k,k} \delta_{im} - n_{m,i}), \\ \partial g_m / \partial n_{i,j} = -(K_{22} + K_{24})(n_m \delta_{ij} - n_j \delta_{im}). \end{cases}$$

Thus δF , as obtained from (23), is identically zero, and the variational problem always is well posed. Note that this fact is related to the nilpotent character of the saddle-splay, already described by Ericksen[33].

Of course, the obtained result holds also in the general case of second-order elasticity, where $f_b(n_i, n_{i,j}, n_{i,jk})$.

4.3. New surfacelike elastic terms. – In the general form (8) of the distortion free energy density, some terms arising from the tensor fields N_{ijklmp} , $D_{ijklmpq}$ and $E_{ijklmpqr}$ can be split in covariant parts, which provide both bulklike and surfacelike contributions.

Let us consider, for instance, the term 3) in table I: it can be written as

$$(26) \quad n_{i,jk} n_{i,jk} = \frac{1}{2} [(\nabla^2 \mathbf{n})^2 + \mathbf{n} \cdot \nabla^2 \nabla^2 \mathbf{n}] + \nabla^2 (n_{i,j} n_{i,j}),$$

where

$$(27) \quad n_{i,j} n_{i,j} = (\operatorname{div} \mathbf{n})^2 + (\mathbf{n} \cdot \operatorname{rot} \mathbf{n})^2 + (\mathbf{n} \times \operatorname{rot} \mathbf{n})^2 - \operatorname{div} (\mathbf{n} \operatorname{div} \mathbf{n} + \mathbf{n} \times \operatorname{rot} \mathbf{n}).$$

The demonstrations of eqs. (26) and (27) are reported in appendix B. Obviously the square brackets in eq. (26) contain only a bulk contribution, whereas $\nabla^2 (n_{i,j} n_{i,j})$ is a surfacelike term. The bulk term is dependent on the \mathbf{n} -derivatives up to the fourth order; the integrated surfacelike free energy has \mathbf{n} -derivatives up to the second order. As a consequence, the variational problem turns out to be well posed[28].

Also other new surfacelike terms are implicitly contained in the free energy density f_{NDE} , like for instance $\nabla^2 (\operatorname{div} \mathbf{n})^2$, $\operatorname{div} (\nabla^2 \mathbf{n}) \operatorname{div} \mathbf{n}$, $\nabla^2 (\mathbf{n} \times \operatorname{rot} \mathbf{n})^2$, and so on; they are coming from squares of derivatives, even though of second order: hence they can be shown with straightforward but tedious calculation to have the above-mentioned nilpotent property. Thus, the surfacelike terms f_{NDE} provide no paradoxes in solving the variational problem of calculating the director profile in the frame of the continuum theory.

Furthermore, such terms can be expressed as functions of square and cubic derivatives of the distortion angles. Hence, in the study of threshold phenomena they can be disregarded[27] with respect to the saddle-splay.

5. – Conclusion.

As is known, the free energy terms relevant to K_{13} , K_{24} often were disregarded by most authors for the only reason that their contribution to the total free energy may be considered as a surface contribution (this opinion is referred as «standard argument»—see, for instance, ref.[20]). But, to drop out the divergence terms is

correct only if the director orientation at the surface is either homeotropic or homogeneous planar and it is fixed (strong anchoring), since only in such a case the equilibrium configuration really is independent of any surface term.

On the other hand, if the n -orientation on the bounding walls of the sample is fixed but neither homeotropic nor homogeneous planar, or if the anchoring is weak, due to the surface treatment, thus the K_{13} -term must be considered in the frame of the generalized elastic theory, and the new bulk elastic constants must be taken into account.

The effect of K_{13} turns out to be a destabilization of the undistorted configuration in the NLC sample [26, 27], K_{13} favouring a high distortion close to the boundary [29, 34].

Here we consider the scalar order parameter S as a constant throughout the whole NLC sample. But, as is well known [35-37], S can vary close to the boundary, thus determining a related change of all elastic «constants». In order to take into account such an effect, instead of eq. (2) it would be necessary to express δf in terms of the virtual variation of the first- and second-order derivatives $Q_{ij,k}$, $Q_{ij,kl}$ of the tensor order parameter $Q_{ij} = S(n_i n_j - \delta_{ij}/3)$.

From preliminary calculation, such a behaviour of S will provide also a high distortion close to the walls of the NLC-cell: this property will be analysed in detail elsewhere.

Furthermore, we stress the fact that, in the presence of spatial distortions in weakly anchored structures, the K_{24} -term plays an important role, as well as, for instance, for what concerns both the behaviour of disclination lines in the bulk, and the features of operating twisted NLC displays. In fact, in a spatial distorted NLC cell, the K_{24} -term affects the effective anchoring energy, whereas in the case of disclination lines the saddle-splay acts as the only contribution to the surface energy, and can stabilize or not the defects themselves. Anyway, the presence of the K_{24} -term never does hinder the solubility of the variational problem of finding the director profile in the set of the continuous functions.

The saddle-splay K_{24} influences also the cholesteric liquid crystals, which presents high bending deformations: the contribution of K_{24} to the stability of the blue phases has been recently analysed by many authors [20-22, 38], concluding that a positive value of K_{24} does stabilize the blue phases.

The same analysis relevant to the effect of K_{13} in the blue phases has been reported only by Kléman [38], whereas in ref. [20-22] the K_{13} -term simply has been neglected.

Our statement is that the latter procedure is correct only in the frame of the ordinary elastic theory, since K_{13} only in this case is zero in liquid crystals.

In conclusion, the principal results of our work are

- i) in the frame of the generalized elastic theory, just one additional bulk elastic constant K^* must be introduced into the free energy density close to a threshold;
- ii) the «standard argument» for disregarding any surfacelike elastic contribution is tautological, thus has no sense;
- iii) in the free energy density of NLC, linear second-order spatial derivatives, concerning the elastic constant K_{13} , are to be considered only in the frame of the generalized elastic theory;
- iv) the K_{24} -term, coming also from squares of first-order derivatives, plays an important role in spatially distorted liquid crystals with weak anchoring;

v) the high-order surfacelike elastic constants have a nilpotent character, as well as K_{24} : but their contribution may be disregarded, close to a threshold, with respect to the latter one.

* * *

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APPENDIX A

Some terms are found to be common to the different tensor fields N_{ijklmp} , $D_{ijklmpq}$ and $E_{ijklmpqr}$. Let us consider, for instance, the term $n_i n_j n_k n_l n_m n_p n_{i,jk} n_{l,mp}$ belonging to the tensor field N_{ijklmp} . Since one can write

$$(A.1) \quad n_i n_j n_k n_{i,jk} = (n_i n_{i,j})_{,k} - n_{i,k} n_{i,j} n_j n_k = -n_i n_{i,j} n_k n_{i,k} = -(\mathbf{n} \times \text{rot } \mathbf{n})^2,$$

thus the previous term becomes

$$(A.2) \quad n_i n_j n_k n_l n_p n_{i,jk} n_{l,mp} = (\mathbf{n} \times \text{rot } \mathbf{n})^4.$$

But, by simple inspection, it is easy to deduce that also the term $n_j n_l n_m n_p n_q n_{i,j} n_{k,l} n_{m,pq}$ and the term (22) in table III, *i.e.* the scalar $n_j n_l n_p n_r n_{i,j} n_{i,l} n_{m,p} n_{m,r}$, arising from the tensor field $D_{ijklmpq}$ and $E_{ijklmpqr}$, respectively, give the same result obtained in eq. (A.2).

By means of analogous straightforward calculations, all the terms marked with * (and with **) in table II and in table III can be derived also from the one of the other tensor fields (or from both ones).

APPENDIX B

In order to demonstrate eqs. (26) and (27), let us to start differentiating twice the scalar $n_{i,j} n_{i,j}$ with respect to k :

$$(B.1) \quad (n_{i,j} n_{i,j})_{,k} = 2n_{i,j} n_{i,jk}$$

and

$$(B.2) \quad (n_{i,j} n_{i,j})_{,kk} = 2(n_{i,jk} n_{i,jk} + n_{i,j} n_{i,jkk}).$$

On the other hand, by differentiating twice $n_i n_{i,kk}$ with respect to j , one obtains

$$(B.3) \quad (n_i n_{i,kk})_{,j} = n_{i,j} n_{i,kk} + n_i n_{i,kkj}$$

and, afterwards,

$$(B.4) \quad (n_i n_{i,kk})_{,jj} = n_{i,jj} n_{i,kk} + 2n_{i,j} n_{i,kkj} + n_i n_{i,kkjj}.$$

But, since \mathbf{n} is a unit vector, one obtains

$$(B.5) \quad n_i n_{i,j} = 0$$

and consequently, from

$$(B.6) \quad (n_i n_{i,j})_{,j} = n_{i,j} n_{i,j} + n_i n_{i,jj} = 0,$$

we deduce

$$(B.7) \quad n_i n_{i,jj} = -n_{i,j} n_{i,j}.$$

By comparing (B.2) with (B.4) and taking into account (B.7), we obtain finally

$$(B.8) \quad n_{i,jk} n_{i,jk} = \frac{1}{2} \{ n_{i,jj} n_{i,kk} + n_i n_{i,jkk} \} + (n_{i,j} n_{i,j})_{,kk},$$

which is eq. (26).

For what is concerning eq. (27), first we observe that

$$(B.9) \quad (\mathbf{n} \cdot \text{rot } \mathbf{n})^2 = n_i \varepsilon_{ijk} n_{k,j} n_l \varepsilon_{lmp} n_{p,m}$$

and, by referring to the identity

$$(B.10) \quad \varepsilon_{ijk} \varepsilon_{lmp} = \delta_{il} \delta_{jm} \delta_{kp} + \delta_{jl} \delta_{km} \delta_{ip} + \delta_{kl} \delta_{im} \delta_{jp} - \delta_{il} \delta_{km} \delta_{jp} - \delta_{kl} \delta_{jm} \delta_{ip} - \delta_{jl} \delta_{im} \delta_{kp},$$

eq. (B.9) becomes

$$(B.11) \quad n_{k,j} n_{k,j} = n_{k,j} n_{j,k} + (\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + (\mathbf{n} \times \text{rot } \mathbf{n})^2.$$

On the other hand, from the symmetry property of differentiation

$$(B.12) \quad n_j n_{k,kj} = n_j n_{k,jk},$$

one can derive

$$(B.13) \quad n_{j,k} n_{k,j} = n_{j,j} n_{k,k} + (n_j n_{k,j})_{,k} - (n_j n_{k,k})_{,j} = (\text{div } \mathbf{n})^2 - \text{div } (\mathbf{n} \text{ div } \mathbf{n} + \mathbf{n} \times \text{rot } \mathbf{n}).$$

By substituting (B.13) into (B.11), eq. (27) is easily obtained.

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