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Comments on free elastic energy for uniaxial nematic liquid crystals

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This paper concerns free elastic energy that is functional for static deformations of a nematic liquid crystal. The free elastic energy density is analysed as a non-negative quadratic form of the first-order derivatives of the director. The resulting conditions imply a system of inequalities to be held by Frank's elastic moduli, which update Ericksen's inequalities. The rejection of surface-like free elastic energy terms from bulk free elastic energy is suggested on the basis of both known and some new arguments.

Keywords: nematic liquid crystals; nematics elastic moduli; Frank's elastic constant; free elastic energy for nematic liquid crystals

1. Introduction

Fifty years ago Frank published the complete theory of static elastic phenomena (Frank–Oseen theory (*1–3*)) and forty years ago Leslie published the complete theory of dynamic phenomena (Ericksen–Leslie theory (*4–7*)) for uniaxial nematic liquid crystals, interpreted as continuous media. During the decades have passed since then, both theories have been confirmed in numerous theoretical and experimental works. In particular, it has been well established that two three-dimensional vector fields, a liquid velocity and a director, are sufficient for the complete description of mechanical phenomena in these materials. Stationary states of nematic liquid crystals are described by a unit dimensionless vector field n (with no defined sense), called a director, which represents a locally-averaged direction of nematic rode-like molecules. The corresponding equations governing static deformations can be derived as the Euler–Lagrange equations for a free energy functional defining the constitutive relationships for the nematics under study. Since nematics are anisotropic liquids, these static deformations are interpreted as equilibrium states of the director fields, enforced in bulk by interactions of confining surfaces and external forces, being referred to the stationary states established by the boundary conditions only.

Let V be a volume filled with nematics, bounded by a sufficiently smooth surface S in three-dimensional real space equipped with Cartesian co-ordinates $x = (x_1, x_2, x_3)$. The free energy functional of confined nematics influenced by external electric and magnetic fields can be considered in the form of a sum of the bulk and the surface functional

$$F = \iiint_V (f_K + f_E + f_M + f_A + f_D)\, dV + \oiint_S f_S\, dS, \tag{1a}$$

or

$$F = \iiint_V (f_K + f_E + f_M)\, dV + \oiint_S (f_S + f_{AS} + f_{DS})\, dS. \tag{1b}$$

The bulk free-energy density consists of three basic terms: the density of the elastic distortion energy f_K, and the densities of the energy of interaction of nematics with an electric or a magnetic field, f_E and f_M. The densities f_E and f_M may be expressed in the commonly accepted form, $f_E = -\frac{1}{2}E \cdot D$, $f_M = -\frac{1}{2}H \cdot B$, with the well-known dependence of electric fields E, D and the magnetic fields H, B on a director field involving constitutive material constants, and are not discussed in this work. The subject of further consideration is the bulk free elastic energy density, which has the commonly accepted basic form, with the splay, twist and bend elastic moduli (Frank's constants k_{11}, k_{22}, k_{33} (*2*)):

$$f_K = \frac{1}{2}\left[k_{11}(\nabla \cdot n)^2 + k_{22}(n \cdot (\nabla \times n))^2 + k_{33}(n \times (\nabla \times n))^2\right], \tag{2}$$

and the surface-like free elastic energy densities f_D (in the form introduced by Frank (*2*)) and f_A (in the form introduced by Nehring and Saupe (*3*)):

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$$f_D = -\tfrac{1}{2}(k_{22}+k_{24})\,\nabla\cdot[(\nabla\cdot n)\,n + n\times(\nabla\times n)]$$
$$= -\tfrac{1}{2}(k_{22}+k_{24})\,\nabla\cdot[(\nabla\cdot n)\,n - (n\cdot\nabla)\,n], \quad (3a)$$

$$f_A = k_{13}\,\nabla\cdot[(\nabla\cdot n)\,n]. \quad (4a)$$

Two questions that remain under discussion (*8–19*) are how to account for the second-order terms with saddle-splay and splay-bend elastic constants k_{24} and k_{13} and how to describe the boundary conditions with the free-energy density of the nematics–substrate interaction f_S. These two questions are either addressed in this work.

Under the assumption that the director field is twice continuously differentiable and the continuous field of unit external normal vectors κ is defined on a confining surface, two surface elasticity terms can be accounted for in the free surface elastic energy functional (1b) with the corresponding surface densities:

$$f_{DS} = -\tfrac{1}{2}(k_{22}+k_{24})\;\kappa\cdot[(\nabla\cdot n)\,n - (n\cdot\nabla)\,n], \quad (3b)$$

$$f_{AS} = k_{13}\;\kappa\cdot[(\nabla\cdot n)\,n]. \quad (4b)$$

These two terms have been extensively discussed recently (*8–19*). The free energy functional can be considered if form (1a) involving terms (3a) or (4a) or in form (1b) involving terms (3b) or (4b). Further, let $f_F \equiv f_K + f_D$ and $f_N \equiv f_K + f_D + f_A$.

2. Free elastic energy functional and elastic moduli for nematic liquid crystals

2.1 Bulk free elastic energy density for nematic liquid crystals

A director field corresponding to static deformations of a nematic liquid crystal, which are enforced by the interaction of a confining surface S (i.e. boundary conditions) and static external fields, should be a minimiser of the free energy functional (1). This description is phenomenological by interpreting liquid crystal as a material continuum. A nematic liquid crystal, being an amorphous anisotropic liquid without a specific shape like a solid, is very unlikely to be a non-simple material, which is characterised by the free elastic energy functional involving higher-order derivatives of a defining field for describing strong deformations. Strong distortions in such continuous media can hardly be imagined. Thus, the free elastic energy functional for nematics should be constructed consequently as a non-negative quadratic form of only first-order derivatives of the director. If it were to be updated with second-order director derivative terms, it should be the sum of two non-negative quadratic forms. In every case this construction should lead to formulating governing equations in the form of Euler–Lagrange equations and well-posed initial-boundary value (evolutional) problems or boundary value (static) problems.

To resume possible forms of the bulk free elastic energy for nematics, the following symbols related to Cartesian co-ordinates $x = (x_1, x_2, x_3)$ will be used.

Director $n(x) \equiv (n_1(x_1, x_2, x_3), n_2(x_1, x_2, x_3), n_3(x_1, x_2, x_3))$, $|n| = 1$ is a unit dimensionless vector with no defined sense; derivatives are denoted with subscripts $\partial_i \equiv \frac{\partial}{\partial x_i}$, $\partial_j n_i \equiv n_{i,j}$, $\nabla \equiv (\partial_1, \partial_2, \partial_3)$, $\nabla g = \operatorname{grad} g = (g_{,i}) = (g_{,1}, g_{,2}, g_{,3})$ for a differentiable scalar field g, $\nabla\cdot n = div\, n = n_{1,1} + n_{2,2} + n_{3,3}$;

$$\nabla\times n = \operatorname{rot} n = \operatorname{curl} n$$
$$= (n_{2,3} - n_{3,2},\, n_{3,1} - n_{1,3},\, n_{1,2} - n_{2,1});$$
$$\nabla n = (n_{1,1}, n_{1,2}, n_{1,3}, n_{2,1}, n_{2,2}, n_{2,3}, n_{3,1}, n_{3,2}, n_{3,3}) \quad (5)$$

is used instead of

$$\nabla n = \begin{bmatrix} n_{1,1} & n_{2,1} & n_{3,1} \\ n_{1,2} & n_{2,2} & n_{3,2} \\ n_{1,3} & n_{2,3} & n_{3,3} \end{bmatrix}; \quad \|\nabla n\| \equiv \left[\sum_{i=1}^{3}\sum_{j=1}^{3}(n_{i,j})^2\right]^{\frac{1}{2}}.$$

The summation over repeated indices is further assumed, e.g. $n_{i,j}n_{i,j} \equiv \sum_{i=1}^{3}\sum_{j=1}^{3} n_{i,j}n_{i,j}$.

For a director as a unit dimensionless vector field, the following equalities hold under assumption of once or twice continuous differentiability:

$$n_i n_i = 1; \quad \nabla(n_i n_i) = 0 \text{ or } n_i n_{i,j} = 0,\ j = 1, 2, 3; \quad n\times(\nabla\times n) = -(n\cdot\nabla)\,n; \quad (6)$$

$$\nabla\cdot((\nabla\cdot n)\,n + n\times(\nabla\times n)) = \partial_i(n_i n_{j,j} - n_j n_{i,j})$$
$$= n_{i,i}n_{j,j} + n_i n_{j,ji} - n_{j,i}n_{i,j} - n_j n_{i,ji}$$
$$= n_{i,i}n_{j,j} - n_{j,i}n_{i,j}. \quad (7)$$

The simplest quadratic form of the first-order director derivative, being the sum of its squares, can be decomposed into four parts (*17, 18*):

$$\|\nabla n\|^2 = (\nabla\cdot n)^2 + (\nabla\times n)^2 - \nabla\cdot((\nabla\cdot n)\,n - (n\cdot\nabla)\,n)$$
$$= (\nabla\cdot n)^2 + (n\cdot(\nabla\times n))^2 + (n\times(\nabla\times n))^2$$
$$- \nabla\cdot((\nabla\cdot n)\,n + n\times(\nabla\times n))$$
$$= n_{i,i}n_{j,j} + (n_{i,j}n_{i,j} - n_{i,j}n_{j,i} - n_j n_k n_{i,j} n_{i,k})$$
$$+ n_j n_k n_{i,j} n_{i,k} - (n_{i,i}n_{j,j} - n_{j,i}n_{i,j}),$$
$$= n_{i,j}n_{i,j} \quad (8)$$

three of which can be recognised in the basic form of free elastic energy density with three Frank's elastic moduli (*2*, *17*, *18*):

$$
\begin{aligned}
f_K(n,\nabla n) = {} & \tfrac{1}{2}k_{11}(\nabla\cdot n)^2 + \tfrac{1}{2}k_{22}(n\cdot(\nabla\times n))^2 \\
& + \tfrac{1}{2}k_{33}(n\times(\nabla\times n))^2 \\
= {} & \tfrac{1}{2}k_{11}n_{i,i}n_{j,j} \\
& + \tfrac{1}{2}k_{22}\left(n_{i,j}n_{i,j} - n_{i,j}n_{j,i} - n_j n_k n_{i,j} n_{i,k}\right) \\
& + \tfrac{1}{2}k_{33}n_j n_k n_{i,j} n_{i,k}. \\
= {} & \tfrac{1}{2}k_{11}n_{i,i}n_{j,j} + \tfrac{1}{2}k_{22}n_{i,j}n_{i,j} \\
& + \tfrac{1}{2}(k_{33}-k_{22})n_j n_{i,j} n_k n_{i,k} \\
& - \tfrac{1}{2}k_{22}n_{i,j}n_{j,i}.
\end{aligned} \tag{9}
$$

This functional has a very specific feature, which constitutes nematic liquid crystals as a unique class of continua, namely the Helmholtz decomposition of the director, which relates its intrinsic structure. According to the Helmholtz theorem (cf. e.g. (*20*)), a three-dimensional differentiable vector field, defined on the whole space and vanishing at infinity or defined on a connected domain confined by a sufficiently smooth surface, may be uniquely decomposed into two additive parts, one of which being irrotational (with a possible harmonic part contained therein) and the other being solenoidal. A vector may be thus written as the sum of the gradient of a scalar potential (the irrotational part with a null curl) and the curl of a vectorial potential (the solenoidal part with a null gradient). Let $n = p + s$, $\nabla\times p = 0$ and $\nabla\cdot s = 0$. Then,

$$
\begin{aligned}
f_K(n,\nabla n) = {} & \tfrac{1}{2}k_{11}(\nabla\cdot p)^2 + \tfrac{1}{2}k_{22}((p+s)\cdot(\nabla\times s))^2 \\
& + \tfrac{1}{2}k_{33}((p+s)\times(\nabla\times s))^2.
\end{aligned} \tag{10}
$$

In this functional, the derivatives of a director are grouped into three terms: the scalar gradient $\nabla\cdot n = \nabla\cdot p$ (for a splay deformation) and two components of the vectorial curl, parallel to a director $(n\cdot(\nabla\times n))\,n = (n\cdot(\nabla\times s))\,n$ (for a twist deformation) and perpendicular to a director $n\times(\nabla\times n) = n\times(\nabla\times s)$ (for a bend deformation). With the three constitutive constants being positive, $k_{11},\ k_{22},\ k_{33} > 0$, the functional (11) is a non-negative definite. It is positive-valued for all director fields with non-null irrotational or solenoidal parts and becomes null only for harmonic fields that satisfy both equalities $\nabla\cdot n = 0$ and $\nabla\times n = 0$. The equilibrium of a stationary state of a nematic is influenced by a balance between these two components of a director, defined by the magnitudes of the constitutive constants $k_{11},\ k_{22},\ k_{33}$ for splay, twist and bend. Evidently, the introduction of an additional term into formula (10) would interfere and perturb this particular structure. Frank left the component (7) with the fourth saddle-splay elastic constant k_{24}, since the term f_D (3) might not be eliminated by accounting symmetry relations defining a uniaxial nematic liquid crystal, and has written the elastic free-energy density (*2, 17*) as:

$$
\begin{aligned}
f_F(n,\nabla n) = {} & \tfrac{1}{2}k_{11}(\nabla\cdot n)^2 + \tfrac{1}{2}k_{22}(n\cdot(\nabla\times n))^2 \\
& + \tfrac{1}{2}k_{33}(n\times(\nabla\times n))^2 \\
& - \tfrac{1}{2}(k_{22}+k_{24})\nabla\cdot((\nabla\cdot n)n + n\times(\nabla\times n)) \\
= {} & \tfrac{1}{2}k_{11}n_{i,i}n_{j,j} \\
& + \tfrac{1}{2}k_{22}(n_{i,j}n_{i,j} - n_{i,j}n_{j,i} - n_j n_k n_{i,j} n_{i,k}) \\
& + \tfrac{1}{2}k_{33}n_j n_k n_{i,j} n_{i,k} \\
& - \tfrac{1}{2}(k_{22}+k_{24})(n_{i,i}n_{j,j} - n_{j,i}n_{i,j}) \\
= {} & \tfrac{1}{2}(k_{22}+k_{24})\,\|\nabla n\|^2 \\
& + \tfrac{1}{2}(k_{11} - k_{22} - k_{24})\,(\nabla\cdot n)^2 \\
& + \tfrac{1}{2}(-k_{24})\,(n\cdot(\nabla\times n))^2 \\
& + \tfrac{1}{2}(k_{33} - k_{22} - k_{24})\,(n\times(\nabla\times n))^2. \\
= {} & \tfrac{1}{2}(k_{11} - k_{22} - k_{24})n_{i,i}n_{j,j} + \tfrac{1}{2}k_{22}n_{i,j}n_{i,j} \\
& + \tfrac{1}{2}(k_{33}-k_{22})n_j n_{i,j} n_k n_{i,k} + \tfrac{1}{2}k_{24}n_{j,i}n_{i,j}.
\end{aligned} \tag{11}
$$

The term f_D (3), in his original notation, contains only the first-order derivative of a director, and may be transformed into a second-order term by virtue of formula (7). Some one-constant, two-constants or three-constant variants of formula (11) can be considered.

The one-constant approximations are:

$$
\begin{gathered}
k_{11} = k_{22} = k_{33} = k,\ \ k_{24} = 0 \\
\text{and then } f_F(n,\nabla n) = \tfrac{1}{2}k\|\nabla n\|^2; \\
k_{11} = k_{22} = k_{33} = k,\ \ k_{24} = -k_{22} \\
\text{and then } f_F(n,\nabla n) = \tfrac{1}{2}k\,((\nabla\cdot n)^2 + (\nabla\times n)^2).
\end{gathered}
$$

The two-constant approximations are:

$$
\begin{aligned}
& k_{22} = k_{33},\ k_{24} = k_{11} - k_{22} \text{ and then} \\
& f_F(n,\nabla n) = \tfrac{1}{2}k_{11}(\,\|\nabla n\|^2 - (\nabla\times n)^2) + \tfrac{1}{2}k_{22}(\nabla\times n)^2; \\
& k_{22} = k_{33},\ k_{24} = -k_{22} \text{ and then} \\
& f_F(n,\nabla n) = \tfrac{1}{2}k_{11}(\nabla\cdot n)^2 + \tfrac{1}{2}k_{22}(\nabla\times n)^2.
\end{aligned}
$$

The three-constant forms are:
with $k_{24} = \tfrac{1}{2}(k_{11} - k_{22})$ (supposed by Nehring and Saupe (*3*))

$$
\begin{aligned}
f_F(n,\nabla n) = {} & \tfrac{1}{4}(k_{11}+k_{22})\,\|\nabla n\|^2 + \tfrac{1}{4}(k_{11}-k_{22})\,(\nabla\cdot n)^2 \\
& - \tfrac{1}{4}(k_{11}-k_{22})\,(n\cdot(\nabla\times n))^2 \\
& + \tfrac{1}{4}(2k_{33} - k_{11} - k_{22})\,(n\times(\nabla\times n))^2;
\end{aligned}
$$

with

$$k_{24}=0:\quad f_F(n,\nabla n)=\tfrac{1}{2}k_{22}\|\nabla n\|^2+\tfrac{1}{2}(k_{11}-k_{22})\,(\nabla\cdot n)^2+\tfrac{1}{2}(k_{33}-k_{22})\,(n\times(\nabla\times n))^2;$$

with $k_{24}=-k_{22}$ (basic form):

$$f_K(n,\nabla n)=\tfrac{1}{2}k_{11}(\nabla\cdot n)^2+\tfrac{1}{2}k_{22}(n\cdot(\nabla\times n))^2+\tfrac{1}{2}k_{33}\times(n\times(\nabla\times n))^2.$$

These forms are non-negative definite under condition $k>0$ or $k_{33}>k_{11}>k_{22}>0$ or only $k_{33},\ k_{22},\ k_{11}>0$ (*17–19*). Term f_D (3) makes it possible to recover the free elastic energy density to a form close to (8), preserving all of the four principal groups of first-order derivatives of the director.

Nehring and Saupe (*3*) have introduced another second-order term f_A (3), which may not be transformed into a first-order term:

$$\begin{aligned}f_N(n,\nabla n,\nabla(\nabla n))&=\tfrac{1}{2}k_{11}(\nabla\cdot n)^2+\tfrac{1}{2}k_{22}(n\cdot(\nabla\times n))^2+\tfrac{1}{2}k_{33}(n\times(\nabla\times n))^2\\&\quad-\tfrac{1}{2}(k_{22}+k_{24})\,\nabla\cdot((\nabla\cdot n)\,n+n\times(\nabla\times n))\\&\quad+k_{13}\nabla\cdot((\nabla\cdot n)\,n).\\&=\tfrac{1}{2}(k_{11}-k_{22}-k_{24})n_{i,i}n_{j,j}+\tfrac{1}{2}k_{22}n_{i,j}n_{i,j}\\&\quad+\tfrac{1}{2}(k_{33}-k_{22})n_jn_{i,j}n_kn_{i,k}+\tfrac{1}{2}k_{24}n_{j,i}n_{i,j}\\&\quad+k_{13}\left(n_{i,i}n_{j,j}+n_in_{j,ji}\right).\end{aligned}\qquad(12)$$

During the recent half-century many attempts, both theoretical and experimental, have been made to verify which form of this functional is adequate. Some conclusions can be formulated, based on the results published to date. The magnitudes of the three Frank's elastic constants, being on order of 10 pN, differ from each other and for all known nematic liquid crystals $k_{33}>k_{11}>k_{22}>0$ or (much less frequently) $k_{11}>k_{33}>k_{22}>0$; a material with equal constants has not been found (*21, 22*). Attempts at determining the magnitudes of these constants, concerning models of molecular interactions, lead to partially contradictory conclusions and rather imprecise values (if any). The question of the significance of surface-like elasticity terms (3) and (4) is still ambiguous (*8–19*). Experiments performed to determine these values have resulted in unclear or negative conclusions. Another important and partially resolved question is the proper description of a nematics–substrate interaction and methods for its experimental verification (*23*). Some discussion is added below.

2.2 Non-negativity of bulk free elastic energy density for nematic liquid crystals as quadratic forms of director derivatives

The free elastic energy density with four Frank's elastic moduli (without second-order terms) is postulated to be a non-negative quadratic form of the first-order derivatives of a director $\nabla n=\left(n_{1,1},\ n_{1,2},\ n_{1,3},\ n_{2,1},\ n_{2,2},\ n_{2,3},\ n_{3,1},\ n_{3,2},\ n_{3,3}\right)$:

$$f_F(n,\nabla n)=\tfrac{1}{2}(\nabla n)M(\nabla n)^T,\qquad(13)$$

with a symmetric form matrix M. This matrix follows from the general expression with four elastic constants developed by Frank (*2*) (originally by considering a particular case when $n=(0,\ 0,\ 1)$). Frank's result is the point of departure for the following considerations. Let the free elastic energy density be given in the form (11):

$$f_F(n,\nabla n)=\tfrac{1}{2}(k_{11}-k_{22}-k_{24})n_{i,i}n_{j,j}+\tfrac{1}{2}k_{22}n_{i,j}n_{i,j}+\tfrac{1}{2}(k_{33}-k_{22})n_jn_{i,j}n_kn_{i,k}+\tfrac{1}{2}k_{24}n_{j,i}n_{i,j}.$$

Let $K_1\equiv k_{11},\ K_2\equiv k_{22},\ K_3\equiv k_{33},\ K_4\equiv k_{24},\ K_5\equiv k_{33}-k_{22},\ K_6\equiv k_{11}-k_{22}-k_{24}$ and $u_{ij}\equiv K_5n_in_j$. Then M takes the form

$$\begin{bmatrix}K_1+u_{11}&u_{12}&u_{13}&0&K_6&0&0&0&K_6\\u_{12}&K_2+u_{22}&u_{23}&K_4&0&0&0&0&0\\u_{13}&u_{23}&K_2+u_{33}&0&0&0&K_4&0&0\\0&K_4&0&K_2+u_{11}&u_{12}&u_{13}&0&0&0\\K_6&0&0&u_{12}&K_1+u_{22}&u_{23}&0&0&K_6\\0&0&0&u_{13}&u_{23}&K_2+u_{33}&0&K_4&0\\0&0&K_4&0&0&0&K_2+u_{11}&u_{12}&u_{13}\\0&0&0&0&0&K_4&u_{12}&K_2+u_{22}&u_{23}\\K_6&0&0&0&K_6&0&u_{13}&u_{23}&K_1+u_{33}\end{bmatrix}.\qquad(14)$$

Firstly, the non-negativity of this quadratic form will be examined without accounting constraints following from the director definition. The conditions for positive or non-negative definiteness of this form and its matrix may be easily obtained by considering special cases of nematic orientations. They follow from requiring positive or non-negative values of the determinants of the principal submatrices of matrix M.

For $n = (0,\ 0,\ 1)$ one obtains M equal to

$$\begin{bmatrix} K_1 & 0 & 0 & 0 & K_6 & 0 & 0 & 0 & K_6 \\ 0 & K_2 & 0 & K_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & K_3 & 0 & 0 & 0 & K_4 & 0 & 0 \\ 0 & K_4 & 0 & K_2 & 0 & 0 & 0 & 0 & 0 \\ K_6 & 0 & 0 & 0 & K_1 & 0 & 0 & 0 & K_6 \\ 0 & 0 & 0 & 0 & 0 & K_3 & 0 & K_4 & 0 \\ 0 & 0 & K_4 & 0 & 0 & 0 & K_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & K_4 & 0 & K_2 & 0 \\ K_6 & 0 & 0 & 0 & K_6 & 0 & 0 & 0 & K_1 + K_5 \end{bmatrix}.$$

This matrix is positive (non-negative) definite if its principal determinants are positive (non-negative):

(1) $K_1 > 0;$
(2) $K_1 \cdot K_2 > 0;$
(3) $K_1 \cdot K_2 \cdot K_3 > 0;$
(4) $K_1 \cdot K_3 \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(5) $\left[K_1{}^2 - (K_1 - K_2 - K_4)^2\right] \cdot K_3 \cdot \left(K_2{}^2 - K_4{}^2\right) > 0$ or $(2K_1 - K_2 - K_4) \cdot (K_2 + K_4) \cdot K_3 \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(6) $\left[K_1{}^2 - (K_1 - K_2 - K_4)^2\right] \cdot K_3{}^2 \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(7) $K_3 \cdot \left[K_1{}^2 - (K_1 - K_2 - K_4)^2\right] \cdot \left(K_2 \cdot K_3 - K_4{}^2\right) \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(8) $\left[K_1{}^2 - (K_1 - K_2 - K_4)^2\right] \cdot \left(K_2 \cdot K_3 - K_4{}^2\right)^2 \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(9) $\left(K_2 \cdot K_3 - K_4{}^2\right)^2 \cdot \left(K_2{}^2 - K_4{}^2\right) \cdot \left\{K_1 \cdot \left[K_1 \cdot (K_2 + K_3 + 2K_4) - (K_2 + K_4)^2\right] - (K_1 - K_2 - K_4)^2 \cdot (K_2 + K_3 + 2K_4)\right\} > 0;$

or equivalently
$\left(K_2 \cdot K_3 - K_4{}^2\right)^2 \cdot \left(K_2{}^2 - K_4{}^2\right) \cdot (K_2 + K_4) \cdot [(K_1 - K_2 - K_4) \cdot (K_2 + K_3 + 2K_4) + K_1 \cdot (K_3 + K_4)] > 0.$

These conditions imply the following constraints for the elastic moduli: $K_1 > 0$; $K_2 > 0$; $K_3 > 0$; $K_2{}^2 - K_4{}^2 > 0$; $2K_1 - K_2 - K_4 > 0$; $K_2 \cdot K_3 - K_4{}^2 > 0$; and $(K_1 - K_2 - K_4) \cdot (K_2 + K_3 + 2K_4) + K_1 \cdot (K_3 + K_4) > 0$.

With $K_4 = -K_2$, which corresponds to the energy density with three Frank's elastic constants $f_F = f_K$, $f_D = 0$, the inequalities (4)–(9) may be satisfied in the weak form only and take the form of identity $0 = 0$; the inequalities (1)–(3) imply the conditions $K_1 > 0$, $K_2 > 0$ and $K_3 > 0$.

For $n = (0, 1, 0)$, one obtains M equal to

$$\begin{bmatrix} K_1 & 0 & 0 & 0 & K_6 & 0 & 0 & 0 & K_6 \\ 0 & K_3 & 0 & K_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & K_2 & 0 & 0 & 0 & K_4 & 0 & 0 \\ 0 & K_4 & 0 & K_2 & 0 & 0 & 0 & 0 & 0 \\ K_6 & 0 & 0 & 0 & K_1 + K_5 & 0 & 0 & 0 & K_6 \\ 0 & 0 & 0 & 0 & 0 & K_2 & 0 & K_4 & 0 \\ 0 & 0 & K_4 & 0 & 0 & 0 & K_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & K_4 & 0 & K_3 & 0 \\ K_6 & 0 & 0 & 0 & K_6 & 0 & 0 & 0 & K_1 \end{bmatrix}.$$

This matrix is positive (non-negative) definite if the principal determinants are positive (non-negative):

(1) $K_1 > 0;$
(2) $K_1 \cdot K_3 > 0;$
(3) $K_1 \cdot K_2 \cdot K_3 > 0;$
(4) $K_1 \cdot K_2 \cdot \left(K_2 \cdot K_3 - K_4{}^2\right) > 0;$
(5) $K_2 \cdot \left[K_1 \cdot (K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right] \cdot \left(K_2 \cdot K_3 - K_4{}^2\right) > 0$ or $K_2 \cdot [K_1 \cdot (K_2 + K_3 + 2K_4) - (K_2 + K_4)^2\Big] \cdot \left(K_2 \cdot K_3 - K_4{}^2\right) > 0;$
(6) $K_2{}^2 \cdot \left[K_1 \cdot (K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right] \cdot \left(K_2 \cdot K_3 - K_4^2\right) > 0;$
(7) $K_2 \cdot \left[K_1 \cdot (K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right] \cdot \left(K_2 \cdot K_3 - K_4{}^2\right) \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(8) $\left[K_1 \cdot (K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right] \cdot \left(K_2 \cdot K_3 - K_4{}^2\right)^2 \cdot \left(K_2{}^2 - K_4{}^2\right) > 0;$
(9) $\left(K_2 \cdot K_3 - K_4{}^2\right)^2 \cdot \left(K_2{}^2 - K_4{}^2\right) \cdot \{K_1 \cdot [(K_1 - K_2 + K_3) \cdot (K_2 + K_3 + 2K_4) - (K_3 + K_4)^2] - (K_1 - K_2 - K_4)^2 \cdot (K_2 + K_3 + 2K_4)\} > 0$

or equivalently

$\left(K_2 \cdot K_3 - K_4{}^2\right)^2 \cdot \left(K_2{}^2 - K_4{}^2\right) \cdot (K_2 + K_4) \cdot [(K_1 - K_2 - K_4) \cdot (K_2 + K_3 + 2K_4) + K_1 \cdot (K_3 + K_4)] > 0.$

These conditions imply the following constraints for the elastic moduli: $K_1 > 0$; $K_2 > 0$; $K_3 > 0$; $K_2{}^2 - K_4{}^2 > 0$; $K_1 \cdot (K_2 + K_3 + 2K_4)(K_2 + K_4)^2 > 0$; $K_2 \cdot K_3 - K_4{}^2 > 0$; and $(K_1 - K_2 - K_4) \cdot (K_2 + K_3 + 2K_4) + K_1 \cdot (K_3 + K_4) > 0$.

With $K_4 = -K_2$, which corresponds to the energy density with three Frank's elastic constants

$f_F = f_K$, $f_D = 0$, the inequalities (7)–(9) may be satisfied in the weak form only and take the form of identity 0 = 0; the inequalities (1)–(6) imply the conditions $K_1 > 0$, $K_2 > 0$ and $K_3 - K_2 > 0$.

For $n = (1,\ 0,\ 0)$, one obtains M equal to

$$\begin{bmatrix} K_1+K_5 & 0 & 0 & 0 & K_6 & 0 & 0 & 0 & K_6 \\ 0 & K_2 & 0 & K_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & K_2 & 0 & 0 & 0 & K_4 & 0 & 0 \\ 0 & K_4 & 0 & K_3 & 0 & 0 & 0 & 0 & 0 \\ K_6 & 0 & 0 & 0 & K_1 & 0 & 0 & 0 & K_6 \\ 0 & 0 & 0 & 0 & 0 & K_2 & 0 & K_4 & 0 \\ 0 & 0 & K_4 & 0 & 0 & 0 & K_3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & K_4 & 0 & K_2 & 0 \\ K_6 & 0 & 0 & 0 & K_6 & 0 & 0 & 0 & K_1 \end{bmatrix}.$$

This matrix is positive (non-negative) definite if the principal determinants are positive (non-negative):

(1) $K_1 - K_2 + K_3 > 0;$
(2) $(K_1 - K_2 + K_3)\cdot K_2 > 0;$
(3) $(K_1 - K_2 + K_3)\cdot {K_2}^2 > 0;$
(4) $(K_1 - K_2 + K_3)\cdot K_2\cdot\left(K_2\cdot K_3 - {K_4}^2\right) > 0;$
(5) $K_2\cdot\left[K_1\cdot(K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right]\cdot(K_2\cdot K_3 - {K_4}^2) > 0$
or $K_2\cdot\left[K_1\cdot(K_2 + K_3 + 2K_4) - (K_2 + K_4)^2\right]\cdot(K_2\cdot K_3 - {K_4}^2) > 0;$
(6) ${K_2}^2\cdot\left[K_1\cdot(K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right]\cdot(K_2\cdot K_3 - {K_4}^2) > 0;$
(7) $K_2\cdot\left[K_1\cdot(K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right]\cdot(K_2\cdot K_3 - {K_4}^2)^2 > 0;$
(8) $\left[K_1\cdot(K_1 - K_2 + K_3) - (K_1 - K_2 - K_4)^2\right]\cdot(K_2\cdot K_3 - {K_4}^2)^2\cdot({K_2}^2 - {K_4}^2) > 0;$
(9) $\left(K_2\cdot K_3 - {K_4}^2\right)^2\cdot\left(K_2^2 - {K_4}^2\right)\cdot(K_2 + K_4)\cdot[(2K_1 - K_2 - K_4)\cdot(K_1 - K_2 + K_3) - 2(K_1 - K_2 - K_4)^2] > 0$

or equivalently

$$({K_2}\cdot K_3 - {K_4}^2)^2\cdot({K_2}^2 - {K_4}^2)\cdot(K_2 + K_4)\cdot[(K_1 - K_2 - K_4)\cdot(K_2 + K_3 + 2K_4) + K_1\cdot(K_3 + K_4)] > 0.$$

These conditions imply the following constraints for the elastic moduli: $K_1 - K_2 + K_3 > 0$; $K_2 > 0$; ${K_2}^2 - {K_4}^2 > 0$; $K_1\cdot(K_2 + K_3 + 2K_4) - (K_2 + K_4)^2 > 0$; $K_2\cdot K_3 - {K_4}^2 > 0$; and $(K_1 - K_2 - K_4)\cdot(K_2 + K_3 + 2K_4) + K_1\cdot(K_3 + K_4) > 0$.

With $K_4 = -K_2$, which corresponds to the energy density with three Frank's elastic constants $f_F = f_K$, $f_D = 0$, the inequalities (8)–(9) may be satisfied in the weak form only and take the form of identity 0 = 0; the inequalities (1)–(7) imply the conditions $K_1 > 0$, $K_2 > 0$ and $K_3 - K_2 > 0$.

It follows from the conditions for positive (or non-negative) definiteness in all these particular co-ordinate system orientations that the form matrix (and free elastic energy density functional) is positive definite if the following inequalities hold:

$$\begin{aligned} &K_1 > 0;\quad K_2 > 0;\quad K_3 > 0;\quad {K_2}^2 - {K_4}^2 > 0;\\ &2K_1 - K_2 - K_4 > 0;\quad K_1 - K_2 + K_3 > 0;\\ &K_2\cdot K_3 - {K_4}^2 > 0; K_1\cdot(K_2 + K_3 + 2K_4) - (K_2 + K_4)^2 > 0; (K_1 - K_2 - K_4)\cdot(K_2 + K_3 + 2K_4) + K_1\cdot(K_3 + K_4) > 0. \end{aligned} \tag{15}$$

The five first conditions are Ericksen inequalities (*4*). The non-negativity is guaranteed if these inequalities are satisfied in the weak form. In the case when $K_4 = -K_2$, two of these inequalities can hold only in the weak form and become identities 0 = 0, while the others are equivalent to the inequalities

$$K_1 > 0;\quad K_2 > 0;\quad K_3 - K_2 > 0. \tag{16}$$

These conditions characterise the quadratic form $f_F(n,\nabla n) = \frac{1}{2}(\nabla n)M(\nabla n)^T$ for arbitrary magnitudes of the components of the director derivative ∇n, that are treated as linearly independent when the constraints following from the assumption $|n| = 1$ are not accounted for. The assumption $n_i n_i = 1$ yields three linear constraints for $n_{i,j}$ (6) and then only six of the nine first-order derivatives of the director components are linearly independent. For $n = (0,\ 0,\ 1)$ with $n_{3,j} = 0,\ j = 1, 2, 3,$ the necessary and sufficient conditions for non-negative definiteness of $f_F(n,\nabla n) = \frac{1}{2}(\nabla n)M(\nabla n)^T$ reduce to requiring non-negativity of the first six principal determinants of the matrix M, which imply Ericksen's inequalities: $K_1 \geq 0$; $K_2 \geq 0$; $K_3 \geq 0$; $K_2^2 - K_4^2 \geq 0$; and $2K_1 - K_2 - K_4 \geq 0$ (*3*, *17–19*), usually written as

$$\begin{aligned} &K_1 \geq 0,\quad K_2 \geq 0,\quad K_3 \geq 0,\quad |K_2| \geq |K_4|,\\ &|K_1| \geq |K_1 - K_2 - K_4|. \end{aligned} \tag{17}$$

For $K_4 = -K_2$ Ericksen's inequalities reduce to three inequalities

$$K_1 \geq 0,\quad K_2 \geq 0,\quad K_3 \geq 0. \tag{18}$$

The same conditions one obtains after re-organising matrix M are in accordance with $\nabla n = (n_{1,1}\ , n_{1,2}\ , n_{1,3}\ , n_{3,1}\ , n_{3,2}\ , n_{3,3}\ , n_{2,1}\ , n_{2,2}\ , n_{2,3})$ for $n = (0,\ 1,\ 0)$ with $n_{2,j} = 0,\ j = 1, 2, 3,$ or $\nabla n = (n_{2,1}\ , n_{2,2}\ , n_{2,3}\ , n_{3,1}\ , n_{3,2}\ , n_{3,3}\ , n_{1,1}\ , n_{1,2}\ , n_{1,3})$ for $n = (1,\ 0,\ 0)$ with $n_{1,j} = 0, j = 1, 2, 3.$

The conditions (15) were deduced for nine-dimensional vector space and include all of Ericksen's conditions (17), deduced for six-dimensional subspace (with three linear constraints). Systems of inequalities (18) and (16) differ only in the last one, which for derivatives of arbitrary three-dimensional vector fields yields $K_3 - K_2 \geq 0$. This inequality is satisfied for all known nematic liquid crystals (cf. e.g. (*21*, *22*)). Moreover, it follows from one of the inequalities (15), $K_2 \cdot K_3 - K_4{}^2 \geq 0$ (which yields the inequality $K_3 - K_2 \geq 0$), that for $K_3 < K_2$ it has to be $|K_4| < K_2$ and $f_D \neq 0$. In view of the properties of real nematics, the last assertion could be treated as an argument for taking $f_D = 0$. It is difficult to decide which systems of inequalities, (15), (16) or (17), (18), approximates physical reality better.

2.3 Saddle-splay elastic constant

The above considerations on the surface-like term f_D in the free elastic energy density for nematic liquid crystals are summarised in this section.

The saddle-splay component (4) of the free-energy density is rather apparently a second-order term, since it can be expressed, using only first-order derivatives of the director components, as a quadratic form (cf. (*2*, *17–19*)). Moreover it is a null Lagrangian (*17*, *18*) that does not contribute to bulk free energy and can be accounted for in the form of a surface integral, as in (1b). It contains the rest of the quadratic terms involving first-order director derivatives that are necessary for obtaining the free elastic energy in the simplest form of the sum of the squares of all director derivatives, when one-constant approximation is assumed. However, such approximation is evidently not suitable for describing nematics, since the splay, bend and twist constants are different for real materials. Moreover, the basic form of the free elastic energy with three elastic moduli involves all partial derivatives of all director components in the form of curl and divergence and is sufficient to describe a director uniquely and adequately. Concerning the free elastic energy functional with the density f_K (1b) as well as $f_K + f_D$ (1a) leads to a well-posed boundary-value problem for non-linear Euler–Lagrange differential equations (*17–19*).

2.4 Splay-bend elastic constant

The splay-bend component (4) of the free-energy density causes serious problem with minimisation of the functional (1a) or (1b) (*8–17*). The functional becomes unbounded from below and a resulting boundary-value problem for the Euler–Lagrange equations (describing static deformations) is ill-posed (*8*, *9*, *13–15*, *17–19*). Moreover, the second-order term (4) cannot be transformed into a first-order term, contrary to the term (3), but it is still a null Lagrangian that contributes only to the surface free energy. Nehring and Saupe (*3*) introduced it in a rather unusual way, by expanding nematics deformation using the Taylor formula with a second-order derivative and introducing this expansion into the free energy functional; this led to the conclusion that the linear term with second-order director derivatives is of the same magnitude order as the other quadratic terms with first-order director derivatives. The method they used for developing the elastic energy density resulted in an intrinsic contradiction; one of two terms originated from the same derivative of the energy density with corresponding coefficient was dropped (the term linear respective first-order derivative of the director), while the other was preserved (the term linear respective second-order derivative of the director). This method is incompatible with the general rule of elasticity theory; a free energy functional should be postulated consequently as a sum of quadratic (at least non-negative definite) forms of derivatives of subsequent orders of a governing field. Frank (*2*), in his considerations, did not account for such a term. By accounting for second-order terms consequently, one achieves well-posed boundary-value problems (*16*, *18*). The experiments for determining saddle-splay and splay-bend elastic constants resulted in rather unclear conclusions (*24*).

Experimental arguments for rejecting this splay-bend term were found from studying planar deformation states enforced in planar cells by a static electric field (*25*, *26*). It was demonstrated that an accurate determination of the boundary condition (i.e. the anchoring characteristics), together with the elastic constants, enabled one to describe planar deformation states of a nematics layer quantitatively and precisely. The boundary-free energy functional depending only on the boundary value of the tilt angle and not on its derivative was sufficient for characterising nematics–substrates interaction adequately and quantitatively. The simulation of the optical retardation, using the same magnitudes of splay and bend elastic constants and anchoring characteristics for nematic cells with thicknesses from 13.9 μm to 64.5 μm (*26*) (and with thicknesses from 1.9 μm to 31.2 μm (*27*)), resulted in reproducing the measured values with the accuracy being inferior to experimental errors. It implied no dependence of the bulk elastic constants on the nematic cell thickness and no need to exploit surface-like elastic constants (and corresponding free elastic energy terms) to describe nematics as material continua.

3. Conclusions

Some additional relations between four bulk elastic constants of nematics can be derived as conditions for non-negative definiteness of the free elastic energy functional. One suggests that the surface-like second-order elastic terms can be omitted from the free elastic energy functional and considered as surface terms together with boundary conditions. A formulation of these conditions that leads to a well-posed boundary-value problem is a separate question, the solution of which must be based on experimental results. The bulk free elastic energy density should be concerned in its basic form with three Frank elastic constants. Accounting only for the boundary free-energy density seems enough to describe the stationary states of the nematics quantitatively when the anchoring characteristics are determined from experimental observations of nematic liquid crystal cells.

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