Statistical Theory of Elastic Constants of Cholesteric Liquid Crystals

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A statistical theory of cholesteric liquid crystals composed of short rigid biaxial molecules is presented. It is derived in the thermodynamic limit at a small density and a small twist. The uniaxial (biaxial) cholesteric phase is regarded as a distorted form of the uniaxial (biaxial) nematic phase. The chirality of the interactions and the implementation of the inversion to the rotation matrix elements are discussed in detail. General microscopic expressions for the elastic constants are derived. The expressions involve the one-particle distribution function and the potential energy of two-body short-range interactions. It is shown that the elastic constants determine the twist of the phase. The stability condition for the cholesteric and nematic phases is presented.

The theory is used to study unary and binary systems. The temperature and concentration dependence of the order parameters, the elastic constants and the twist of the phase are obtained. The possibility of phase separation is not investigated.

Key words: Liquid Crystals; Cholesterics; Elastic Constants; Mixtures.

1. Introduction

The cholesteric phase can be considered as a special case of the nematic phase [1]. The long axes of the anisotropic molecules are on the average aligned parallel to each other within planes. The direction of this alignment rotates smoothly as one proceeds in a direction perpendicular to the parallel planes. Such a phase (the twisted uniaxial nematic phase) will be called the uniaxial cholesteric phase. By analogy, the twisted biaxial nematic phase will be called the biaxial cholesteric phase. We note that in the case of the twisted biaxial nematic phase three twists around three perpendicular axes of biaxial symmetry should be considered simultaneously.

There are many models of the uniaxial cholesteric phase where molecules are assumed to be uniaxial. In 1970 Goossens[2] showed within the extended Maier-Saupe model that the quadrupole interactions give rise to the twist. In 1976 Straley [3] presented a statistical-mechanical theory of the elastic constants and of the spontaneous twisting of a cholesteric. He expressed the pitch by means of the elastic constants. We note that he gave the geometric interpretation of the chiral term which is often present in microscopic theories of cholesterics. This term can approximately describe the minimum approach distance of a pair of threaded rods. We will derive similar terms in the case of biaxial molecules. In 1977 Lin-Liu *et al.* [4] presented a molecular theory of cholesteric liquid crystals and showed the general form of the chiral potential energy of interactions for uniaxial molecules. They discussed different types of the temperature dependence of the pitch.

Real molecules forming liquid crystalline phases are never uniaxial and it is more realistic to assume less symmetric biaxial molecules. Some properties of the cholesteric phase formed by biaxial molecules were investigated in the past. In 1974 Priest and Lubensky [5] found the order of the biaxial order parameter and predicted a fluctuation instability. Van der Meer and Vertogen [6] discussed the dependence of the pitch on the biaxial order parameter. They also derived expressions for the temperature dependence of the pitch and the elastic constants [7] in the case of uniaxial cholesteric phases. Finally, in 1992 Evans [8] presented a hard body model for chiral nematic liquid crystals. The density functional theory was used, and molecules were represented by a hard convex twisted ellipsoidal core, with and without an encircling isotropic square well. The pitch was found to be density and temperature independent with values in the visible region of the spectrum. Long range potential softness could account for the increase of the pitch with decreasing temperature.

The phase behaviour of liquid crystalline mixtures has been studied, using a number of theoretical methods. In 1980 Sivardiere [9] introduced the Ising-like model and obtained a large variety of phase diagrams. Brochard *et al.* [10] considered the Maier-Saupe model and gave a catalogue of allowed diagrams for mixtures of nematogens. As far as the cholesteric mixtures are concerned, the theoretical and experimental works describe usually uniaxial cholesteric phases composed of uniaxial molecules. In 1971 Nakagiri *et al.* [11] studied the helical twisting power in nematic-cholesteric mixtures as functions of concentration. It was found that, as the concentration of the cholesteric material increases, the twisting power of the mixtures increases lineary up to a certain concentration, beyound which it increases more slowly, taking a maximum value at some specific concentration. Then, in the high-concentra tion region, the twisting power falls. We note that typically the additivity rule is satisfied as described in Section 5. In 1977 Lin-Liu *et al.* [4] presented a molecular theory of binary cholesteric mixtures. They considered uniaxial molecules and derived a formula showing how the pitch depends on temperature and concentration. Under certain conditions the formula reduces at fixed $T - T_\mathrm{C}$ to a simple quadratic rational fraction in the composition.

The forming of the cholesteric phase is closely connected with chirality. Some authors tried to establish quantitative relationships between molecular properties and measurable properties that result from chiral molecular structures. Osipov *et al.* [12] proposed an intrinsic molecular chirality tensor based only on nuclear position. The chirality tensor gives rise to two universal chirality indices, the first giving information about absolute chirality, and the second about anisotropy of the chirality. Recently Harris *et al.* [13] showed that any chiral measure of a geometric object is a pseudoscalar and must involve three-point correlations that only come into play when the molecule has at least four atoms. In general, a molecule is characterized by an infinite set of chiral parameters. However, one can also consider chirality of interactions [14, 15], and we will use this approach.

Our aim is to describe the uniaxial and biaxial cholesteric phases that consist of biaxial or uniaxial molecules. We would like to derive the microscopic expressions for the elastic constants and the pitch. We will investigate the inversion in the context of chirality. Our paper is organized as follows. In Sect. 2 we present a phenomenological continuum theory of cholesteric liquid crystals. In Sect. 3 we describe a statistical theory of cholesteric phases that consist of rigid biaxial molecules, and in Sect. 4 we derive general expressions for the elastic constants and the cholesteric pitch. A condition of stability is obtained that concerns both nematics and cholesterics. Exemplary calculations are presented in Sect. 5, were the Corner potential energy is applied. By means of symmetry considerations we will identyfy main chiral terms for biaxial molecules. In the limit of uniaxial molecules we will recover the results from [4]. In Sect. 6 we summarize the results of this work.

2. Phenomenological Approach

In this section we describe a uniform phase from a phenomenological point of view [16]. We assume that at every point $\vec{r}$ inside a considered phase we can define three orthonormal vectors $(\vec{L}(\vec{r}), \vec{M}(\vec{r}), \vec{N}(\vec{r}))$ reflecting orientational properties of this phase. In the case of the biaxial phase they determine directions of its two-fold 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

$$\vec{L} = L_\alpha \vec{e}_\alpha, \; \vec{M} = M_\alpha \vec{e}_\alpha, \; \vec{N} = N_\alpha \vec{e}_\alpha, \qquad (1)$$

where repeated indices imply summation. The completely ordered uniform phase is described by $(\vec{L}, \vec{M}, \vec{N}) = (\vec{e}_x, \vec{e}_y, \vec{e}_z)$.

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 $f_\mathrm{d}(\vec{r})$ was derived in [16] in the case of small distortions. When a considered phase has a D_2 symmetry group (the biaxial cholesteric phase) we get

$$\begin{aligned} f_\mathrm{d} = {} & K_{11}D_{11} + K_{22}D_{22} + K_{33}D_{33} \\ & + \frac{1}{2}K_{1111}(D_{11})^2 + \frac{1}{2}K_{1212}(D_{12})^2 + \frac{1}{2}K_{1313}(D_{13})^2 \\ & + \frac{1}{2}K_{2121}(D_{21})^2 + \frac{1}{2}K_{2222}(D_{22})^2 + \frac{1}{2}K_{2323}(D_{23})^2 \\ & + \frac{1}{2}K_{3131}(D_{31})^2 + \frac{1}{2}K_{3232}(D_{32})^2 + \frac{1}{2}K_{3333}(D_{33})^2 \end{aligned}$$

$$
\begin{aligned}
&+\frac{1}{2}(K_{1221}+K_{1122})(D_{12}D_{21}+D_{11}D_{22})\\
&+\frac{1}{2}(K_{1331}+K_{1133})(D_{13}D_{31}+D_{11}D_{33})\\
&+\frac{1}{2}(K_{2332}+K_{2233})(D_{23}D_{32}+D_{22}D_{33})\\
&+\frac{1}{2}(K_{1221}-K_{1122})(D_{12}D_{21}-D_{11}D_{22})\\
&+\frac{1}{2}(K_{1331}-K_{1133})(D_{13}D_{31}-D_{11}D_{33})\\
&+\frac{1}{2}(K_{2332}-K_{2233})(D_{23}D_{32}-D_{22}D_{33})\\
&+L_{123}\partial_\alpha(L_\alpha D_{23}+M_\alpha D_{13})\\
&+L_{231}\partial_\alpha(M_\alpha D_{31}+N_\alpha D_{21})\\
&+\ L_{312}\partial_\alpha(N_\alpha D_{12}+L_\alpha D_{32}),
\end{aligned}\tag{2}
$$

where $K_{ij}, K_{ijkl}=K_{klij}, L_{ijk}=L_{jik}$ are the elastic constants,

$$
\begin{aligned}
&D_{11}=L_\alpha M_\beta\partial_\alpha N_\beta, D_{12}=L_\alpha N_\beta\partial_\alpha L_\beta,\\
&D_{13}=L_\alpha L_\beta\partial_\alpha M_\beta,\\
&D_{21}=M_\alpha M_\beta\partial_\alpha N_\beta, D_{22}=M_\alpha N_\beta\partial_\alpha L_\beta,\\
&D_{23}=M_\alpha L_\beta\partial_\alpha M_\beta,\\
&D_{31}=N_\alpha M_\beta\partial_\alpha N_\beta, D_{32}=N_\alpha N_\beta\partial_\alpha L_\beta,\\
&D_{33}=N_\alpha L_\beta\partial_\alpha M_\beta.
\end{aligned}\tag{3}
$$

The terms with K_{ii} give 3 bulk terms, the terms with L_{ijk} give 3 surface terms, the terms with K_{ijkl} give 12 bulk and 3 surface terms of the form

$$
\begin{aligned}
&\partial_\alpha(L_\beta\partial_\beta L_\alpha-L_\alpha\partial_\beta L_\beta)=2(D_{23}D_{32}-D_{22}D_{33}),\\
&\partial_\alpha(M_\beta\partial_\beta M_\alpha-M_\alpha\partial_\beta M_\beta)=2(D_{31}D_{13}-D_{11}D_{33}),\\
&\partial_\alpha(N_\beta\partial_\beta N_\alpha-N_\alpha\partial_\beta N_\beta)=2(D_{12}D_{21}-D_{11}D_{22}).
\end{aligned}\tag{4}
$$

The total numbers of bulk and surface terms are 15 and 6, respectively.

If a considered phase possesses a D_∞ symmetry group (the uniaxial cholesteric phase), the number of elastic constants is smaller, because some constants from the previous case become dependent or zero. Let the z axis be oriented along the axis of symmetry. Then the distortion free-energy density has the form of the Frank expression

$$
\begin{aligned}
f_\mathrm{d}={}&K_0\vec{N}\cdot(\nabla\times\vec{N})+\frac{1}{2}K_1(\nabla\cdot\vec{N})^2\\
&+\frac{1}{2}K_2[\vec{N}\cdot(\nabla\times\vec{N})]^2+\frac{1}{2}K_3[\vec{N}\times(\nabla\times\vec{N})]^2\\
&+\frac{1}{2}K_4\nabla\cdot[(\vec{N}\cdot\nabla)\vec{N}-\vec{N}(\nabla\cdot\vec{N})]\\
&+\ \frac{1}{2}K_5\nabla\cdot[(\vec{N}\cdot\nabla)\vec{N}+\vec{N}(\nabla\cdot\vec{N})],
\end{aligned}\tag{5}
$$

where the relations among the nonzero elastic constants are

$$
\begin{aligned}
&K_0=K_{11}=K_{22},\ K_1=K_{1212}=K_{2121},\\
&K_2=K_{1111}=K_{2222},\ K_3=K_{3131}=K_{3232},\\
&K_4=(K_{1221}-K_{1122}+K_1+K_2)/2,\\
&K_5=2L_{231}=-2L_{312}.
\end{aligned}\tag{6}
$$

Therefore, in the case of the uniaxial phase we have 4 bulk (from K_0 to K_3) and 2 surface terms (K_4 and K_5). Therefore in the case of the uniaxial phase we have 4 bulk (from K_0 to K_3) and 2 surface terms (K_4 and K_5).

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; if not, the undistorted nematic conformation would not correspond to a minimum of the free energy F_d. In [17], 18 basic deformations proper for the continuum theory of biaxial nematics were given. They were divided into five groups and connected with relevant elastic constants: 3 twists (for K_{iiii}), 6 splays and bends (for K_{ijij}), 3 modified twists (for L_{ijk}) and two groups of 3 double twists (for K_{iijj} and for

K_{ijji}). Inside the formulas for deformations a parameter q was used ($1/q$ was a certain length). Small q meant a small deformation and a conformation close to the uniform one ($\vec{L}^{(0)}, \vec{M}^{(0)}, \vec{N}^{(0)}$). The vectors of the local frame were expanded into a power series with respect to q:

$$\vec{L} = \vec{L}^{(0)} + q\vec{L}^{(1)} + q^2\vec{L}^{(2)} + \ldots,$$

$$\vec{M} = \vec{M}^{(0)} + q\vec{M}^{(1)} + q^2\vec{M}^{(2)} + \ldots,$$

$$\vec{N} = \vec{N}^{(0)} + q\vec{N}^{(1)} + q^2\vec{N}^{(2)} + \ldots . \qquad (7)$$

It appeared that the most important terms in (7) were linear in q. They were sufficient to calculate the distortion free energy up to the second order in q, and to calculate the elastic constants of biaxial nematic liquid crystals. We add that for K_{ii} one should use the same deformations as for K_{iiii} because the relevant terms have different dependences on the parameter q and they do not mix.

3. Microscopic Approach

In this section we focus on the microscopic analysis of cholesteric liquid crystals. Let us consider a dilute gas of N molecules contained in a volume V, at the temperature T (in Kelvine). Let it be a binary mixture of N_A molecules A and N_B molecules B, where $N = N_A + N_B$. We assume that molecules are rigid blocks with three translational and three rotational degrees of freedom. The state of a molecule i is described by a vector of the position $\vec{r}_i$ and the orientation $R_i = (\phi_i, \theta_i, \psi_i)$, where ϕ_i, θ_i and ψ_i are the three Euler angles. On the other hand, one can use 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 as

$$\vec{l} = l_\alpha \vec{e}_\alpha,\ \vec{m} = m_\alpha \vec{e}_\alpha,\ \vec{n} = n_\alpha \vec{e}_\alpha. \qquad (8)$$

Let m_I, J_{Ix}, J_{Iy} and J_{Iz} denote the mass of a molecule I ($I = A$ or B) and the three moments of inertia, respectively. Apart from that, we denote $\vec{u} = \vec{r}_2 - \vec{r}_1 = u\vec{\Delta}$. $R_u = (\phi, \theta, \psi)$ are the three Euler angles for $\vec{\Delta}$. In fact, ψ is not used, because $\vec{\Delta} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, and R_u will appear inside the rotation matrix elements $D^{(l)}_{\mu 0}$.

We assume that molecules interact via two-body short-range forces which depend on the distance between molecules and their orientations; $\Phi^{IJ}_{12}(u, R_u, R_1, R_2)$ gives the potential energy of interactions ($I, J = A, B$). Now we would like to discuss in detail symmetries of the energy Φ^{IJ}_{12} and molecules, because it is crucial for the forming of the cholesteric phase. We note that the Euler angles always enter any formulas via the standard rotation matrix elements $D^{(l)}_{\mu\nu}$. There is a problem how to incorporate the inversion $\mathrm{C_i}$ into this formalism, because the inversion can not be expressed by means of rotations. However, one can try to simulate the inversion. We start from the vector $\vec{\Delta}$. After the inversion operation it gives $-\vec{\Delta}$. Let us denote the Euler angles after the inversion by $\mathbf{I}R_u$.

$$D^{(l)}_{\mu 0}(\mathbf{I}R_u) = D^{(l)}_{\mu 0}(\phi + \pi, \pi - \theta, \Psi(\psi))$$
$$= (-1)^l D^{(l)}_{\mu 0}(R_u). \qquad (9)$$

We used an unknown function Ψ of the angle ψ because the third Euler angle is not determined before and after the inversion. Note that the relation (9) is often generalized to the form [18]

$$D^{(l)}_{\mu\nu}(\mathbf{I}R_u) = (-1)^l D^{(l)}_{\mu\nu}(R_u). \qquad (10)$$

The relation (10) in general is not true because it cancels the matrix elements $D^{(l)}_{\mu\nu}$ with l odd. On the other hand such elements have to be used as described in [17].

Let us rewrite (9) in the form

$$D^{(l)}_{\mu 0}(\mathbf{I}R_u) = (-1)^l D^{(l)}_{\mu 0}(R_u) = D^{(l)}_{\mu 0}(R_u R_z(\pi)). \quad (11)$$

Thus, for the matrix elements $D^{(l)}_{\mu 0}$ the inversion can be connected with the rotation $R_z(\pi) = (0, \pi, 0)$ and the $\mathrm{C_2}$ symmetry group. This means that there is no difference between D_∞ and $\mathrm{D}_{\infty h}$ within the considered formalism.

We postulate that the invariance with respect to the inversion means the invariance with respect to the three separate rotations $R_x(\pi)$, $R_y(\pi)$ and $R_z(\pi)$ and one should replace $D^{(l)}_{\mu\nu}(\mathbf{I}R_u)$ with $D^{(l)}_{\mu\nu}(R_u R_x(\pi))$, $D^{(l)}_{\mu\nu}(R_u R_y(\pi))$ and $D^{(l)}_{\mu\nu}(R_u R_z(\pi))$, respectively. This connects C_i with the $\mathrm{D_2}$ symmetry group. This means that there is no difference between $\mathrm{D_2}$ and $\mathrm{D_{2h}}$ within the considered formalism. It is known that

$R_x(\pi) = R_y(\pi)R_z(\pi)$, so only two rotations have to be used.

Now we are in a position to discuss all symmetries of the potential energy Φ_{12}^{IJ}.

1. *Translational invariance:* It is satisfied because Φ_{12}^{IJ} depends on $\vec{u}$.

2. *Rotational invariance:* Φ_{12}^{IJ} should not depend on a choice of a reference frame. It means that for any rotation R

$$\Phi_{12}^{IJ}(u, RR_u, RR_1, RR_2) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2). \quad (12)$$

We add that generally it does not have to be satisfied because the interactions between two molecules can be modified by the presence of other molecules, especially in an ordered phase.

3. *Invariance with respect to the permutation of identical molecules:*

$$\Phi_{12}^{II}(u, \mathbf{I}R_u, R_2, R_1) = \Phi_{12}^{II}(u, R_u, R_1, R_2). \quad (13)$$

4. *Invariance with respect to the symmetry operations of molecules:* for biaxial molecules we apply operations from the D$_{2\mathrm{h}}$ symmetry group. For the molecule I

$$\Phi_{12}^{IJ}(u, R_u, R_1R_z(\pi), R_2) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2),$$
$$\Phi_{12}^{IJ}(u, R_u, R_1R_y(\pi), R_2) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2), \quad (14)$$

and for the molecule J

$$\Phi_{12}^{IJ}(u, R_u, R_1, R_2R_z(\pi)) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2),$$
$$\Phi_{12}^{IJ}(u, R_u, R_1, R_2R_y(\pi)) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2). \quad (15)$$

If the molecule I is uniaxial, we should add operations from the D$_{\infty\mathrm{h}}$ symmetry group. For any α

$$\Phi_{12}^{IJ}(u, R_u, R_1R_z(\alpha), R_2) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2). \quad (16)$$

5. *Invariance with respect to complex conjugation:* Φ_{12}^{IJ} should be a real function.

6. *Chirality of the interactions:* the interactions between molecules are *nonchiral* when

$$\Phi_{12}^{IJ}(u, \mathbf{I}R_u, \mathbf{I}R_1, \mathbf{I}R_2) = \Phi_{12}^{IJ}(u, R_u, R_1, R_2), \quad (17)$$

where $\mathbf{I}R$ denotes the Euler angles R after the inversion. In the opposite case the interactions are chiral, and this leads to the forming of the cholesteric phase.

The microscopic free energy of the binary mixture has the form [19]

$$\beta F = \sum_{I=A,B} \int \mathrm{d}(1) G_I(1) \left\{ \ln[G_I(1)\Lambda_I] - 1 \right\} - \frac{1}{2} \sum_{I,J=A,B} \int \mathrm{d}(1)\mathrm{d}(2) G_I(1) G_J(2) f_{12}^{IJ}, \quad (18)$$

where $G_I(1) = G_I(\vec{r}_1, R_1)$ are the one-particle distribution functions with the normalizations

$$\int \mathrm{d}(1) G_I(1) = N_I, \quad (19)$$

$d(1) = d\vec{r}_1 dR_1$. $f_{12}^{IJ} = \exp(-\beta\Phi_{12}^{IJ}) - 1$ are the Mayer functions, $\beta = 1/k_{\mathrm{B}}T$, and

$$\Lambda_I = \left(\frac{h^2\beta}{2\pi}\right)^3 \left(m_I^3 J_{Ix} J_{Iy} J_{Iz}\right)^{-1/2}. \quad (20)$$

Our set of state variables consists of T, V, N_A and N_B. The free energy (18) consists of the ideal terms (with Λ_I) and the excess terms directly related to intermolecular forces. The ideal terms are those of the ideal gas.

The expression (18) was derived systematically for binary mixtures from the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy equations in the thermodynamic limit ($N \to \infty, V \to \infty, N/V = \text{const}$) [19]. The two-particle distribution functions were expressed in terms of the one-particle distribution functions and the two-particle correlation functions of the simple form $\exp(-\beta\Phi_{12}^{IJ})$. This assumption guarantees the proper limit of the unary system.

The equilibrium distributions G_I minimizing the free energy (18) satisfy

$$\ln[G_I(1)\Lambda_I] - \sum_{J=A,B} \int \mathrm{d}(2) G_J(2) f_{12}^{IJ} = \text{const.} \quad (21)$$

In the homogeneous phase the distribution functions G_I do not depend on the position of a molecule and $G_I(1) = G_{0I}(R_1)$. In order to obtain G_{0I} one should solve the equations (21) together with (19).

In order to define the microscopic distortion free-energy density f_{d} one should also identify the homogeneous free-energy density f_0. Note that the terms with Λ_I in (18) are local: the integrands involve the distribution function for a single point only. Other terms couple the distributions at neighbouring points. The dependence of the free energy on the spatial variations of the ordering will be found by expanding this term in the gradients of G_J [3]. Substituting the Taylor expansion of $G_J(\vec{r}_1+\vec{u})$ into (18) we get

$$F = \int \mathrm{d}\vec{r}[f_0(\vec{r}) + f_d(\vec{r})], \tag{22}$$

where

$$\beta f_0(\vec{r}) = \sum_{I=A,B} \int \mathrm{d}R G_I(\vec{r},R)\{\ln[G_I(\vec{r},R)\Lambda_I] - 1\}$$
$$- \frac{1}{2} \sum_{I,J=A,B} \int \mathrm{d}R_1 dR_2 \mathrm{d}\vec{u} G_I(\vec{r},R_1) G_J(\vec{r},R_2) f_{12}^{IJ}, \tag{23}$$

$$\beta f_d(\vec{r}) = -\frac{1}{2} \sum_{I,J=A,B} \int \mathrm{d}R_1 dR_2 d\vec{u} G_I(\vec{r},R_1)$$
$$\cdot [(\vec{u}\cdot\nabla) G_J(\vec{r},R_2)] f_{12}^{IJ}$$
$$+ \frac{1}{4} \sum_{I,J=A,B} \int \mathrm{d}R_1 dR_2 \mathrm{d}\vec{u} [(\vec{u}\cdot\nabla) G_I(\vec{r},R_1)]$$
$$\cdot [(\vec{u}\cdot\nabla) G_J(\vec{r},R_2)] f_{12}^{IJ}. \tag{24}$$

Note that an integration by parts has been used to combine the second order terms, and the surface terms have been neglected thanks to the thermodynamic limit. The definition () is equivalent to that by Poniewierski and Stecki [20]. This is a well-founded assumption if we also assume slow variations of the vectors $(\vec{L},\vec{M},\vec{N})$. We will also restrict the one-particle distribution function G_I to the class of G_{0I} functions. This method was succesfully used in the past [21, 22]. As we expect, for the homogeneous phase f_{d} becomes equal to zero.

It was shown in [23, 17] that in the case of the homogeneous biaxial nematic phase composed of biaxial molecules, the one-particle distribution function G_{0I} depends on four arguments:

$$G_{0I}(R) = G_{0I}(\vec{l}\cdot\vec{e}_x, \vec{l}\cdot\vec{e}_z, \vec{n}\cdot\vec{e}_x, \vec{n}\cdot\vec{e}_z). \tag{25}$$

We postulate that the distribution of the distorted phase $G_I(\vec{r},R)$ can be written as

$$G_I(\vec{r},R) = G_{0I}(\vec{l}\cdot\vec{L}(\vec{r}), \vec{l}\cdot\vec{N}(\vec{r}), \vec{n}\cdot\vec{L}(\vec{r}), \vec{n}\cdot\vec{N}(\vec{r})), \tag{26}$$

where the reference frame $(\vec{e}_x,\vec{e}_y,\vec{e}_z)$ is replaced with the local frame $(\vec{L}(\vec{r}),\vec{M}(\vec{r}),\vec{N}(\vec{r}))$.

4. Elastic Constants

Now we are in a position to substitute the basic deformations into the microscopic distortion free-energy density (24) and the phenomenological distortion free-energy density (2) and (5). As a result of the comparison we get the microscopic formulas for the elastic constants. To make them more compact, we write

$$U_\alpha^I = \partial_1 G_{0I} l_\alpha + \partial_3 G_{0I} n_\alpha,$$
$$W_\alpha^I = \partial_2 G_{0I} l_\alpha + \partial_4 G_{0I} n_\alpha. \tag{27}$$

The microscopic expressions for the chiral elastic constants of the biaxial cholesteric phase are as follows:

$$\beta K_{11} = -\frac{1}{2} \int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x \sum_{I,J=A,B} f_{12}^{IJ} G_{0I}(R_1) W_{2y}^J,$$

$$\beta K_{22} = -\frac{1}{2} \int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y$$
$$\cdot \sum_{I,J=A,B} f_{12}^{IJ} G_{0I}(R_1)(U_{2z}^J - W_{2x}^J),$$

$$\beta K_{33} = \frac{1}{2} \int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_z \sum_{I,J=A,B} f_{12}^{IJ} G_{0I}(R_1) U_{2y}^J. \tag{28}$$

Microscopic expressions for the nonchiral elastic constants are the following. The first group is

$$\beta K_{1111} = \frac{1}{2} \int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1y}^I W_{2y}^J, \tag{29}$$

$$\beta K_{2222} = \frac{1}{2} \int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y^2$$
$$\cdot \sum_{I,J=A,B} f_{12}^{IJ} (U_{1z}^I - W_{1x}^I)(U_{2z}^J - W_{2x}^J), \tag{30}$$

$$\beta K_{3333} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} U_{1y}^I U_{2y}^J. \quad (31)$$

The second group is

$$\beta K_{1212} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x^2 \cdot \sum_{I,J=A,B} f_{12}^{IJ}(U_{1z}^I - W_{1x}^I)(U_{2z}^J - W_{2x}^J), \quad (32)$$

$$\beta K_{1313} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} U_{1y}^I U_{2y}^J, \quad (33)$$

$$\beta K_{2121} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1y}^I W_{2y}^J, \quad (34)$$

$$\beta K_{2323} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} U_{1y}^I U_{2y}^J, \quad (35)$$

$$\beta K_{3131} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1y}^I W_{2y}^J, \quad (36)$$

$$\beta K_{3232} = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_z^2 \cdot \sum_{I,J=A,B} f_{12}^{IJ}(U_{1z}^I - W_{1x}^I)(U_{2z}^J - W_{2x}^J). \quad (37)$$

The third group is

$$L_{123} = L_{231} = L_{312} = 0. \quad (38)$$

The fourth group is

$$\beta K_{1122} = \frac{1}{4}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x u_y \sum_{I,J=A,B} f_{12}^{IJ} \cdot [(U_{1z}^I - W_{1x}^I)W_{2y}^J + W_{1y}^I(U_{2z}^J - W_{2x}^J)], \quad (39)$$

$$\beta K_{2233} = \frac{1}{4}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y u_z \sum_{I,J=A,B} f_{12}^{IJ} \cdot [-U_{1y}^I(U_{2z}^J - W_{2x}^J) - (U_{1z}^I - W_{1x}^I)U_{2y}^J], \quad (40)$$

$$\beta K_{1133} = \frac{1}{4}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x u_z \cdot \sum_{I,J=A,B} f_{12}^{IJ}[-U_{1y}^I W_{2y}^J - W_{1y}^I U_{2y}^J]. \quad (41)$$

The fifth group is

$$K_{1221} = K_{1122},\ K_{1331} = K_{1133},\ K_{2332} = K_{2233}. \quad (42)$$

In the case of the uniaxial cholesteric phase the expression for the chiral elastic constant is

$$\beta K_0 = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y \sum_{I,J=A,B} f_{12}^{IJ} G_{0I}(R_1) W_{2x}^J. \quad (43)$$

The expressions for the nonchiral elastic constants are as follows:

$$\beta K_1 = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1x}^I W_{2x}^J, \quad (44)$$

$$\beta K_2 = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1x}^I W_{2x}^J, \quad (45)$$

$$\beta K_3 = \frac{1}{2}\int \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\vec{u} u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1x}^I W_{2x}^J, \quad (46)$$

$$K_4 = \frac{1}{2}(K_1 + K_2), \quad (47)$$

$$K_5 = 0. \quad (48)$$

Let us show how the elastic constants determine the state of cholesteric liquid crystals. It is very important that, when we look for the physical state of the liquid crystal in the thermodynamic limit, we should remove all surface terms from the phenomenological free-energy densities. The reason is that in the thermodynamic limit all surface terms are negligible. We used the surface terms to derive the expressions for the elastic constants to assure the consistency because the surface terms are present in hidden form in the microscopic free-energy density. The equilibrium distortion of the uniaxial cholesteric phase is a pure twist

$$\vec{N}(\vec{r}) = [0, -\sin(qx), \cos(qx)], \quad (49)$$

where $q = K_0/K_2$, $P = 2\pi/|q|$ is the cholesteric pitch and $f_\mathrm{d} = -K_0^2/2K_2$. Note that the sign of K_0 distinguishes between right- and left-handed helices.

For the biaxial cholesteric liquid crystals the equilibrium distortion is composed of three twists with respect to the orthogonal axes. In the limit of small distortions the vectors of the local frame have the form

$$\begin{aligned}\vec{L} &= (1, q_3 z, -q_2 y),\\ \vec{M} &= (-q_3 z, 1, q_1 x),\\ \vec{N} &= (q_2 y, -q_1 x, 1),\end{aligned} \tag{50}$$

where $q_i = W_i/W$,

$$\begin{aligned}W &= K_{1111}K_{2222}K_{3333} + 2K_{1122}K_{1133}K_{2233}\\ &\quad - K_{1111}K_{2233}^2 - K_{2222}K_{1133}^2 - K_{3333}K_{1122}^2,\\ W_1 &= K_{11}(K_{2222}K_{3333} - K_{2233}^2)\\ &\quad + K_{22}(K_{1133}K_{2233} - K_{1122}K_{3333})\\ &\quad + K_{33}(K_{1122}K_{2233} - K_{1133}K_{2222}),\\ W_2 &= K_{11}(K_{1133}K_{2233} - K_{1122}K_{3333})\\ &\quad + K_{22}(K_{1111}K_{3333} - K_{1133}^2)\\ &\quad + K_{33}(K_{1122}K_{1133} - K_{1111}K_{2233}),\\ W_3 &= K_{11}(K_{1122}K_{2233} - K_{1133}K_{2222})\\ &\quad + K_{22}(K_{1133}K_{1122} - K_{1111}K_{2233})\\ &\quad + K_{33}(K_{1111}K_{2222} - K_{1122}^2).\end{aligned} \tag{51}$$

The distortion free-energy density at the minimum is

$$\begin{aligned}f_\mathrm{d} &= [2K_{11}K_{22}(K_{3333}K_{1122} - K_{1133}K_{2233})\\ &\quad + 2K_{11}K_{33}(K_{2222}K_{1133} - K_{1122}K_{2233})\\ &\quad + 2K_{22}K_{33}(K_{1111}K_{2233} - K_{1122}K_{1133})\\ &\quad + K_{11}^2(K_{2233}^2 - K_{2222}K_{3333})\\ &\quad + K_{22}^2(K_{1133}^2 - K_{1111}K_{3333})\\ &\quad + K_{33}^2(K_{1122}^2 - K_{1111}K_{2222})]/2W^2.\end{aligned} \tag{52}$$

It is important that a global minimum of f_d exists only if the matrix

$$\begin{bmatrix} K_{1111} & K_{1122} & K_{1133}\\ K_{1122} & K_{2222} & K_{2233}\\ K_{1133} & K_{2233} & K_{3333}\end{bmatrix} \tag{53}$$

is positive definite. In the opposite case there is no stable biaxial cholesteric (and nematic) phase. Taking the uniaxial phase limit, we get simpler conditions. We can say that there is a stable cholesteric or nematic phase only if

$$K_1 < 3K_2. \tag{54}$$

As far as we know almost all theories and all real and computer experiments agree with the relation (54). The equality $K_1 = 3K_2$ appears in some theories with hard molecules [21, 24].

5. Exemplary Calculations

The aim of this section is to express the elastic constants by means of the order parameters which can be measured in experiments. We will apply the Corner potential energy of the interactions because in principle it allows detailed calculations without any additional approximations. On the other hand, it is quite realistic. The Corner potential energy has the form $\Phi_{12}^{IJ}(u/\sigma^{IJ})$, where σ^{IJ} depends on the orientations R_1, R_2, and R_u. For σ^{IJ} one can write the general expansion proposed by Blum and Torruela [18]. It involvs the 3-j Wigner symbols and the standard rotation matrix elements. The same expression was used to describe the interactions of biaxial molecules in [23]. In the case of biaxial molecules the lowest order terms of the expansion give

$$\begin{aligned}\sigma^{IJ} &= \sigma_0^{IJ} + \sigma_{11}^{IJ}(\vec{\Delta}\cdot\vec{n}_1)^2 + \sigma_{12}^{IJ}(\vec{\Delta}\cdot\vec{n}_2)^2\\ &\quad + \sigma_2^{IJ}(\vec{n}_1\cdot\vec{n}_2)^2 + \sigma_{31}^{IJ}(\vec{\Delta}\cdot\vec{l}_1)^2 + \sigma_{32}^{IJ}(\vec{\Delta}\cdot\vec{l}_2)^2\\ &\quad + \sigma_4^{IJ}(\vec{l}_1\cdot\vec{l}_2)^2 + \sigma_{51}^{IJ}(\vec{l}_1\cdot\vec{n}_2)^2 + \sigma_{52}^{IJ}(\vec{n}_1\cdot\vec{l}_2)^2\\ &\quad + \sigma_6^{IJ}(\vec{n}_1\cdot\vec{n}_2)(\vec{n}_1\times\vec{n}_2)\cdot\vec{\Delta}\\ &\quad + \sigma_{71}^{IJ}[(\vec{l}_1\cdot\vec{n}_2)(\vec{l}_1\times\vec{n}_2)\cdot\vec{\Delta} - (\vec{m}_1\cdot\vec{n}_2)(\vec{m}_1\times\vec{n}_2)\cdot\vec{\Delta}]\\ &\quad + \sigma_{72}^{IJ}[(\vec{n}_1\cdot\vec{l}_2)(\vec{n}_1\times\vec{l}_2)\cdot\vec{\Delta} - (\vec{n}_1\cdot\vec{m}_2)(\vec{n}_1\times\vec{m}_2)\cdot\vec{\Delta}]\\ &\quad + \sigma_8^{IJ}[(\vec{l}_1\cdot\vec{l}_2)(\vec{l}_1\times\vec{l}_2)\cdot\vec{\Delta} + (\vec{m}_1\cdot\vec{m}_2)(\vec{m}_1\times\vec{m}_2)\cdot\vec{\Delta}\\ &\quad - (\vec{l}_1\cdot\vec{m}_2)(\vec{l}_1\times\vec{m}_2)\cdot\vec{\Delta} - (\vec{m}_1\cdot\vec{l}_2)(\vec{m}_1\times\vec{l}_2)\cdot\vec{\Delta}].\end{aligned} \tag{55}$$

There are 13 molecular parameters that determine the main features of the interactions between biaxial molecules. We would like to add some comments to this long expression. The terms with $\sigma_0^{IJ}, \sigma_{11}^{IJ}, \sigma_{12}^{IJ}$, and σ_2^{IJ} describe the nonchiral interactions of uniaxial molecules. The term with σ_6^{IJ} describes the chiral part of their interactions. A similar term was used in the past [4, 25]. The terms with $\sigma_0^{IJ}, \sigma_{11}^{IJ}, \sigma_{12}^{IJ}, \sigma_2^{IJ}, \sigma_{31}^{IJ}, \sigma_{32}^{IJ}, \sigma_4^{IJ}, \sigma_{51}^{IJ}$, and σ_{52}^{IJ} describe the nonchiral interactions of biaxial molecules [23, 17]. The additional terms with $\sigma_6^{IJ}, \sigma_{71}^{IJ}, \sigma_{72}^{IJ}$ and σ_8^{IJ} allow to decribe the chiral interactions of biaxial molecules. As far as we know they were not presented in the literature. Note that the terms with $\vec{\Delta}$ couple the translational and rotational degrees of freedom.

In order to set the proper values of the parameters σ_i^{IJ} one should investigated the equipotential surfaces of the potential energy. The excluded volume method described in [23] can be helpful. Molecules I are described by $\sigma_0^{II}, \sigma_1^{II} \equiv \sigma_{11}^{II} = \sigma_{12}^{II}, \sigma_2^{II}, \sigma_3^{II} \equiv \sigma_{31}^{II} = \sigma_{32}^{II}$, σ_4^{II}, $\sigma_5^{II} \equiv \sigma_{51}^{II} = \sigma_{52}^{II}$, σ_6^{II}, $\sigma_7^{II} \equiv \sigma_{71}^{II} = \sigma_{72}^{II}$, and σ_8^{II}. The interactions between molecles I and J we describe by

$$\sigma_0^{IJ} = (\sigma_0^{II} + \sigma_0^{JJ})/2,\ \sigma_{11}^{IJ} = \sigma_1^{II},\ \sigma_{12}^{IJ} = \sigma_1^{JJ},$$

$$\sigma_2^{IJ} = (\sigma_2^{II} + \sigma_2^{JJ})/2,\ \sigma_{31}^{IJ} = \sigma_3^{II},\ \sigma_{32}^{IJ} = \sigma_3^{JJ},$$

$$\sigma_4^{IJ} = (\sigma_4^{II} + \sigma_4^{JJ})/2,\ \sigma_{51}^{IJ} = \sigma_{52}^{IJ} = (\sigma_5^{II} + \sigma_5^{JJ})/2,$$

$$\sigma_6^{IJ} = (\sigma_6^{II} + \sigma_6^{JJ})/2,\ \sigma_{71}^{IJ} = \sigma_{72}^{IJ} = (\sigma_7^{II} + \sigma_7^{JJ})/2,$$

$$\sigma_8^{IJ} = (\sigma_8^{II} + \sigma_8^{JJ})/2. \tag{56}$$

The parameters σ_i^{IJ} are the molecular constants that in our model determine the ordering of the phase, the value of the elastic constants and the twist of the phase. As far as the functional dependence of the potential energy on u/σ^{IJ} is concerned, we have many possibilities and we will mention two of them, together with a function $B_s(T)$ defined as

$$B_s(T) = \int_0^\infty \mathrm{d}x x^s f_{12}^{IJ}(x)$$

$$= \int_0^\infty \mathrm{d}x x^s [\exp(-\beta \Phi_{12}^{IJ}(x)) - 1]. \tag{57}$$

Let ϵ denotes a depth of the potential energy (we assume for simplicity that it is the same for both types of molecules).

1. The *soft-core potential energy:*

$$\Phi_{12}^{IJ}(u/\sigma^{IJ}) = \epsilon(\sigma^{IJ}/u)^m, \tag{58}$$

$$B_s(T) = \frac{-1}{s+1} \Gamma \left(\frac{m-s-1}{m} \right) \left(\frac{\epsilon}{k_{\mathrm{B}} T} \right)^{(s+1)/m}. \tag{59}$$

2. The *square-well potential energy:*

$$\Phi_{12}^{IJ}(u/\sigma^{IJ}) = \begin{cases} +\infty & \text{for } (u/\sigma^{IJ}) < 1 \\ -\epsilon & \text{for } 1 < (u/\sigma^{IJ}) < R_{\mathrm{SW}} \\ 0 & \text{for } (u/\sigma^{IJ}) > R_{\mathrm{SW}}, \end{cases} \tag{60}$$

$$B_s(T) = \frac{1}{s+1} \left[\left(\exp(\epsilon/k_B T) - 1 \right) (R_{SW}^{s+1} - 1) - 1 \right]. \tag{61}$$

Let us define dimensionless functions $f_I(R) = G_{0I}(R) V/N_I$ with the normalization

$$\int \mathrm{d}R f_I(R) = 1. \tag{62}$$

In order to describe systems with biaxial symmetry it is convenient to introduce the complete set of basic functions (invariants) proper for that kind of symmetry. They are closely connected with the rotation matrix elements and have the form

$$F_{\mu\nu}^{(j)}(R) = \left(\frac{1}{\sqrt{2}} \right)^{2+\delta_{\mu 0}+\delta_{0\nu}}$$

$$\cdot \sum_{\rho,\sigma=\pm 1} (-1)^{j(\sigma-\rho)/2} D_{\rho\cdot\mu,\sigma\cdot\nu}^{(j)}(R), \tag{63}$$

where j is a nonnegative integer, μ, ν are even. 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 $2 \le \nu \le j$. The invariants are real and orthogonal functions

$$\int \mathrm{d}R F_{\mu\nu}^{(j)}(R) F_{\rho\sigma}^{(k)}(R) = \delta_{jk} \delta_{\mu\rho} \delta_{\nu\sigma} 8\pi^2/(2j+1). \tag{64}$$

The properties of the invariants were described in [17]. It was shown that all $F_{\mu\nu}^{(j)}$ can be expressed by means of $(\vec{l} \cdot \vec{e}_x)^2$, $(\vec{l} \cdot \vec{e}_z)^2$, $(\vec{n} \cdot \vec{e}_x)^2$ and $(\vec{n} \cdot \vec{e}_z)^2$. Let us show the most important invariants with $j = 2$:

$$F_{00}^{(2)} = [-1 + 3(\vec{n} \cdot \vec{e}_z)^2]/2,$$

$$F_{02}^{(2)} = [-1 + (\vec{n}\cdot\vec{e}_z)^2 + 2(\vec{l}\cdot\vec{e}_z)^2]\sqrt{3}/2,$$

$$F_{20}^{(2)} = [-1 + (\vec{n}\cdot\vec{e}_z)^2 + 2(\vec{n}\cdot\vec{e}_x)^2]\sqrt{3}/2,$$

$$F_{22}^{(2)} = [-3 + (\vec{n}\cdot\vec{e}_z)^2 + 2(\vec{l}\cdot\vec{e}_z)^2 + 2(\vec{n}\cdot\vec{e}_x)^2 + 4(\vec{l}\cdot\vec{e}_x)^2]/2. \quad (65)$$

For the first time all four invariants (with different normalization) appeared in the paper by Straley [26]. Let us define the order parameters for our system as

$$\langle F_{\mu\nu}^{(j)}\rangle_I \equiv \int \mathrm{d}R f_I(R) F_{\mu\nu}^{(j)}(R). \quad (66)$$

Note that for the completely ordered biaxial phase we have $\langle F_{\mu\nu}^{(j)}\rangle_I = \delta_{\mu\nu}$, thus the most important are $\langle F_{00}^{(2)}\rangle_I$ and $\langle F_{22}^{(2)}\rangle_I$ (S and V in the Straley notation).

Let us rewrite (21) for the one-particle distribution function of the uniform phase. It is identical to one in the theory with nonchiral interactions. We define

$$K^{IJ}(R_1, R_2) = \int \mathrm{d}\vec{\Delta}(\sigma^{IJ}/\sigma_0^{IJ})^3, \quad (67)$$

$$\lambda^{IJ} = B_2(T)(\sigma_0^{IJ})^3 N_J/V. \quad (68)$$

The kernel K^{IJ} and the distribution functions f_I can be expressed in terms of the invariants

$$K^{IJ}(R, 0) = \sum_j \sum_{\mu\nu} K_{\mu\nu}^{(j)IJ} F_{\mu\nu}^{(j)}(R), \quad (69)$$

$$\ln f_I(R) = \sum_j \sum_{\mu\nu} S_{\mu\nu}^{(j)I} F_{\mu\nu}^{(j)}(R). \quad (70)$$

Note that for σ^{IJ} given by (55) both sums (69) and (70) are *finite* series. Thus the distribution function f_I is fully described by 35 coefficients $S_{\mu\nu}^{(j)I}$. We calculate the coefficients $S_{\mu\nu}^{(j)I}$ from the equations

$$S_{\mu\nu}^{(j)I} = \sum_{J=A,B} \lambda^{IJ} \sum_{\rho} K_{\rho\nu}^{(j)IJ} \langle F_{\mu\rho}^{(j)}\rangle_J \text{ for } j > 0, \quad (71)$$

$$\langle F_{00}^{0}\rangle_I = 1 \quad \text{(the normalization condition)}. \quad (72)$$

Now we move to the elastic constants. We can expand the distribution function f_I in an infinite series with respect to invariants

$$f_I(R) = \sum_j \sum_{\mu\nu} \langle F_{\mu\nu}^{(j)}\rangle_I F_{\mu\nu}^{(j)}(R)(2j + 1)/(8\pi^2). \quad (73)$$

All elastic constants can be written as *finite* sums of the form

$$K_{ii} = \sum \xi^{IJ} \langle F_{\mu\nu}^{(j)}\rangle_I \langle F_{\rho\sigma}^{(k)}\rangle_J B_{ii,\mu\nu\rho\sigma}^{(j)(k)IJ}, \quad (74)$$

$$K_{ijkl} = \sum \eta^{IJ} \langle F_{\mu\nu}^{(j)}\rangle_I \langle F_{\rho\sigma}^{(k)}\rangle_J A_{ijkl,\mu\nu\rho\sigma}^{(j)(k)IJ}, \quad (75)$$

where

$$\xi^{IJ} = k_\mathrm{B} T B_3(T)(\sigma_0^{IJ})^4 N_I N_J/V^2, \quad (76)$$

$$\eta^{IJ} = k_\mathrm{B} T B_4(T)(\sigma_0^{IJ})^5 N_I N_J/V^2, \quad (77)$$

The coefficients $K_{\mu\nu}^{(j)IJ}$, $A_{ijkl,\mu\nu\rho\sigma}^{(j)(k)IJ}$, and $B_{ii,\mu\nu\rho\sigma}^{(j)(k)IJ}$ are polynomials in $(\sigma_i^{IJ}/\sigma_0^{IJ})$ that can be calculated analytically.

5.1. Unary Phase of Biaxial Molecules

For simplicity in our calculations we took into account only the dependence on the order parameters $\langle F_{00}^{(2)}\rangle$ and $\langle F_{22}^{(2)}\rangle$. We assumed the square-well potential energy of interactions with $R_\mathrm{SW} = 2$. Note that σ_0 determines the length scale, whereas ϵ determines the energy scale. The elastic constants will be expressed in ϵ/σ_0 and ϵ/σ_0^2, temperatures will be given in ϵ/k_B. We assumed that molecules are similar to ellipsoids with three different axes $(\sigma_0/2) \times (\sigma_0) \times (2\sigma_0)$. We used $V/N = 8\sigma_0^3$, and our set of the molecular parameters is

$$\sigma_1 = \sigma_0/2,\ \sigma_2 = \sigma_0/2,\ \sigma_3 = -\sigma_0/4,$$

$$\sigma_4 = \sigma_5 = 0,\ \sigma_6 = \sigma_7 = \sigma_8 = \sigma_0/10. \quad (78)$$

In our system, on decreasing the temperature we meet the first-order transition to the uniaxial cholesteric phase at $T = 1.94$ and the second-order transition to the biaxial cholesteric phase at $T = 0.41$. The temperature dependence of the order parameters $\langle F_{00}^{(2)}\rangle$ and $\langle F_{22}^{(2)}\rangle$ is presented in Figure 1. The order parameters were used to calculate the temperature dependence of the elastic constants. It appeared that the factors ξ and

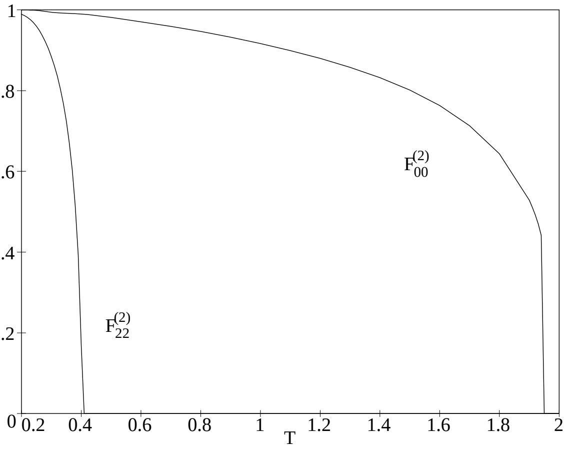

Fig. 1. Temperature dependence of the order parameters $\langle F^{(2)}_{00} \rangle$ and $\langle F^{(2)}_{22} \rangle$.

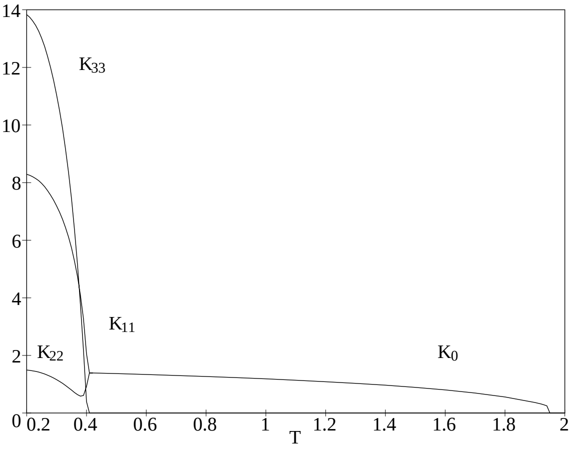

Fig. 2. Temperature dependence of the chiral elastic constants K_{ii}/ξ. In the uniaxial cholesteric phase (between T = 1.94 and T = 0.41) we have $K_0 = K_{11} = K_{22}$ and K_{33} = 0. In the biaxial cholesteric phase (below T = 0.41) K_0 splits into two constants and K_{33} becomes nonzero.

η introduce very strong variations with temperature, and it was more comfortable to present the elastic constant divided by those factors as shown in Figs. 2 and 3. The corresponding twist parameters q and q_i are shown in Figure 4.

In the uniaxial cholesteric phase there is one chiral constant (K_0) and three nonchiral ones (K_1, K_2 and K_3). The twist parameter q describing the pure twist is decreasing with temperature. For some potential energies one can obtain also the increasing temperature dependence, more often present in cholesterics. We have also the accidental equality $K_1 = K_3$ caused by the omission of the order parameters $\langle F^{(j)}_{\mu\nu} \rangle$ with j greater than 2. Typically, for rodlike molecules we get the inequalities $K_2 < K_1 < K_3$.

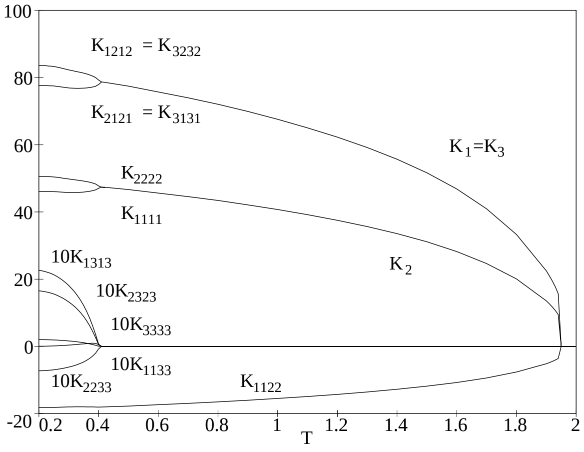

Fig. 3. Temperature dependence of the nonchiral elastic constants K_{ijkl}/η. In the uniaxial cholesteric phase (between T = 1.94 and T = 0.41) we have $K_1 = K_{1212} = K_{2121}$ equal to $K_3 = K_{3131} = K_{3232}$ and $K_2 = K_{1111} = K_{2222}$. We have also $K_{1122} = (K_2 - K_1)/2$. In the biaxial cholesteric phase (below T = 0.41) K_1, K_2, and K_3 split into two constants, K_{1122} becomes an independent constant, five constants become nonzero (K_{1133}, K_{2233}, K_{1313}, K_{2323}, and K_{3333}).

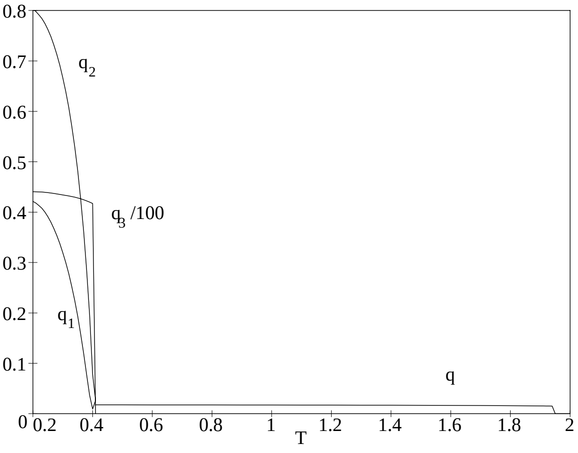

Fig. 4. Temperature dependence of the twist parameters q and q_i. In the uniaxial cholesteric phase (between T = 1.94 and T = 0.41) we have $q > 0$. In the biaxial cholesteric phase (below T = 0.41) all q_i are positive and $q_1 < q_2 < q_3$.

In the biaxial cholesteric phase we have three chiral constants (K_{11}, K_{22} and K_{33}) and twelve nonchiral ones. On decreasing the temperature, K_0 splits into $K_{11} > K_{22}$ and K_{33} becomes nonzero. K_1 splits

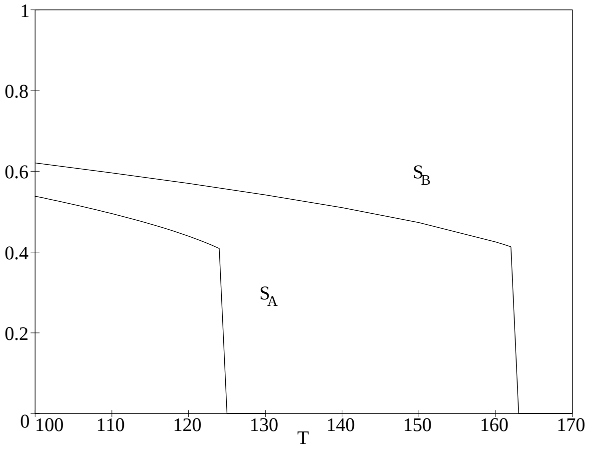

Fig. 5. Temperature dependence of the order parameters $S_A = \langle P_2 \rangle_A$ (Cholesteric) and $S_B = \langle P_2 \rangle_B$ (Nematic) for the unary systems.

into $K_{1212} > K_{2121}$, K_3 splits into $K_{3232} > K_{3131}$, K_2 splits into $K_{2222} > K_{1111}$, 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}. They are about two orders of magnitude smaller then the previous ones. The twist parameters q_i are quickly increasing with decreasing temperature and satisfy the inequalities $q_1 < q_2 < q_3$.

5.2. Binary Phase of Uniaxial Molecules

We mixed the prolate molecules interacting via the soft core potential with $m = 12$. The set of molecular parameters is

$$\sigma_0^{AA} = \sigma_0, \ \sigma_1^{AA} = 0.2\sigma_0,$$

$$\sigma_2^{AA} = -0.2\sigma_0, \ \sigma_6^{AA} = -0.1\sigma_0,$$

$$\sigma_0^{BB} = \sigma_0, \ \sigma_1^{BB} = 0.3\sigma_0,$$

$$\sigma_2^{BB} = -0.2\sigma_0, \ \sigma_6^{BB} = 0, \tag{79}$$

where σ_0 denotes some molecular length and $V/N = 4.471\sigma_0^3$. The elastic constants will be expressed in $10^{-6}\epsilon/\sigma_0^2$ and $10^{-6}\epsilon/\sigma_0$, the temperature in $10^{-6}\epsilon/k_\mathrm{B}$.

For simplicity reasons we assume that only one phase is present. It corresponds to the stable solution with the minimum free energy. The possibility of phase separation will not be investigated. We checked the stability against perturbations of nematic symmetry and the stability against deformations of the phase.

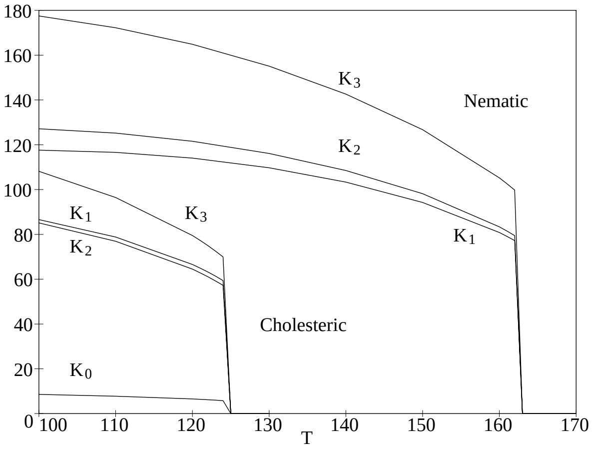

Fig. 6. Temperature dependence of the elastic constants for the unary systems.

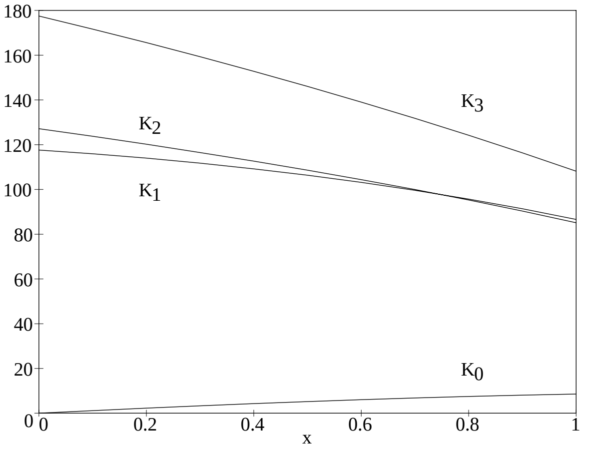

Fig. 7. Elastic constants vs. composition of the mixture at the temperature $T = 100$ ($x = N_A/N$).

The molecules A and B in the unary phase form the uniaxial cholesteric and nematic phase, respectively. The transition temperatures of unary systems from the isotropic to the uniaxial cholesteric or nematic phase are $T_A = 124$ and $T_B = 162$. The temperature dependence of the order parameters $\langle P_2 \rangle_I$ and the elastic constants for unary systems are shown in Figs. 5 and 6. The pitch of the system of molecules A is a falling concave function of the temperature.

In the considered range of temperatures the isotropic or uniaxial cholesteric phase was present in the mixture. The transition temperature T_C of the binary system from the isotropic to the uniaxial cholesteric phase can be described approximately as

$$T_{\mathrm{C}} = \sum_{I=A,B} x_I T_I . \tag{80}$$

We performed a detailed analysis of the mixture at the temperature $T = 100$ where the uniaxial cholesteric phase was present for all concentrations. The order parameters and the elastic constants are continous and concave functions of the concentration x_A. The dependence of the elastic constants on the concentration is plotted in Figure 7. The twist of the mixture is approximately described by the equation

$$q = \sum_{I=A,B} x_I q_I , \tag{81}$$

where the q_I are related to the unary systems at the same temperature. The additivity rule (81) is satisfied for most mixtures between cholesterol derivatives [1] but there are some exceptions [27]. Note that in general q_I may be positive or negative.

6. Conclusions

In this paper we developed the statistical theory for the uniaxial and biaxial cholesteric phases. Rigid molecules interacting via two-body short-range forces were assumed. We derived the microscopic formulas for the elastic constants and the pitch of the phase. In order to calculate the values of the elastic constants one needs the one-particle distribution function and the potential energy of the molecular interactions. It is showed that the elastic constants determine the twist of the phase. The obtained stability condition is to our knowledge not to be found in the literature. In the case of the uniaxial cholesteric or nematic phase it has the simple form $K_1 < 3K_2$. It seems that it is satisfied for all known substances.

Our theory was applied to the unary and binary systems of molecules similar to ellipsoids with three different axes. Thanks to the Corner potential energy the elastic constants were expressed as a finite series of the order parameters. Apart from this the role of the temperature is more transparent: the function $B_2(T)$ determines the order parameters; the functions $B_3(T)$ and $B_4(T)$ are closely related to the chiral and nonchiral elastic constants, respectively. The temperature dependence of the order parameters, the elastic constants and the twists in uniaxial and biaxial cholesteric phases was obtained.

The results concernig the nonchiral elastic constants K_{ijkl} are the same as in the case of nematic phases described in [17]. We focus on the new results on the chiral elastic constants K_{ii}. During the transition from a uniaxial to a biaxial cholesteric phase K_0 splits into K_{11} and K_{22}, whereas K_{33} becomes nonzero. Below a certain temperature they satisfy the inequalities $K_{11} < K_{22} < K_{33}$. The corresponding twist parameters satisfy the similar relations $q_1 < q_2 < q_3$. Note that those relations depend on the type of molecular interactions and do not have to be always satisfied.

In the binary mixture it appeared that the transition temperatures and the twist of the mixture approximately satisfy the simple additivity rules.

Our theory is a starting point for further research. It is desirable to go beyound the low density limit where the Mayer function is replaced with a better approximation of the direct correlation function c_2. The theory can be generalized to the case of many component liquid crystalline mixtures. We are also waiting for experimental data on the biaxial nematic and cholesteric phases and the elastic constants as, according to Kini and Chandrasekhar, experiments are feasible [28]. The experiments can verify the theoretical predictions and provide new problems.

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