Statistical theory of elastic constants of biaxial nematic liquid crystals

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Microscopic expressions for the elastic constants of liquid crystals composed of biaxial or uniaxial molecules are derived in the case of a weak anchoring, small distortions, and a small density. Both biaxial and uniaxial phases are considered. The expressions involve the one-particle distribution function and the potential energy of two-body short-range interactions. The theory was used to calculate the temperature dependence of the elastic constants for a system of rigid molecules similar to elipsoids with three different axes. [S1063-651X(97)04106-8]

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I. INTRODUCTION

The understanding of the elastic constants of liquid crystals is important for a number of reasons. In the first place, they appear in the description of virtually all phenomena where the variation of the director is manipulated by external fields (display devices) [1]. Second, they provide unusually sensitive probes of the microscopic structure of the ordered state. Valuable information regarding the nature and importance of various anisotropies of the intermolecular potentials and of the spatial and angular correlation functions can be derived from the study of the elastic constants. Knowledge of the elasticity of the liquid crystals is also needed in the study of defects in them [2]. There are microscopic theories [3–8] that give working expressions for the elastic constants of uniaxial nematic liquid crystals. Contrary to this, biaxial nematic liquid crystals are poorly examined because they require more complex theoretical description and are difficult to obtain experimentally. In this paper we would like to present a statistical theory of the elastic constants of biaxial nematic liquid crystals. To provide a context for our derivations we remind the reader of the main results in this field.

In 1970 Freiser [9] generalized the Maier-Saupe theory by incorporating molecules with nonaxial quadrupole symmetry in the interaction potential and predicted a phase transition sequence from isotropic to uniaxial order and then to biaxial order on cooling the sample. In 1972 Shin and Alben [10] considered a generalization of Flory's lattice model to describe a fluid of rectangular platelike objects of any length and width. They found that plates that are neither very square nor very rodlike in shape may exist in a biaxial phase at high pressure. On decreasing the pressure first a uniaxial phase and next an isotropic phase appear. In 1973 Alben [11] considered a simple Landau theory to study phase transitions in a fluid of biaxial particles. His results suggest that the phase diagram of such fluid exhibits a special critical point where two second-order critical lines meet a first-order boundary in a sharp cusp. In 1974 Straley [12] presented a generalization of the Maier-Saupe theory for biaxial particles. He identified the four main order parameters necessary to describe an ordered phase of biaxial molecules.

In 1980 Yu and Saupe observed experimentally the biaxial phase in lyotropic systems [13]. The phenomenological theory of elastic constants and viscosity coefficients of biaxial nematic liquid crystals was developed by Saupe in 1981 [14]. It was based on a generalization of the concepts used in the Frank-Oseen theory for uniaxial nematics. The author introduced twelve bulk elastic constants (and three additional surface elastic constants). Three of them were assigned to twist deformations, six to bend deformations, and three to coupling between bend and twist deformations. In Sec. VI we will present predictions of our model for the Saupe elastic constants.

Brand and Pleiner presented hydrodynamics of biaxial nematic liquid crystals and similarly to Saupe they showed that there are twelve bulk elastic constants and three surface terms in the elastic energy [15,16]. In our opinion, the most transparent derivation of the phenomenological elastic energy of biaxial nematic liquid crystals was given by Stallinga and Vertogen [17]. That is why we will use this paper as a basis for our considerations.

Kini and Chandrasekhar in 1989 discussed the feasibility of determining some of the twelve curvature elastic constants of an orthorhombic nematic liquid crystal using Saupe's continuum theory. They studied the effects of external magnetic and electric fields applied in different geometries [18]. In the same year Mulder considered the isotropic-symmetry-breaking bifurcations occurring in a class of liquid-crystal models describing particles with the symmetry of rectangular slabs [19]. His main result was the classification of the symmetries of the bifurcating solutions to the equations describing the stationary phases in terms of eigenvalues of the effective pair interactions. He also introduced the set of symmetry-adapted functions, but it was not complete [20].

Finally, we would like to mention the most important work by Singh *et al.* They used a density-functional theory to derive an expression for the distorsion free energy of molecular ordered phases and expanded it in terms of the order parameters characterizing the structure of the phase and the molecular correlation function of an effective isotropic liquid [21]. Next they derived expressions for the 12 elastic constants of a biaxial nematic phase [22]. The expressions were written in terms of order parameters and the structural parameters that involve the generalized spherical-harmonic coefficients of the direct pair correlation function of an effec-

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tive isotropic liquid. The authors tried to estimate the relative magnitudes of these constants using a reasonable guess for the values of order and structural parameters. We postpone the discussion of their results until Sec. VI.

Among problems discussed in omitted papers we would like to mention a Monte Carlo study of a biaxial lattice model [23,24], chiral biaxial liquid crystals [25,26], and phase diagrams of binary mixtures of biaxial nematogens [27].

Our paper is organized as follows. In Sec. II we present a phenomenological continuum theory of nematic liquid crystals and define basic deformations that allow us to extract all elastic constants from the distortion free energy. In Sec. III we describe a statistical theory of a nematic phase and define the microscopic distortion free energy. Then, in Sec. IV we derive general expressions for elastic constants of biaxial and uniaxial nematic liquid crystals. Exemplary calculations of the values of elastic constants for a simple model are presented in Sec. V. Some comments on the theory presented are given in Sec. VI.

II. PHENOMENOLOGICAL APPROACH

A. Description of a phase

In this section we will describe nematic liquid crystals from a phenomenological point of view [17]. We assume that at every point $\vec{r}$ inside a considered phase we can define three orthonormal vectors $(\vec{L}(\vec{r}),\vec{M}(\vec{r}),\vec{N}(\vec{r}))$ that reflect some properties of this phase. In the case of a biaxial phase they determine the directions of its twofold axes of symmetry. The vectors $(\vec{L},\vec{M},\vec{N})$ create the local frame, which can be expressed by means of a space-fixed reference frame $(\vec{e}_x,\vec{e}_y,\vec{e}_z)$ as

$$\vec{L}=R_{1\alpha}\vec{e}_\alpha, \quad \vec{M}=R_{2\alpha}\vec{e}_\alpha, \quad \vec{N}=R_{3\alpha}\vec{e}_\alpha, \quad (1)$$

where the matrix elements $R_{i\alpha}$ ($i=1,2,3$ and $\alpha=x,y,z$) satisfy the conditions

$$R_{i\alpha}R_{j\alpha}=\delta_{ij}, \quad (2)$$

$$R_{i\alpha}R_{i\beta}=\delta_{\alpha\beta}. \quad (3)$$

Relations (2) and (3) express the orthogonality and the completeness of the local frame. Note that repeated indices imply summation. The matrix elements can be expressed in terms of the three Euler angles $\phi(\vec{r})$, $\theta(\vec{r})$, and $\psi(\vec{r})$,

$$R_{1x}=\cos\theta\cos\phi\cos\psi-\sin\phi\sin\psi, \quad (4)$$

$$R_{1y}=\cos\theta\sin\phi\cos\psi+\cos\phi\sin\psi,$$

$$R_{1z}=-\sin\theta\cos\psi,$$

$$R_{2x}=-\cos\theta\cos\phi\sin\psi-\sin\phi\cos\psi,$$

$$R_{2y}=-\cos\theta\sin\phi\sin\psi+\cos\phi\cos\psi,$$

$$R_{2z}=\sin\theta\sin\psi,$$

$$R_{3x}=\sin\theta\cos\phi,$$

$$R_{3y}=\sin\theta\sin\phi,$$

$$R_{3z}=\cos\theta.$$

The ideal phase is described by $\phi(\vec{r})=\theta(\vec{r})=\psi(\vec{r})=0$ for all $\vec{r}$.

B. Distortion free energy

Let us call F_d the free energy due to the distortion of the local frame $(\vec{L},\vec{M},\vec{N})$. A general form of its density $f_d(\vec{r})$ was derived in Ref. [17] in the case of small distortions. It has the form

$$f_d(\vec{r})=k_{ij}D_{ij}+\frac{1}{2}K_{ijkl}D_{ij}D_{kl}+\frac{1}{2}L_{ijk}S_{ijk}, \quad (5)$$

where k_{ij},K_{ijkl},L_{ijk} are elastic constants,

$$D_{ij}=\frac{1}{2}\epsilon_{jkl}R_{i\alpha}R_{k\beta}\partial_\alpha R_{l\beta},$$

$$S_{ijk}=S_{jik}=\partial_\alpha(R_{i\alpha}D_{jk}+R_{j\alpha}D_{ik}),$$

$$S_{ij}=S_{ji}=\partial_\alpha(R_{i\beta}\partial_\beta R_{j\alpha}-R_{i\alpha}\partial_\beta R_{j\beta}),$$

$$S_{ij}=(\epsilon_{kim}\epsilon_{ljn}-\epsilon_{lim}\epsilon_{kjn})D_{lm}D_{kn},$$

$$\partial_\alpha R_{i\alpha}=-\epsilon_{ijk}D_{jk}, \quad (6)$$

and ϵ_{ijk} is an element of antisymmetric tensor (we set up the convention $\epsilon_{123}=+1$). The elastic constants satisfy the symmetry relations

$$K_{ijkl}=K_{klij}, \quad (7)$$

$$L_{ijk}=L_{jik}. \quad (8)$$

In general, the linear first-order terms with k_{ij} give 6 bulk and 3 surface terms ($\partial_\alpha R_{i\alpha}$); the quadratic first-order terms with K_{ijkl} give 39 bulk and 6 surface terms (S_{ij}); the terms with L_{ijk} give 18 surface terms (S_{ijk}). The total numbers of bulk and surface terms are 45 and 27, respectively.

Let us briefly recall how the number of independent elastic constants have to be determined with the help of symmetry requirements. The different cases of symmetry can be described as the orthogonal transformation with the matrix elements T_{ij} ($i,j=1,2,3$). This transformation changes the local frame into the new one

$$R'_{i\alpha}=T_{ij}R_{j\alpha}. \quad (9)$$

The distortion free energy density may be expressed in terms of new variables with new (primed) elastic constants. As elastic constants do not change under symmetry operations, we can identify the independent elastic constants.

C. Biaxial phase

Let us assume that a considered phase has a D_{2h} symmetry group. Then the distortion free-energy density has the form

$$f_d = \frac{1}{2} K_{1111}(D_{11})^2 + \frac{1}{2} K_{1212}(D_{12})^2 + \frac{1}{2} K_{1313}(D_{13})^2$$

$$+ \frac{1}{2} K_{2121}(D_{21})^2 + \frac{1}{2} K_{2222}(D_{22})^2 + \frac{1}{2} K_{2323}(D_{23})^2$$

$$+ \frac{1}{2} K_{3131}(D_{31})^2 + \frac{1}{2} K_{3232}(D_{32})^2 + \frac{1}{2} K_{3333}(D_{33})^2$$

$$+ K_{1122}D_{11}D_{22} + K_{1133}D_{11}D_{33} + K_{2233}D_{22}D_{33}$$

$$+ K_{1221}D_{12}D_{21} + K_{1331}D_{13}D_{31} + K_{2332}D_{23}D_{32} + L_{123}S_{123}$$

$$+ L_{231}S_{231} + L_{312}S_{312}. \tag{10}$$

The terms with K_{ijkl} give 12 bulk and 3 surface terms (S_{11}, S_{22}, S_{33}), whereas the terms with L_{ijk} give 3 surface terms ($S_{123}, S_{231}, S_{312}$). The total numbers of bulk and surface terms are 12 and 6, respectively.

For the sake of future discussion we will rewrite here the distortion free-energy density of a biaxial phase from the paper of Saupe [14] using the notation (6)

$$f_d^S = \frac{1}{2} K_{aa}(D_{11})^2 + \frac{1}{2} K_{bb}(D_{22})^2 + \frac{1}{2} K_{cc}(D_{33})^2$$

$$+ \frac{1}{2} K_{ab}(D_{13})^2 + \frac{1}{2} K_{ac}(D_{12})^2 + \frac{1}{2} K_{ba}(D_{23})^2$$

$$+ \frac{1}{2} K_{bc}(D_{21})^2 + \frac{1}{2} K_{ca}(D_{32})^2 + \frac{1}{2} K_{cb}(D_{31})^2$$

$$- C_{ab}D_{12}D_{21} - C_{bc}D_{23}D_{32} - C_{ca}D_{13}D_{31} + k_{0,a}S_{11}$$

$$+ k_{0,b}S_{22} + k_{0,c}S_{33}. \tag{11}$$

The relations among the elastic constants from Eqs. (10) and (11) are

$$K_{1111} = K_{aa}, \quad K_{1122} = -2k_{0,c},$$

$$K_{1212} = K_{ac}, \quad K_{1133} = -2k_{0,b},$$

$$K_{1313} = K_{ab}, \quad K_{2233} = -2k_{0,a},$$

$$K_{2121} = K_{bc}, \quad K_{1221} = -C_{ab} + 2k_{0,c},$$

$$K_{2222} = K_{bb}, \quad K_{1331} = -C_{ca} + 2k_{0,b}, \tag{12}$$

$$K_{2323} = K_{ba}, \quad K_{2332} = -C_{bc} + 2k_{0,a},$$

$$K_{3131} = K_{cb}, \quad L_{123} = 0,$$

$$K_{3232} = K_{ca}, \quad L_{231} = 0,$$

$$K_{3333} = K_{cc}, \quad L_{312} = 0.$$

D. Uniaxial phase

Let us assume that a considered phase possesses a $D_{\infty h}$ symmetry group. Let the z axis be oriented along the axis of symmetry. It is known that D_{2h} is a subgroup of the $D_{\infty h}$ symmetry group. It is interesting to study how higher symmetry reduces the number of independent constants from Eq.

(10). We write the implicit definitions of the new independent elastic constants K_s ($s=1, \ldots, 9$),

$$K_{3333} = 4 K_8,$$

$$K_{1313} = K_{2323} = K_7,$$

$$K_{3131} = K_{3232} = K_3,$$

$$K_{1331} = K_{2332} = K_6,$$

$$K_{1133} = K_{2233} = K_9 + 2 K_8 - K_6,$$

$$L_{123} = 0, \tag{13}$$

$$L_{231} = -L_{312} = \frac{1}{2} K_5,$$

$$K_{1111} = K_{2222} = K_2 + K_8 + K_9,$$

$$K_{1212} = K_{2121} = K_1,$$

$$K_{1122} = K_2 - K_4 + K_8 + K_9,$$

$$K_{1221} = K_4 - K_1.$$

The distortion free-energy density has the form

$$f_d = \frac{1}{2} K_1(\text{div}\vec{N})^2 + \frac{1}{2} K_2(\vec{N} \cdot \text{rot}\vec{N})^2 + \frac{1}{2} K_3(\vec{N} \times \text{rot}\vec{N})^2$$

$$+ \frac{1}{2} K_4 S_{33} + \frac{1}{2} K_5(S_{231} - S_{312}) + \frac{1}{2} K_6(S_{11} + S_{22})$$

$$+ \frac{1}{2} K_7[(\vec{N} \cdot \text{rot}\vec{L})^2 + (\vec{N} \cdot \text{rot}\vec{M})^2] + \frac{1}{2} K_8[(\vec{L} \cdot \text{rot}\vec{L})^2$$

$$+ (\vec{M} \cdot \text{rot}\vec{M})^2] + \frac{1}{2} K_9(\vec{N} \cdot \text{rot}\vec{N})[(\vec{L} \cdot \text{rot}\vec{L})$$

$$+ (\vec{M} \cdot \text{rot}\vec{M})]. \tag{14}$$

Therefore, in the case of the uniaxial phase we have six bulk (K_1, K_2, K_3, K_7, K_8, and K_9) and three surface terms (K_4, K_5, and K_6). Note that usually authors use only terms from K_1 to K_5, i.e., those that can be expressed by the vector $\vec{N}$ only. But the remaining terms from K_6 to K_9 are not excluded by the symmetry conditions and that is why we take them into account.

E. Basic deformations of a biaxial phase

In the continuum theory of uniaxial nematic liquid crystals three basic types of deformations, i.e., splay, twist, and bend, appear, which extract from the distortion free energy terms with K_1, K_2, and K_3, respectively. Thus each constant K_i must be positive; otherwise the undistorted nematic conformation would not correspond to a minimum of the free energy F_d.

Our aim in this section is to construct basic deformations proper for the continuum theory of biaxial nematic liquid crystals, where the distortion free-energy density is expressed by Eq. (10). A biaxial phase has lower symmetry

than a uniaxial one, so as a special case basic deformations from the uniaxial continuum theory should appear.

The ideal conformation is defined as

$$\vec{L}^{(0)} = (1,0,0),$$

$$\vec{M}^{(0)} = (0,1,0), \tag{15}$$

$$\vec{N}^{(0)} = (0,0,1).$$

Let us define the operator $\hat{O}(\vec{e},\phi)$, which is turning a given vector $\vec{p}$ around a unit vector $\vec{e}$ with an angle ϕ. We can write

$$\hat{O}(\vec{e},\phi)\vec{p} = (1-\cos\phi)(\vec{p}\cdot\vec{e})\vec{e} + (\cos\phi)\vec{p} + (\sin\phi)\vec{e}\times\vec{p}. \tag{16}$$

Now we define the basic deformations with the help of the operator $\hat{O}$. The deformations can be divided into five groups and connected with relevant elastic constants. The first group (twists) is, for K_{1111},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_x,\epsilon x)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

for K_{2222},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_y,\epsilon y)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

and for K_{3333},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_z,\epsilon z)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}). \tag{17}$$

The second group (splays and bends) is, for K_{1212},

$$\vec{L} = \frac{(z+1/\epsilon,0,-x)}{\sqrt{x^2+(z+1/\epsilon)^2}},$$

$$\vec{M} = \vec{M}^{(0)},$$

$$\vec{N} = \frac{(x,0,z+1/\epsilon)}{\sqrt{x^2+(z+1/\epsilon)^2}};$$

for K_{1313},

$$\vec{L} = \frac{(y+1/\epsilon,-x,0)}{\sqrt{x^2+(y+1/\epsilon)^2}},$$

$$\vec{M} = \frac{(x,y+1/\epsilon,0)}{\sqrt{x^2+(y+1/\epsilon)^2}},$$

$$\vec{N} = \vec{N}^{(0)};$$

for K_{2121},

$$\vec{L} = \vec{L}^{(0)},$$

$$\vec{M} = \frac{(0,z+1/\epsilon,-y)}{\sqrt{y^2+(z+1/\epsilon)^2}},$$

$$\vec{N} = \frac{(0,y,z+1/\epsilon)}{\sqrt{y^2+(z+1/\epsilon)^2}};$$

for K_{2323},

$$\vec{L} = \frac{(x+1/\epsilon,y,0)}{\sqrt{(x+1/\epsilon)^2+y^2}},$$

$$\vec{M} = \frac{(-y,x+1/\epsilon,0)}{\sqrt{(x+1/\epsilon)^2+y^2}},$$

$$\vec{N} = \vec{N}^{(0)};$$

for K_{3131},

$$\vec{L} = \vec{L}^{(0)},$$

$$\vec{M} = \frac{(0,y+1/\epsilon,z)}{\sqrt{(y+1/\epsilon)^2+z^2}},$$

$$\vec{N} = \frac{(0,-z,y+1/\epsilon)}{\sqrt{(y+1/\epsilon)^2+z^2}};$$

and for K_{3232},

$$\vec{L} = \frac{(x+1/\epsilon,0,z)}{\sqrt{(x+1/\epsilon)^2+z^2}},$$

$$\vec{M} = \vec{M}^{(0)},$$

$$\vec{N} = \frac{(-z,0,x+1/\epsilon)}{\sqrt{(x+1/\epsilon)^2+z^2}}. \tag{18}$$

The third group (modified twists) is, for L_{123},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_z,\epsilon x)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

for L_{231},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_x,\epsilon y)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

and for L_{312},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_y,\epsilon z)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}). \tag{19}$$

The fourth group (double twists) is, for K_{1122},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_y,\epsilon y)\hat{O}(\vec{e}_x,\epsilon x)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

for K_{1133},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_x,\epsilon x)\hat{O}(\vec{e}_z,\epsilon z)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

and for K_{2233},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}(\vec{e}_z,\epsilon z)\hat{O}(\vec{e}_y,\epsilon y)(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}). \tag{20}$$

The fifth group (double twists) is, for K_{1221},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}((-\vec{e}_x+\vec{e}_y)/\sqrt{2},\epsilon(x-y)/\sqrt{2})$$
$$\times \hat{O}((\vec{e}_x+\vec{e}_y)/\sqrt{2},\epsilon(x+y)/\sqrt{2})$$
$$\times (\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

for K_{1331},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}((\vec{e}_x-\vec{e}_z)/\sqrt{2},\epsilon(-x+z)/\sqrt{2})$$
$$\times \hat{O}((\vec{e}_x+\vec{e}_z)/\sqrt{2},\epsilon(x+z)/\sqrt{2})(\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}),$$

and for K_{2332},

$$(\vec{L},\vec{M},\vec{N}) = \hat{O}((-\vec{e}_y+\vec{e}_z)/\sqrt{2},\epsilon(y-z)/\sqrt{2})$$
$$\times \hat{O}((\vec{e}_y+\vec{e}_z)/\sqrt{2},\epsilon(y+z)/\sqrt{2})$$
$$\times (\vec{L}^{(0)},\vec{M}^{(0)},\vec{N}^{(0)}). \quad (21)$$

Inside the formulas for deformations we used a small parameter ϵ ($1/\epsilon$ is a length). As this measure of a deformation goes to zero, a considered conformation becomes the ideal one. The vectors of the local frame can be expanded into a power series with respect to ϵ,

$$\vec{L} = \vec{L}^{(0)} + \epsilon\vec{L}^{(1)} + \epsilon^2\vec{L}^{(2)} + \cdots,$$

$$\vec{M} = \vec{M}^{(0)} + \epsilon\vec{M}^{(1)} + \epsilon^2\vec{M}^{(2)} + \cdots, \quad (22)$$

$$\vec{N} = \vec{N}^{(0)} + \epsilon\vec{N}^{(1)} + \epsilon^2\vec{N}^{(2)} + \cdots.$$

Let us consider expansion of f_d given by Eq. (10) with respect to ϵ. It is clear that the lowest order ϵ is the second one (with ϵ^2). These terms contain linear parts of the local frame with the exception of S_{ijk} terms, but later they will apper to be unimportant. That is why we write below only linear parts of the vectors for all deformations. The first group is, for K_{1111},

$$\vec{L}^{(1)} = (0,0,0), \quad \vec{M}^{(1)} = (0,0,x), \quad \vec{N}^{(1)} = (0,-x,0);$$

for K_{2222},

$$\vec{L}^{(1)} = (0,0,-y), \quad \vec{M}^{(1)} = (0,0,0), \quad \vec{N}^{(1)} = (y,0,0);$$

and for K_{3333},

$$\vec{L}^{(1)} = (0,z,0), \quad \vec{M}^{(1)} = (-z,0,0), \quad \vec{N}^{(1)} = (0,0,0). \quad (23)$$

The second group is, for K_{1212},

$$\vec{L}^{(1)} = (0,0,-x), \quad \vec{M}^{(1)} = (0,0,0), \quad \vec{N}^{(1)} = (x,0,0);$$

for K_{1313},

$$\vec{L}^{(1)} = (0,-x,0), \quad \vec{M}^{(1)} = (x,0,0), \quad \vec{N}^{(1)} = (0,0,0);$$

for K_{2121},

$$\vec{L}^{(1)} = (0,0,0), \quad \vec{M}^{(1)} = (0,0,-y), \quad \vec{N}^{(1)} = (0,y,0);$$

for K_{2323},

$$\vec{L}^{(1)} = (0,y,0), \quad \vec{M}^{(1)} = (-y,0,0), \quad \vec{N}^{(1)} = (0,0,0);$$

for K_{3131},

$$\vec{L}^{(1)} = (0,0,0), \quad \vec{M}^{(1)} = (0,0,z), \quad \vec{N}^{(1)} = (0,-z,0);$$

and for K_{3232},

$$\vec{L}^{(1)} = (0,0,z), \quad \vec{M}^{(1)} = (0,0,0), \quad \vec{N}^{(1)} = (-z,0,0). \quad (24)$$

The third group is, for L_{123},

$$\vec{L}^{(1)} = (0,x,0), \quad \vec{M}^{(1)} = (-x,0,0), \quad \vec{N}^{(1)} = (0,0,0),$$

for L_{231},

$$\vec{L}^{(1)} = (0,0,0), \quad \vec{M}^{(1)} = (0,0,y), \quad \vec{N}^{(1)} = (0,-y,0),$$

and for L_{312},

$$\vec{L}^{(1)} = (0,0,-z), \quad \vec{M}^{(1)} = (0,0,0), \quad \vec{N}^{(1)} = (z,0,0). \quad (25)$$

The fourth group is, for K_{1122},

$$\vec{L}^{(1)} = (0,0,-y), \quad \vec{M}^{(1)} = (0,0,x), \quad \vec{N}^{(1)} = (y,-x,0),$$

for K_{1133},

$$\vec{L}^{(1)} = (0,z,0), \quad \vec{M}^{(1)} = (-z,0,x), \quad \vec{N}^{(1)} = (0,-x,0),$$

and for K_{2233},

$$\vec{L}^{(1)} = (0,z,-y), \quad \vec{M}^{(1)} = (-z,0,0), \quad \vec{N}^{(1)} = (y,0,0). \quad (26)$$

The fifth group is, for K_{1221},

$$\vec{L}^{(1)} = (0,0,-x), \quad \vec{M}^{(1)} = (0,0,y), \quad \vec{N}^{(1)} = (x,-y,0),$$

for K_{1331},

$$\vec{L}^{(1)} = (0,x,0), \quad \vec{M}^{(1)} = (-x,0,z), \quad \vec{N}^{(1)} = (0,-z,0),$$

and for K_{2332},

$$\vec{L}^{(1)} = (0,y,-z), \quad \vec{M}^{(1)} = (-y,0,0), \quad \vec{N}^{(1)} = (z,0,0). \quad (27)$$

One can calculate the distortion free energy from its density by

$$F_d = \int d\vec{r} f_d. \quad (28)$$

Below we write the lowest order of F_d for all deformations labeled by the relevant elastic constants. The first group is, for K_{1111},

$$F_d = \frac{1}{2} K_{1111}\epsilon^2 V,$$

for K_{2222},

$$F_d = \frac{1}{2} K_{2222} \epsilon^2 V, \qquad (29)$$

and for K_{3333},

$$F_d = \frac{1}{2} K_{3333} \epsilon^2 V.$$

The second group is, for K_{1212},

$$F_d = \frac{1}{2} K_{1212} \epsilon^2 V,$$

for K_{1313},

$$F_d = \frac{1}{2} K_{1313} \epsilon^2 V,$$

for K_{2121},

$$F_d = \frac{1}{2} K_{2121} \epsilon^2 V,$$

for K_{2323},

$$F_d = \frac{1}{2} K_{2323} \epsilon^2 V,$$

for K_{3131},

$$F_d = \frac{1}{2} K_{3131} \epsilon^2 V,$$

and for K_{3232},

$$F_d = \frac{1}{2} K_{3232} \epsilon^2 V. \qquad (30)$$

The third group is, for L_{123},

$$F_d = \frac{1}{2} (K_{1313} + 4L_{123}) \epsilon^2 V,$$

for L_{231},

$$F_d = \frac{1}{2} (K_{2121} + 4L_{231}) \epsilon^2 V,$$

and for L_{312},

$$F_d = \frac{1}{2} (K_{3232} + 4L_{312}) \epsilon^2 V. \qquad (31)$$

The fourth group is, for K_{1122},

$$F_d = \left(K_{1122} + \frac{1}{2} K_{1111} + \frac{1}{2} K_{2222} + L_{123} - L_{231} + L_{312} \right) \epsilon^2 V,$$

for K_{1133},

$$F_d = \left(K_{1133} + \frac{1}{2} K_{1111} + \frac{1}{2} K_{3333} - L_{123} + L_{231} + L_{312} \right) \epsilon^2 V,$$

for K_{2233},

$$F_d = \left(K_{2233} + \frac{1}{2} K_{2222} + \frac{1}{2} K_{3333} + L_{123} + L_{231} - L_{312} \right) \epsilon^2 V. \qquad (32)$$

The fifth group is, for K_{1221},

$$F_d = \left(K_{1221} + \frac{1}{2} K_{1212} + \frac{1}{2} K_{2121} + L_{231} - L_{312} \right) \epsilon^2 V,$$

for K_{1331},

$$F_d = \left(K_{1331} + \frac{1}{2} K_{1313} + \frac{1}{2} K_{3131} + L_{123} - L_{231} \right) \epsilon^2 V,$$

and for K_{2332},

$$F_d = \left(K_{2332} + \frac{1}{2} K_{2323} + \frac{1}{2} K_{3232} - L_{123} + L_{312} \right) \epsilon^2 V. \qquad (33)$$

Note that only deformations from the first and the second group extract one constant from the distortion free energy. Deformations from remaining groups always give a new constant together with previously found ones.

III. MICROSCOPIC APPROACH

A. Description of a system

In this section we focus on the microscopic analysis of nematic liquid crystals. Let us consider a dilute gas of N molecules contained in a volume V at temperature T. We assume that the molecules are rigid blocks with three translational and three rotational degrees of freedom. The state of a molecule is described by a vector of position $\vec{r}$ and the orientation $R = (\phi, \theta, \psi)$, where ϕ, θ, and ψ are the three Euler angles. Let m, J_x, J_y, and J_z denote the mass of a molecule and the three moments of inertia, respectively. We assume that the molecules interact via two-body short-range forces that depend on the distance between the molecules and their orientations; Φ_{12} gives the potential energy of interactions.

The free energy for our system can be derived in the thermodynamic limit $(N \to \infty, V \to \infty, N/V = \text{const})$ from the Born-Bogoliubov-Green-Kirkwood-Yvon hierarchy [20]. It is given by

$$\beta F = \int d(1) G(1) \{ \ln[G(1)\Lambda_6] - 1 \}$$
$$- \frac{1}{2} \int d(1) d(2) G(1) G(2) f_{12}, \qquad (34)$$

where $G(1) = G(\vec{r}_1, R_1)$ is the one-particle distribution function with the normalization

$$\int d(1) G(1) = N, \qquad (35)$$

$d(1) = d\vec{r}_1 dR_1 = d\vec{r}_1 d\phi_1 d\theta_1 \sin\theta_1 d\psi_1$, $f_{12} = \exp(-\beta \Phi_{12}) - 1$ is the Mayer function, $\beta = 1/k_B T$, and

$$\Lambda_6 = \left(\frac{h^2\beta}{2\pi}\right)^3 (m^3 J_x J_y J_z)^{-1/2}. \quad (36)$$

The equilibrium distribution G minimizing the free energy (34) satisfies

$$\ln[G(1)\Lambda_6] - \int d(2)G(2)f_{12} = \text{const.} \quad (37)$$

In the case of the homogeneous phase the distribution $G(1)$ does not depend on the position of a molecule and we can write $G(1) = G_0(R_1)$. It is convenient to use a dimensionless function $f(R) = G_0(R)V/N$ with the normalization

$$\int dR f(R) = 1. \quad (38)$$

In Ref. [20] the influence of symmetry of molecules and a phase on $f(R)$ was discussed. We have to distinguish four different cases. Note that in our paper a biaxial phase (molecule) has the D_{2h} symmetry group whereas a uniaxial phase (molecule) has the $D_{\infty h}$ symmetry group.

(i) If a biaxial phase is composed of biaxial molecules then $f(R)$ can be expressed in terms of the invariants $F_{\mu\nu}^{(j)}(R)$.

(ii) If a biaxial phase is composed of uniaxial molecules then $f(R)$ can be expressed in terms of the invariants $F_{\mu 0}^{(j)}(R)$.

(iii) If a uniaxial phase is composed of biaxial molecules then $f(R)$ can be expressed in terms of the invariants $F_{0\nu}^{(j)}(R)$.

(iv) If a uniaxial phase is composed of uniaxial molecules then $f(R)$ can be expressed in terms of the invariants $F_{00}^{(j)}(R) = P_j(\cos\theta)$.

The definition and the main properties of the invariants $F_{\mu\nu}^{(j)}$ are recalled in Appendix A.

B. Distribution function for a distorted phase

First we recall the simplest case of a uniaxial phase composed of uniaxial molecules. When the phase symmetry axis coincides with the z axis, the homogeneous distribution function depends only on the cosine of the angle between the molecule symmetry axis and the phase symmetry axis [6]

$$G_0(\vec{n}) = G_0(\cos\theta) = G_0(\vec{n}\cdot\vec{e}_z), \quad (39)$$

where $\vec{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ describes the orientation of the molecule. For a distorted phase the following observation is often used: In a weakly distorted system, at any point, the local properties are still those of a homogeneous system; only the optical axis has been rotated. In terms of the distribution function this means that [6]

$$G(\vec{r},\vec{n}) = G_0(\vec{n}\cdot\vec{N}(\vec{r})), \quad (40)$$

where $\vec{N}(\vec{r})$ is a director field.

Let us consider the most complex case of a biaxial phase composed of biaxial molecules. We can describe the orientation of a molecule both by the three Euler angles and by the set of the three orthonormal vectors $(\vec{l},\vec{m},\vec{n})$. In a space-fixed reference frame $(\vec{e}_x,\vec{e}_y,\vec{e}_z)$ we can express them just like the vectors of the local frame (1),

$$\vec{l} = R_{1\alpha}\vec{e}_\alpha = l_\alpha\vec{e}_\alpha,$$

$$\vec{m} = R_{2\alpha}\vec{e}_\alpha = m_\alpha\vec{e}_\alpha,$$

$$\vec{n} = R_{3\alpha}\vec{e}_\alpha = n_\alpha\vec{e}_\alpha, \quad (41)$$

but now the matrix elements $R_{i\alpha}$ do not depend on the position. We can say that the orientation is described by the nine elements $R_{i\alpha}$ instead of the three angles. It is clear that nine is more than enough. Because of symmetry $f(R)$ should depend only on $(R_{i\alpha})^2$. Below we show that using the four elements R_{1x}, R_{1z}, R_{3x}, and R_{3z} we can express the remaining ones

$$(R_{1y})^2 = 1 - (R_{1x})^2 - (R_{1z})^2,$$

$$(R_{2x})^2 = 1 - (R_{1x})^2 - (R_{3x})^2,$$

$$(R_{2y})^2 = (R_{1x})^2 + (R_{1z})^2 + (R_{3x})^2 + (R_{3z})^2 - 1,$$

$$(R_{2z})^2 = 1 - (R_{1z})^2 - (R_{3z})^2,$$

$$(R_{3y})^2 = 1 - (R_{3x})^2 - (R_{3z})^2. \quad (42)$$

Our four distinguished elements are still not independent because of the identity linking them,

$$2R_{1x}R_{1z}R_{3x}R_{3z} = 1 - (R_{1x})^2 - (R_{1z})^2 - (R_{3x})^2 - (R_{3z})^2$$
$$+ (R_{1x}R_{3z})^2 + (R_{1z}R_{3x})^2. \quad (43)$$

It is not difficult to express one element in terms of the three remaining ones, but this leads to complicated formulas and, more importantly, it is not necessary. We should only give the one possible functional dependence of $f(R)$ [and invariants $F_{\mu\nu}^{(j)}(R)$] on four elements R_{1x}, R_{1z}, R_{3x}, and R_{3z}. It will not have to be the unique dependence. Note that during computations we should use only one fixed functional dependence.

Now we will find the functional dependence of the invariants on R_{1x}, R_{1z}, R_{3x}, and R_{3z} because $f(R)$ depends on the invariants. We expect that $F_{\mu\nu}^{(j)}$ could be a sum of terms proportional to products

$$(R_{1x})^a (R_{1z})^b (R_{3x})^c (R_{3z})^d, \quad (44)$$

where a, b, c, and d are non-negative even numbers. Apart from this we expect that $F_{\mu\nu}^{(j)}$ with $j = 2s-1$ and $j = 2s$ should contain products with $a+b+c+d \leq 2s$. We know that for $j = 2s-1$ ($s > 0$) there are $(s-1)^2$ invariants, whereas for $j = 2s$ ($s \geq 0$) there are $(s+1)^2$ invariants. Let us compare the number N_s of products with $a+b+c+d = 2s$ with the number $\tilde{N}_s$ of $F_{\mu\nu}^{(j)}$ with $j = 2s-1$ and $j = 2s$:

$$N_0 = 1, \quad \tilde{N}_0 = 1, \quad (45)$$

$$N_1 = 2\times 3\times 4/6 = 4, \quad \tilde{N}_1 = 4,$$

$$N_2 = 3 \times 4 \times 5/6 = 10, \quad \widetilde{N}_2 = 1^2 + 3^2 = 10,$$

$$N_3 = 4 \times 5 \times 6/6 = 20, \quad \widetilde{N}_3 = 2^2 + 4^2 = 20,$$

$$N_4 = 5 \times 6 \times 7/6 = 35, \quad \widetilde{N}_4 = 3^2 + 5^2 = 34,$$

$$N_5 = 6 \times 7 \times 8/6 = 56, \widetilde{N}_5 = 4^2 + 6^2 = 52,$$

$$N_s = (s+3)!/(s!3!),$$

$$\widetilde{N}_s = (s-1)^2 + (s+1)^2 = 2s^2 + 2 \quad \text{for } s > 0.$$

Note that when $s > 3$, N_s is greater than $\widetilde{N}_s$. This can be easily understood by keeping in mind the identity (43) linking our four elements. For instance, for $s = 4$ the product $p \equiv (R_{1x}R_{1z}R_{3x}R_{3z})^2$ can be expressed by means of others. We have the same for $s = 5$ and products $p(R_{1x})^2$, $p(R_{1z})^2$, $p(R_{3x})^2$, and $p(R_{3z})^2$.

Now we are in a position to present the procedure to determine the functional dependence of $F_{\mu\nu}^{(j)}$ on R_{1x}, R_{1z}, R_{3x}, and R_{3z}. First we choose the number of products (44) equal to $\widetilde{N}_s$ for any s. Next we look for coefficients of every product in a space created by the invariants (the orthogonality of $F_{\mu\nu}^{(j)}$ should be used). We get products expressed in terms of invariants. Finally, we revert these relations to obtain invariants expressed in terms of products. Exemplary results of this procedure are listed in Appendix B.

Let Q_i ($i = 1,2,3,4$) denote the arguments of the distribution G_0, i.e.,

$$Q_1(R) = R_{1x} = \vec{l} \cdot \vec{e}_x,$$

$$Q_2(R) = R_{1z} = \vec{l} \cdot \vec{e}_z,$$

$$Q_3(R) = R_{3x} = \vec{n} \cdot \vec{e}_x,$$

$$Q_4(R) = R_{3z} = \vec{n} \cdot \vec{e}_z. \tag{46}$$

We know the functional dependence G_0 on Q_i and we postulate that the distribution of the distorted phase $G(\vec{r},R)$ can be written as

$$G(\vec{r},R) = G_0(Q_1,Q_2,Q_3,Q_4), \tag{47}$$

but the reference frame $(\vec{e}_x,\vec{e}_y,\vec{e}_z)$ should be replaced with the local frame $(\vec{L}(\vec{r}),\vec{M}(\vec{r}),\vec{N}(\vec{r}))$. Thus

$$Q_1(\vec{r},R) = \vec{l} \cdot \vec{L}(\vec{r}),$$

$$Q_2(\vec{r},R) = \vec{l} \cdot \vec{N}(\vec{r}),$$

$$Q_3(\vec{r},R) = \vec{n} \cdot \vec{L}(\vec{r}),$$

$$Q_4(\vec{r},R) = \vec{n} \cdot \vec{N}(\vec{r}). \tag{48}$$

We assume that the vectors of the local frame can be expanded into a power series with respect to the parameter ϵ (similarly to the phenomenological approach). We can write

$$Q_i = Q_i^{(0)} + \epsilon Q_i^{(1)} + \epsilon^2 Q_i^{(2)} + \cdots, \tag{49}$$

where

$$Q_1^{(p)}(\vec{r},R) = \vec{l} \cdot \vec{L}^{(p)}(\vec{r}),$$

$$Q_2^{(p)}(\vec{r},R) = \vec{l} \cdot \vec{N}^{(p)}(\vec{r}),$$

$$Q_3^{(p)}(\vec{r},R) = \vec{n} \cdot \vec{L}^{(p)}(\vec{r}),$$

$$Q_4^{(p)}(\vec{r},R) = \vec{n} \cdot \vec{N}^{(p)}(\vec{r}). \tag{50}$$

Let us write the expansion of G

$$G(\epsilon) = G(0) + \epsilon G'(0) + \frac{\epsilon^2}{2} G''(0) + \cdots, \tag{51}$$

or, more accurately,

$$G(\vec{r},R) = G_0(R) + \epsilon \sum_{i=1}^{4} \partial_i G_0(R) Q_i^{(1)}(\vec{r},R)$$

$$+ \epsilon^2 \sum_{i=1}^{4} \partial_i G_0(R) Q_i^{(2)}(\vec{r},R)$$

$$+ \frac{\epsilon^2}{2} \sum_{i,j=1}^{4} \partial_i \partial_j G_0(R) Q_i^{(1)}(\vec{r},R) Q_j^{(1)}(\vec{r},R) + O(\epsilon^3).$$

$$\tag{52}$$

C. Distortion free energy

It is known in the literature [6] that to obtain the distortion free energy F_d one should substract a homogeneous part F_0 from the total free energy F. It is important that F_0 is not equal to the free energy of a homogeneous phase F^H,

$$\beta F^H = \int d(1) G_0(R_1) \{\ln[G_0(R_1)\Lambda_6] - 1\}$$

$$- \frac{1}{2} \int d(1)d(2) G_0(R_1) G_0(R_2) f_{12}. \tag{53}$$

It is not obvious what we should choose as F_0. We postulate that

$$\beta F_0 = \int d(1) G(1) \{\ln[G(1)\Lambda_6] - 1\}$$

$$- \frac{1}{4} \int d(1)d(2) G(\vec{r}_1,R_1) G(\vec{r}_1,R_2) f_{12}$$

$$- \frac{1}{4} \int d(1)d(2) G(\vec{r}_2,R_1) G(\vec{r}_2,R_2) f_{12} \tag{54}$$

and

$$\beta F_d = \beta F - \beta F_0. \tag{55}$$

This is a generalization of the expression for uniaxial nematic liquid crystals [5].

We substitute the expansion (52) into the deformation free energy (55). When we make use of various identities that come from the normalizations of G_0 and vectors of the local frame we get

$$\beta F_d = \frac{1}{4}\int d(1)d(2)f_{12}\epsilon^2 \sum_{i,j=1}^{4} \partial_i G_0(R_1)\partial_j G_0(R_2)$$
$$\times[-2Q_i^{(1)}(\vec{r}_1,R_1)Q_j^{(1)}(\vec{r}_2,R_2)+Q_i^{(1)}(\vec{r}_1,R_1)$$
$$\times Q_j^{(1)}(\vec{r}_1,R_2)+Q_i^{(1)}(\vec{r}_2,R_1)Q_j^{(1)}(\vec{r}_2,R_2)]+O(\epsilon^3).$$

$$(56)$$

Let us substitute the basic deformations (23)–(27) into the free energy (56). We denote

$$U_\alpha=\partial_1 G_0 l_\alpha+\partial_3 G_0 n_\alpha,$$
$$W_\alpha=\partial_2 G_0 l_\alpha+\partial_4 G_0 n_\alpha. \qquad (57)$$

We write the distortion energies for all deformations. The first group is, for K_{1111},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_x^2 W_{1y}W_{2y},$$

for K_{2222},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_y^2(U_{1z}-W_{1x})(U_{2z}-W_{2x}),$$

and for K_{3333},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_z^2 U_{1y}U_{2y}. \qquad (58)$$

The second group is, for K_{1212},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_x^2(U_{1z}-W_{1x})(U_{2z}-W_{2x}),$$

for K_{1313},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_x^2 U_{1y}U_{2y},$$

for K_{2121},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_y^2 W_{1y}W_{2y},$$

for K_{2323},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_y^2 U_{1y}U_{2y},$$

for K_{3131},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_z^2 W_{1y}W_{2y},$$

and for K_{3232},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_z^2(U_{1z}-W_{1x})(U_{2z}-W_{2x}). \qquad (59)$$

The third group is, for L_{123},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_x^2 U_{1y}U_{2y},$$

for L_{231},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_y^2 W_{1y}W_{2y},$$

and for L_{312},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}u_z^2(U_{1z}-W_{1x})(U_{2z}-W_{2x}). \qquad (60)$$

The fourth group is, for K_{1122},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}\{u_y^2(U_{1z}-W_{1x})(U_{2z}-W_{2x})$$
$$+u_x^2 W_{1y}W_{2y}+u_x u_y[(U_{1z}-W_{1x})W_{2y}$$
$$+W_{1y}(U_{2z}-W_{2x})]\},$$

for K_{1133},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}[u_x^2 W_{1y}W_{2y}+u_z^2 U_{1y}U_{2y}$$
$$-u_x u_z(U_{1y}W_{2y}+W_{1y}U_{2y})],$$

and for K_{2233},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}\{u_y^2(U_{1z}-W_{1x})(U_{2z}-W_{2x})$$
$$+u_z^2 U_{1y}U_{2y}-u_y u_z[U_{1y}(U_{2z}-W_{2x})$$
$$+(U_{1z}-W_{1x})U_{2y}]\}. \qquad (61)$$

The fifth group is, for K_{1221},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}\{u_x^2(U_{1z}-W_{1x})(U_{2z}-W_{2x})$$
$$+u_y^2 W_{1y}W_{2y}+u_x u_y[(U_{1z}-W_{1x})W_{2y}$$
$$+W_{1y}(U_{2z}-W_{2x})]\},$$

for K_{1331},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12}\epsilon^2 V\frac{1}{4}[u_x^2 U_{1y}U_{2y}+u_z^2 W_{1y}W_{2y}$$
$$-u_x u_z(U_{1y}W_{2y}+W_{1y}U_{2y})],$$

and for K_{2332},

$$\beta F_d = \int dR_1 dR_2 d\vec{u} f_{12} \epsilon^2 V \frac{1}{4} \{u_z^2 (U_{1z} - W_{1x})(U_{2z} - W_{2x})$$

$$+ u_y^2 U_{1y} U_{2y} - u_y u_z [U_{1y}(U_{2z} - W_{2x})$$

$$+ (U_{1z} - W_{1x}) U_{2y}]\}. \tag{62}$$

Note that we changed the variables

$$\vec{r}_2 - \vec{r}_1 = \vec{u} = u_\alpha \vec{e}_\alpha, \quad \vec{r}_2 + \vec{r}_1 = \vec{\eta} = \eta_\alpha \vec{e}_\alpha \tag{63}$$

and we integrated over $\vec{\eta}$ because f_{12} does not depend on it.

IV. ELASTIC CONSTANTS

A. Biaxial phase composed of biaxial molecules

In the previous sections we calculated the distortion free energy from both macroscopic and microscopic points of view. Now we compare these expressions to obtain microscopic formulas for the elastic constants of the biaxial phase. The first group is

$$\beta K_{1111} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_x^2 W_{1y} W_{2y},$$

$$\beta K_{2222} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_y^2 (U_{1z} - W_{1x})(U_{2z} - W_{2x}),$$

$$\tag{64}$$

$$\beta K_{3333} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_z^2 U_{1y} U_{2y}.$$

The second group is

$$\beta K_{1212} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_x^2 (U_{1z} - W_{1x})(U_{2z} - W_{2x}),$$

$$\beta K_{1313} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_x^2 U_{1y} U_{2y},$$

$$\beta K_{2121} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_y^2 W_{1y} W_{2y},$$

$$\beta K_{2323} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_y^2 U_{1y} U_{2y},$$

$$\beta K_{3131} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_z^2 W_{1y} W_{2y},$$

$$\beta K_{3232} = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_z^2 (U_{1z} - W_{1x})(U_{2z} - W_{2x}).$$

$$\tag{65}$$

The third group is

$$L_{123} = L_{231} = L_{312} = 0. \tag{66}$$

The fourth group is

$$\beta K_{1122} = \frac{1}{4} \int dR_1 dR_2 d\vec{u} f_{12} u_x u_y [(U_{1z} - W_{1x}) W_{2y}$$

$$+ W_{1y}(U_{2z} - W_{2x})],$$

$$\beta K_{1133} = \frac{1}{4} \int dR_1 dR_2 d\vec{u} f_{12} u_x u_z [- U_{1y} W_{2y} - W_{1y} U_{2y}],$$

$$\tag{67}$$

$$\beta K_{2233} = \frac{1}{4} \int dR_1 dR_2 d\vec{u} f_{12} u_y u_z [- U_{1y}(U_{2z} - W_{2x})$$

$$- (U_{1z} - W_{1x}) U_{2y}].$$

The fifth group is

$$K_{1221} = K_{1122}, \quad K_{1331} = K_{1133}, \quad K_{2332} = K_{2233}. \tag{68}$$

We note that three constants vanished and three others appeared to be dependent. The total number of independent constants is equal to 12.

B. Uniaxial phase composed of biaxial molecules

This phase is described by the distribution $f(R)$ that depends on the invariants $F_{0\nu}^{(j)}(R)$. There is no dependence on the ϕ angle, thus

$$\partial_1 G_0 = \partial_3 G_0 = 0, \quad U_\alpha = 0. \tag{69}$$

The expressions for the elastic constants are

$$\beta K_1 = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_x^2 W_{1x} W_{2x}, \tag{70}$$

$$\beta K_2 = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_y^2 W_{1x} W_{2x}, \tag{71}$$

$$\beta K_3 = \frac{1}{2} \int dR_1 dR_2 d\vec{u} f_{12} u_z^2 W_{1x} W_{2x}, \tag{72}$$

$$K_4 = \frac{1}{2}(K_1 + K_2). \tag{73}$$

The remaining constants are equal to zero

$$K_5 = K_6 = K_7 = K_8 = K_9 = 0. \tag{74}$$

Note that formulas (70)–(72) differ from the case of uniaxial molecules, but we have the same number (3) of independent constants.

C. Biaxial phase composed of uniaxial molecules

The phase is described by the distribution $f(R)$ that depends on the invariants $F_{\mu 0}^{(j)}(R)$. As there is no dependence on the ψ angle one gets

$$\partial_1 G_0 = \partial_2 G_0 = 0. \tag{75}$$

The formulas for the elastic constants are just like the expressions (64)–(68) for biaxial molecules, but we should use the substitutions

$$U_\alpha = \partial_3 G_0 n_\alpha, \quad W_\alpha = \partial_4 G_0 n_\alpha. \qquad (76)$$

D. Uniaxial phase composed of uniaxial molecules

This is the simplest case and we show that our model recovers the famous formulas by Poniewierski and Stecki [6] with the direct correlation function replaced by f_{12}. The phase is described by the invariants $F_{00}^{(j)}(R)$. There is no dependence on either ϕ or ψ; thus

$$\partial_1 G_0 = \partial_2 G_0 = \partial_3 G_0 = 0, \quad U_\alpha = 0. \qquad (77)$$

The formulas for the elastic constants are just like the expressions (70)–(74) for biaxial molecules, but we should use the substitution

$$W_\alpha = \partial_4 G_0 n_\alpha. \qquad (78)$$

V. EXEMPLARY CALCULATIONS

In this section, by means of the present general theory we carry out analytical and numerical calculations for a relatively simple model with the interaction energy of the form $\Phi_{12}(u/\sigma)$ [7,28], where u is the distance between molecules ($\vec{u} = u\vec{\Delta}$) and

$$
\sigma(R_1, R_2, \vec{\Delta}) = \sigma_0 + \sigma_1[(\vec{\Delta}\cdot\vec{n}_1)^2 + (\vec{\Delta}\cdot\vec{n}_2)^2] + \sigma_2(\vec{n}_1\cdot\vec{n}_2)^2
$$
$$
+ \sigma_3[(\vec{\Delta}\cdot\vec{l}_1)^2 + (\vec{\Delta}\cdot\vec{l}_2)^2] + \sigma_4(\vec{l}_1\cdot\vec{l}_2)^2
$$
$$
+ \sigma_5[(\vec{l}_1\cdot\vec{n}_2)^2 + (\vec{l}_2\cdot\vec{n}_1)^2]. \qquad (79)
$$

The function σ is real and invariant under rotations and permutation of molecules. Also the symmetry operations on molecules from the D_{2h} symmetry group leave σ invariant [20].

There are a number of possibilities for the functional dependence of Φ_{12} on u/σ. We give four examples, together with a function $B_s(T^*)$, defined as

$$B_s(T^*) = \int_0^\infty dx\, x^s f_{12}(x) = \int_0^\infty dx\, x^s \{\exp[-\beta\Phi_{12}(x)] - 1\}, \qquad (80)$$

where $T^* = 1/\beta\epsilon$ is a dimensionless temperature and ϵ is a depth of the potential energy: (i) the *hard-core potential energy*

$$\Phi_{12}(u/\sigma)_{HC} = \begin{cases} +\infty & \text{for } u/\sigma < 1 \\ 0 & \text{for } u/\sigma > 1, \end{cases} \qquad (81)$$

$$B_s(T^*)_{HC} = \frac{-1}{s+1} = \text{const}; \qquad (82)$$

(ii) the *soft-core potential energy*

$$\Phi_{12}(u/\sigma)_{SC} = \epsilon_{SC}(\sigma/u)^m, \qquad (83)$$

$$B_s(T^*)_{SC} = \frac{-1}{s+1}\Gamma\left(\frac{m-s-1}{m}\right)\left(\frac{1}{T^*}\right)^{(s+1)/m}\exp(1/T^*); \qquad (84)$$

(iii) the *square-well potential energy*

$$\Phi_{12}(u/\sigma)_{SW} = \begin{cases} +\infty & \text{for } u/\sigma < 1 \\ -\epsilon_{SW} & \text{for } 1 < u/\sigma < R_{SW} \\ 0 & \text{for } u/\sigma > R_{SW}, \end{cases} \qquad (85)$$

$$B_s(T^*)_{SW} = \frac{1}{s+1}\{[\exp(1/T^*) - 1](R_{SW}^{s+1} - 1) - 1\}; \qquad (86)$$

and (iv) the *Lennard-Jones m-n potential energy*

$$\Phi_{12}(u/\sigma)_{LJ} = 4\epsilon_{LJ}[(\sigma/u)^m - (\sigma/u)^n], \qquad (87)$$

$$B_s(T^*)_{LJ} = \frac{-1}{s+1}\sum_{p=0}^\infty \frac{1}{p!}\left(\frac{4}{T^*}\right)^{[p(m-n)+s+1]/m}$$
$$\times \Gamma\left(\frac{pn+m-s-1}{m}\right) \qquad (88)$$

$$+ \frac{1}{s+1}\sum_{p=0}^\infty \frac{1}{p!}\frac{n}{m}\left(\frac{4}{T^*}\right)^{[p(m-n)+m-n+s+1]/m}$$
$$\times \Gamma\left(\frac{pn+n-s-1}{m}\right) \qquad (89)$$

The function $B_s(T^*)$ is of great importance, i.e., to the problem of the existence of the ordered phase.

We rewrite the general equation (37) for the distribution function in the case of a homogeneous phase. Let us define

$$K(R_1, R_2) = \int d\vec{\Delta}(\sigma/\sigma_0)^3, \qquad (90)$$

$$\lambda = B_2(T^*)(\sigma_0^3 N/V). \qquad (91)$$

The kernel K and the distribution function f can be expressed in terms of invariants $F^{[I]}$ (see Appendix A),

$$K(R,0) = \sum_{[I]=[1]}^{[35]} K^{[I]} F^{[I]}(R), \qquad (92)$$

$$\ln f(R) = \sum_{[I]=[1]}^{[35]} S^{[I]} F^{[I]}(R). \qquad (93)$$

Note that for σ given by Eq. (79) both sums (92) and (93) are *finite* series. Thus the distribution function of the homogeneous phase is fully described by 35 coefficients $S^{[I]}$. Let us define order parameters as

$$\langle F^{[I]}\rangle \equiv \int dR f(R) F^{[I]}(R). \qquad (94)$$

The set of coefficients $S_{\mu\nu}^j$ we derive from the equations

$$S_{\mu\nu}^j = \lambda \sum_\rho K_{\rho\nu}^j \langle F_{\mu\rho}^{(j)}\rangle \quad \text{for } j > 0, \qquad (95)$$

$$\langle F_{00}^{(0)}\rangle = 1 \quad \text{(the normalization condition).} \qquad (96)$$

Note that there is a mistake in these equations in Ref. [20]. Now we move to the elastic constants. We can expand the distribution function f in an infinite series with respect to invariants $F_{\mu\nu}^{(j)}$,

$$f(R) = \sum_j \sum_{\mu,\nu} \langle F_{\mu\nu}^{(j)} \rangle F_{\mu\nu}^{(j)}(R)(2j+1)/8\pi^2. \quad (97)$$

When we insert the series (97) into definitions of W_α and U_α we get

$$W_\alpha = (N/V) \sum_{[I]} \langle F^{[I]} \rangle W_\alpha^{[I]},$$

$$U_\alpha = (N/V) \sum_{[I]} \langle F^{[I]} \rangle U_\alpha^{[I]}. \quad (98)$$

We can write all elastic constants as *finite* sums of the form

$$K_{ijkl} = \eta \sum_{[I]=[2]}^{[121]} \sum_{[J]=[2]}^{[121]} \langle F^{[I]} \rangle \langle F^{[J]} \rangle A_{ijkl}^{[I][J]}, \quad (99)$$

where

$$\eta = (\epsilon/\sigma_0)T^* B_4(T^*)(\sigma_0^3 N/V)^2 \quad (100)$$

and $A^{[I][J]}$ are functions of parameters σ_i. They are defined as follows: for

$$A_{1111}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_x^2 W_{1y}^{[I]} W_{2y}^{[J]},$$

$$A_{2222}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_y^2(U_{1z}^{[I]} - W_{1x}^{[I]})$$
$$\times(U_{2z}^{[J]} - W_{2x}^{[J]}),$$

$$A_{3333}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_z^2 U_{1y}^{[I]} U_{2y}^{[J]},$$

$$A_{1212}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_x^2(U_{1z}^{[I]} - W_{1x}^{[I]})$$
$$\times(U_{2z}^{[J]} - W_{2x}^{[J]}),$$

$$A_{1313}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_x^2 U_{1y}^{[I]} U_{2y}^{[J]},$$

$$A_{2121}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_y^2 W_{1y}^{[I]} W_{2y}^{[J]},$$

$$A_{2323}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_y^2 U_{1y}^{[I]} U_{2y}^{[J]},$$

$$A_{3131}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_z^2 W_{1y}^{[I]} W_{2y}^{[J]},$$

$$A_{3232}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_z^2(U_{1z}^{[I]} - W_{1x}^{[I]})$$
$$\times(U_{2z}^{[J]} - W_{2x}^{[J]}),$$

$$A_{1122}^{[I][J]} = \frac{1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_x \Delta_y(U_{1z}^{[I]} - W_{1x}^{[I]})W_{2y}^{[J]},$$

$$A_{1133}^{[I][J]} = \frac{-1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_x \Delta_z U_{1y}^{[I]} W_{2y}^{[J]},$$

$$A_{2233}^{[I][J]} = \frac{-1}{2} \int dR_1 dR_2 d\vec{\Delta}(\sigma/\sigma_0)^5 \Delta_y \Delta_z(U_{1z}^{[I]} - W_{1x}^{[I]})U_{2y}^{[J]}. \quad (101)$$

We would like to stress that all $A^{[I][J]}$ can be calculated analytically. As there are 12 different elastic constants with $120 \times 120 = 14\,400$ functions $A^{[I][J]}$, which have an eightfold integration, it is a very time consuming task. In order to get some estimation of the values of the elastic constants we performed calculations numerically with a rather rough approximation that the most important are two order parameters $\langle F_{00}^{(2)} \rangle$ and $\langle F_{22}^{(2)} \rangle$. We assumed the square-well potential energy of interactions with $R_{SW} = 2$ and a density equal to 1/5 of close-packed density. We show how to calculate the close-packed density. The mutually excluded volume V_e of two molecules with fixed orientations R_1 and R_2 is equal to

$$V_e(R_1,R_2) = \int d\vec{\Delta}\sigma^3/3 = K(R_1,R_2)\sigma_0^3/3. \quad (102)$$

We assume that the volume of a molecule is equal to

$$V_{mol} = V_e(0,0)/8 = K(0,0)\sigma_0^3/24 = \sum_j \sum_\mu K_{\mu\mu}^j \sigma_0^3/24. \quad (103)$$

We used $V/N = 5 V_{mol}$. According to Ref. [20], we assumed that molecules are similar to ellipsoids with three different axes $(2a) \times (2b) \times (2c)$, where $a < b < c$. Then, by means of the excluded volume method [20] we get

$$\sigma_0 = 2b, \quad \sigma_1 = c-b, \quad \sigma_3 = a-b, \quad \sigma_2 = \sigma_4 = \sigma_5 = 0. \quad (104)$$

In our calculations we applied $c = 3b = 9a$. Note that σ_0 determines the length scale, whereas ϵ_{SW} determines the energy scale. The elastic constants can be expressed in ϵ_{SW}/σ_0.

In our system, on decreasing the temperature we meet the first-order transition to the uniaxial nematic phase at $T^* = 0.64$ and the second-order transition to the biaxial nematic phase at $T^* = 0.32$ [20]. The temperature dependence of the two order parameters $\langle F_{00}^{(2)} \rangle$ and $\langle F_{22}^{(2)} \rangle$ is presented in Fig. 1. The order parameters were used to calculate the temperature dependence of the elastic constants shown in Fig. 2.

In the nematic phase generally three independent constants are present: $K_1 = K_{1212} = K_{2121}$, $K_3 = K_{3131} = K_{3232}$, and $K_2 = K_{1111} = K_{2222}$. We plotted also the negative constant K_{1122}, which in this phase is equal to $(K_2 - K_1)/2$. Note that the equality $K_1 = K_3$ is accidental and results from simplifying the assumption that we take into account only two
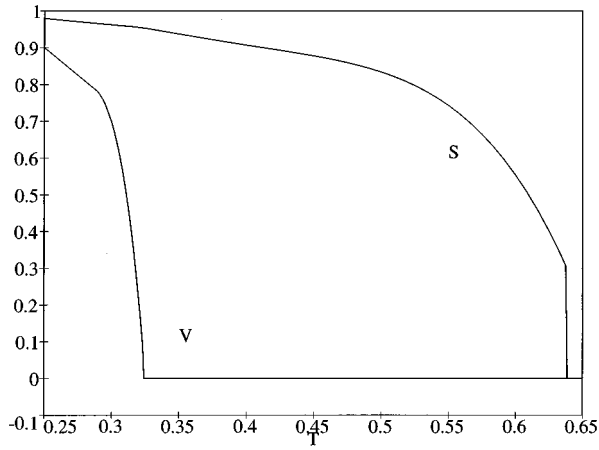
FIG. 1. Temperature dependence of the order parameters $S = \langle F_{00}^2 \rangle$ and $V = \langle F_{22}^2 \rangle$ (we use the Straley notation). T denotes the dimensionless temperature T^*.

order parameters $\langle F_{00}^{(2)} \rangle$ and $\langle F_{22}^{(2)} \rangle$. Typically, for rodlike molecules we get inequalities $K_3 > K_1 > K_2$.

In the biaxial phase we have 12 independent constants. K_1 splits into K_{1212} and K_{2121} ($K_{1212} > K_{2121}$), K_3 splits into K_{3232} and K_{3131} ($K_{3232} > K_{3131}$), K_2 splits into K_{2222} and K_{1111} ($K_{2222} > K_{1111}$), and K_{1122} becomes a new independent constant. Other new independent constants are four positive $K_{1133} > K_{1313} > K_{2323} > K_{3333}$ and one negative K_{2233}. Note that K_{1313}, K_{2323}, and K_{3333} are about an order of magnitude smaller than K_{1133}, but they have a similar temperature dependence. We noticed that in the biaxial phase in the neighborhood of the transition point four constants reveal unusual behavior. K_{3131}, K_{2121}, and K_{1111} *decrease* on decreasing the temperature and K_{1122} *increases* on decreasing the temperature. Unfortunately, it is not clearly visible in the picture.
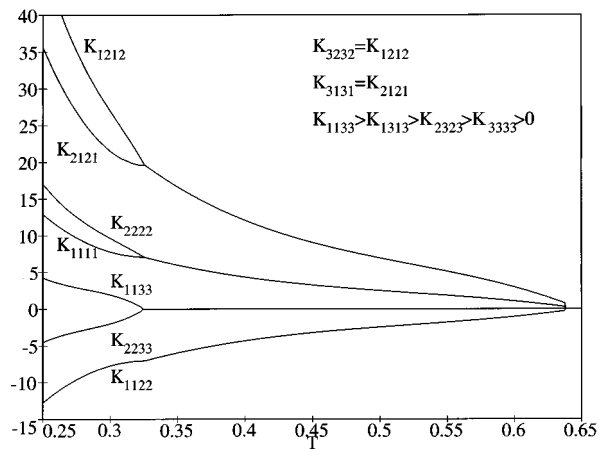

FIG. 2. Temperature dependence of the elastic constants. In the uniaxial nematic phase (between $T^* = 0.64$ and $T^* = 0.32$) we have $K_1 = K_{1212} = K_{2121}$ equal to $K_3 = K_{3131} = K_{3232}$ and $K_2 = K_{1111} = K_{2222}$. In addition we have $K_{1122} = (K_2 - K_1)/2$. In the biaxial nematic phase (below $T^* = 0.32$) K_1, K_3, and K_2 split into two constants and K_{1122} becomes an independent constant. Apart from that, one negative (K_{2233}) and four positive ($K_{1133} > K_{1313} > K_{2323} > K_{3333}$) constants appear. T denotes the dimensionless temperature T^*.

VI. CONCLUSION

In this paper we derived the microscopic formulas for elastic constants of biaxial nematic liquid crystals. In order to calculate the values of elastic constants one needs the one-particle distribution function and the potential energy of molecular interactions. The theory was developed for rigid molecules interacting via two-body short-range forces. We showed that the potential energy of the form $\Phi_{12}(r/\sigma)$ is extremely useful for calculations. It allows us to express the elastic constants as a *finite* series in terms of the order parameters. Apart from that the potential energy $\Phi_{12}(r/\sigma)$ makes the role of the temperature more visible. The temperature determines the order parameters via the function $B_2(T^*)$ in λ [Eq. (91)] and it has a direct influence on the elastic constants via the function $B_4(T^*)$ in η [Eq. (100)].

Our theory was applied to a system of molecules similar to ellipsoids and the temperature dependence of the elastic constants in uniaxial and biaxial nematics phase was obtained.

We sum up our results by a comparison to the paper by Singh *et al.* [22] because both works have a lot in common. We will list predictions of Singh *et al.* using our notation and will add our comments.

(i) During the transition from a uniaxial to a biaxial phase K_1 splits into K_{1212} and K_{2121}, K_3 splits into K_{3232} and K_{3131}, K_2 splits into K_{2222} and K_{1111}, and K_{1122} becomes a new independent constant.

(ii) Seven constants, viz., K_{1212}, K_{2121}, K_{3232}, K_{3131}, K_{2222}, K_{1111}, and K_{1122}, have a nearly equal value and are of the order of the values found in a uniaxial phase.

(iii) Three constants, viz., K_{3333}, K_{1313}, and K_{2323}, are three or four orders of magnitude smaller than the value of the constants found in a uniaxial phase.

(iv) K_{1133} and K_{2233} are about one order of magnitude smaller than K_{1122}.

(v) $K_{1122} < 0$, $K_{1133} > 0$, and $K_{2233} < 0$.

(vi) If $\langle F_{02}^{(2)} \rangle = \langle F_{20}^{(2)} \rangle = 0$ (and also higher-order parameters) then $K_1 = K_3$, $K_{3232} = K_{1212}$, and $K_{3131} = K_{2121}$.

All predictions are confirmed by our results except (iii) and (iv). It is easy to find the origin. Singh *et al.* assumed that $\langle F_{22}^{(2)} \rangle / \langle F_{00}^{(2)} \rangle \sim 0.01$, but it is true only near the transition point. For low temperatures our $\langle F_{22}^{(2)} \rangle$ and $\langle F_{00}^{(2)} \rangle$ have the same order of magnitude.

We would like to stress that contrary to Singh *et al.*, we obtained a full temperature dependence of the elastic constants, not only an estimation of their values. We could also establish the relations between split constants in our model.

Our result (68) implies that there are the following relations among the elastic constants from the paper of Saupe [14]:

$$C_{ab} = 4 k_{0,c}, \quad C_{bc} = 4 k_{0,a}, \quad C_{ca} = 4 k_{0,b}. \quad (105)$$

As far as we know, these relations have not been presented in the literature. In the case of the uniaxial phase they give the Cauchy relation from the paper of Nehring and Saupe [3] [Eq. (73) in our notation].

The uniaxial version of the present theory was successfuly applied 15 years ago [7]. We are convinced that the biaxial version can be a useful tool for experimenters dealing with biaxial nematic liquid crystals. In the future we expect experimental data for the elastic constants of biaxial nematogens as, according to Kini and Chandrasekhar, experiments are feasible [18] and the number of known biaxial materials increased [29].

APPENDIX A

Let us recall the main properties of the invariants $F_{\mu\nu}^{(j)}$, which describe biaxial and uniaxial molecules in biaxial and uniaxial phases.

(i) The definition is

$$F_{\mu\nu}^{(j)}(R) = \left(\frac{1}{\sqrt{2}}\right)^{2+\delta_{\mu 0}+\delta_{0\nu}} \sum_{\rho,\sigma=\pm 1} (-1)^{j(\sigma-\rho)/2}$$
$$\times D_{\rho\mu,\sigma\nu}^{(j)}(R), \qquad (A1)$$

where j is a non-negative integer. If j is even, then $0\le\mu\le j$ and $0\le\nu\le j$. If j is odd, then $2\le\mu\le j$ and $2\le\nu\le j$. Functions $D_{\mu\nu}^{(j)}(R)$ are standard rotation matrix elements.

(ii) The invariants are real functions.

(iii) Let $R^{-1}=(-\psi,-\theta,-\phi)$ denote the rotation inverse to $R=(\phi,\theta,\psi)$. Then

$$F_{\mu\nu}^{(j)}(R^{-1}) = F_{\nu\mu}^{(j)}(R). \qquad (A2)$$

(iv) For the zero rotation we have

$$F_{\mu\nu}^{(j)}(0) = \delta_{\mu\nu}. \qquad (A3)$$

(v) The invariants satisfy the orthogonality relations

$$\int dR F_{\mu\nu}^{(j)}(R) F_{\rho\sigma}^{(k)}(R) = \delta_{jk}\delta_{\mu\rho}\delta_{\nu\sigma} 8\pi^2/(2j+1). \qquad (A4)$$

More generally, we can write

$$\int dR F_{\mu\nu}^{(j)}(R) F_{\rho\sigma}^{(k)}(R_1^{-1}R)$$
$$= \delta_{jk} F_{\mu\rho}^{(j)}(R_1) F_{\nu\sigma}^{(j)}(0) 8\pi^2/(2j+1). \qquad (A5)$$

(vi) For a given $j=2s$ and $j=2s+1$ there are $(s+1)^2$ and s^2 invariants, respectively.

(vii) In order to get a more transparent form of certain formulas we introduce alternative labeling of invariants. We replace indicators (j,μ,ν) with an indicator $[I]$, where I runs from 1 by 1 to infinity. For two indicators $[I]=(j,\mu,\nu)$ and $[J]=(k,\rho,\sigma)$ we can write that $[I]<[J]$ only when $j<k$, or when $j=k$ and $\mu<\rho$, or when $j=k$, $\mu=\rho$, and $\nu<\sigma$. We have, for example,

$$[1]=(0,0,0),$$
$$[2]=(2,0,0),$$
$$[3]=(2,0,2),$$
$$[4]=(2,2,0),$$
$$[5]=(2,2,2),$$
$$[6]=(3,2,2),$$
$$[7]-[15] \quad \text{for} \quad (4,\mu,\nu),$$
$$[16]-[19] \quad \text{for} \quad (5,\mu,\nu),$$
$$[20]-[35] \quad \text{for} \quad (6,\mu,\nu),$$
$$[36]-[44] \quad \text{for} \quad (7,\mu,\nu),$$
$$[45]-[69] \quad \text{for} \quad (8,\mu,\nu),$$
$$[70]-[85] \quad \text{for} \quad (9,\mu,\nu),$$
$$[86]-[121] \quad \text{for} \quad (10,\mu,\nu). \qquad (A6)$$

APPENDIX B

We list the invariants $F_{\mu\nu}^{(j)}$ expressed in terms of products $(R_{1x})^a(R_{1z})^b(R_{3x})^c(R_{3z})^d$ for $j=0, 2, 3,$ and 4 as an exemplary result of the procedure described in Sec. III D:

$$F_{00}^{(0)}=1,$$

$$F_{00}^{(2)}=\frac{1}{2}[-1+3(R_{3z})^2],$$

$$F_{02}^{(2)}=\frac{\sqrt{3}}{2}[-1+(R_{3z})^2+2(R_{1z})^2],$$

$$F_{20}^{(2)}=\frac{\sqrt{3}}{2}[-1+(R_{3z})^2+2(R_{3x})^2],$$

$$F_{22}^{(2)}=\frac{1}{2}[-3+(R_{3z})^2+2(R_{1z})^2+2(R_{3x})^2+4(R_{1x})^2],$$

$$F_{22}^{(3)}=-(R_{3z})^2+(R_{1z})^2+(R_{3x})^2-(R_{1x})^2+3(R_{1x})^2(R_{3z})^2$$
$$-3(R_{1z})^2(R_{3x})^2,$$

$$F_{00}^{(4)}=\frac{1}{8}[3-30(R_{3z})^2+35(R_{3z})^4],$$

$$F_{02}^{(4)}=\frac{\sqrt{5}}{4}[1-8(R_{3z})^2-2(R_{1z})^2+7(R_{3z})^4$$
$$+14(R_{1z})^2(R_{3z})^2],$$

$$F_{04}^{(4)}=\frac{\sqrt{35}}{8}[1-2(R_{3z})^2-8(R_{1z})^2+(R_{3z})^4$$
$$+8(R_{1z})^2(R_{3z})^2+8(R_{1z})^4],$$

$$F_{20}^{(4)} = \frac{\sqrt{5}}{4}[1 - 8(R_{3z})^2 - 2(R_{3x})^2 + 7(R_{3z})^4$$
$$+ 14(R_{3x})^2(R_{3z})^2],$$

$$F_{22}^{(4)} = \frac{11}{2} - 10(R_{3z})^2 - 6(R_{3x})^2 + \frac{7}{2}(R_{3z})^4 + 7(R_{3x})^2(R_{3z})^2$$
$$- 6(R_{1z})^2 + 7(R_{1z})^2(R_{3z})^2 - 5(R_{1x})^2 + 7(R_{1z})^2(R_{3x})^2$$
$$+ 7(R_{1x})^2(R_{3z})^2,$$

$$F_{24}^{(4)} = \frac{\sqrt{7}}{4}[7 - 8(R_{3z})^2 - 6(R_{3x})^2 + (R_{3z})^4 + 2(R_{3x})^2(R_{3z})^2$$
$$- 16(R_{1z})^2 + 8(R_{1z})^2(R_{3z})^2 - 8(R_{1x})^2$$
$$+ 8(R_{1z})^2(R_{3x})^2 + 8(R_{1x})^2(R_{3z})^2 + 8(R_{1z})^4$$
$$+ 16(R_{1x})^2(R_{1z})^2],$$

$$F_{40}^{(4)} = \frac{\sqrt{35}}{8}[1 - 2(R_{3z})^2 - 8(R_{3x})^2 + (R_{3z})^4 + 8(R_{3x})^2(R_{3z})^2$$
$$+ 8(R_{3x})^4],$$

$$F_{42}^{(4)} = \frac{\sqrt{7}}{4}[7 - 8(R_{3z})^2 - 16(R_{3x})^2 + (R_{3z})^4 + 8(R_{3x})^2(R_{3z})^2$$
$$- 6(R_{1z})^2 + 2(R_{1z})^2(R_{3z})^2 - 8(R_{1x})^2 + 8(R_{1z})^2(R_{3x})^2$$
$$+ 8(R_{1x})^2(R_{3z})^2 + 8(R_{3x})^4 + 16(R_{1x})^2(R_{3x})^2],$$

$$F_{44}^{(4)} = \frac{33}{8} - \frac{13}{4}(R_{3z})^2 - 5(R_{3x})^2 + \frac{1}{8}(R_{3z})^4 + (R_{3x})^2(R_{3z})^2$$
$$- 5(R_{1z})^2 + (R_{1z})^2(R_{3z})^2 - 12(R_{1x})^2 + (R_{3x})^4$$
$$+ 4(R_{1z})^2(R_{3x})^2 + 4(R_{1x})^2(R_{3z})^2 + (R_{1z})^4$$
$$+ 8(R_{1x})^2(R_{1z})^2 + 8(R_{1x})^2(R_{3x})^2 + 8(R_{1x})^4.$$

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