# Elastic Constants of Binary Liquid Crystalline Mixtures

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Microscopic expressions for the elastic constants of binary liquid crystalline mixtures composed of short rigid uniaxial molecules are derived in the thermodynamic limit at small distorsions and a small density. Uniaxial and biaxial nematic phases are considered. The expressions involve the one-particle distribution functions and the potential energy of two-body short-range interactions. The theory is used to calculate the phase diagram of a mixture of rigid prolate and oblate molecules. The concentration dependence of the order parameters and the elastic constants are obtained. The possibility of phase separation is not investigated.

*Key words:* Liquid Crystals; Nematics; Elastic Constants; Mixtures.

## 1. Introduction

The elastic constants of liquid crystals are the material constants that appear in the description of almost all phenomena where the variation of the director is manipulated by external fields [1]. They are of technological importance because liquid crystals have found wide application, e. g., in display devices, laser technique, holography, termography, nuclear and microwave techniques. On the other hand, the elastic constants give information on the microscopic anisotropic intermolecular forces. They are also needed in the study of defects in liquid crystals [2].

There are microscopic theories [3 - 8] that give working expressions for the elastic constants of one-component uniaxial nematic liquid crystals. But in technical applications very often some special properties are required, and chemically pure substances with the desired ones are hard to find. That is why mixtures are widely used. It is clear that theories which allow to understand the physical properties of mixtures are helpful in designing mixtures with the prescribed technical parameters. Miscibility studies are also important from a more fundamental point of view – to identify new phases. The rule that is used is the following: if two phases are continuously miscible without crossing any (first- or second-order) transition line, they have the same symmetry. This method can often be carried out under the microscope (in a concentration gradient) and is faster than taking an X-ray picture [1].

In this paper we present a statistical theory of the elastic constants of binary liquid crystalline mixtures. Uniaxial and biaxial nematic phases will be considered. Since a theoretical description of biaxial phases (and mixtures) is rather complex [9, 10] we developed our theory with some approximations: rigid molecules, small density and the thermodynamic limit. Our aim is to express the elastic constants by means of the one-particle distribution functions and the potential energy of molecular interactions. The thermodynamic limit suggests that we neglect surface effects. Nevertheless we will obtain some known relations for the surface elastic constants and we will interprete those relations as consistency conditions.

The phase behaviour of liquid crystal mixtures has been studied using a number of theoretical methods. A large variety of phase diagrams was presented in the paper by Sivardiere [11] where the Ising-like model was introduced. Brochard *et al.* [12] considered the less artificial Maier-Saupe model and gave a catalogue of allowed diagrams for mixtures of nematogens. In 1973 Alben [13] considered a mean-field lattice model with discrete orientations to describe steric interactions in mixtures of rods and discs. He predicted the existence of a biaxial phase in the composition range between two uniaxial phases. Similar results have been obtained for van der Waals lattice models in mean-field [14] and renormalization group [15] theories. The question of thermodynamical stability

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against phase separation was addressed by Palffy-Muhoray *et al.* [16] within a mean-field theory. The geometric mean assumption about the pseudopotential leads to instability of a biaxial phase, whereas a deviation from this assumption leads to a stable biaxial phase [17]. A mean-field theory was also used to describe binary mixtures of biaxial molecules [18, 19]. Mixtures of rods and spheres were studied by Agren [20], Humphries and Luckhurst [21], and Martire *et al.* [22]. The result is that the introduction of spheres induces, via a small two-phase region, a transition to an isotropic phase. Mixtures of rods of different length-to-width ratios were analysed by Peterson *et al.* [23], Warner and Flory [24], and Lekkerkerker *et al.* [25]. Recently, different demixing mechanisms in hard rod [26] and rod-plate mixtures [27] were analysed by van Roij and Mulder.

As far as the elastic constants are concerned, to our knowlwdge there are no experimental data on biaxial phases. In 1989 Kini and Chandrasekhar [28] studied the effects of external magnetic and electric fields applied in different geometries. They showed that it is feasible to determine some of the twelve elastic constants. Our theory could help to predict the temperature and concentration dependence of them in the case of binary mixtures.

Our paper is organized as follows: In Sect. 2 we present a phenomenological continuum theory of nematic liquid crystals. In Sect. 3 we describe a statistical theory of nematic phases and derive general expressions for the elastic constants in the case of uniaxial and biaxial nematic phases. Exemplary calculations of the values of the elastic constants are presented in Sect. 4, where the Corner potential energy is applied and a mixture of rods and discs is analysed. In Sect. 5 we summarize the results of this work.

## 2. Phenomenological Approach

### 2.1. Description of a Phase

In this section we describe nematic liquid crystals from a phenomenological point of view [29]. We assume that at every point $\boldsymbol{r}$ inside a considered phase we can define three orthonormal versors $(\boldsymbol{L}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r}), \boldsymbol{N}(\boldsymbol{r}))$ which reflect properties of this phase. In case of a biaxial phase they determine directions of its two-fold axes of symmetry. The vectors $(\boldsymbol{L}, \boldsymbol{M}, \boldsymbol{N})$ create the local frame which can be expressed by means of a space-fixed reference frame $(\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z)$ as

$$\boldsymbol{L} = R_{1\alpha}\boldsymbol{e}_\alpha,\ \boldsymbol{M} = R_{2\alpha}\boldsymbol{e}_\alpha,\ \boldsymbol{N} = R_{3\alpha}\boldsymbol{e}_\alpha, \tag{1}$$

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

$$R_{i\alpha}R_{j\alpha} = \delta_{ij}, \tag{2}$$

$$R_{i\alpha}R_{i\beta} = \delta_{\alpha\beta}. \tag{3}$$

Relations (2) and (3) express the orthogonality and the completeness of the local frame. Note that repeated indices imply summation. The homogeneous phase is described by $R_{i\alpha} = \delta_{i\alpha}$.

### 2.2. Distorsion Free Energy

Let us call $F_\mathrm{d}$ the free energy due to the distorsion of the local frame $(\boldsymbol{L}, \boldsymbol{M}, \boldsymbol{N})$. A general expression of its density $f_d(\boldsymbol{r})$ was derived in [29] in the case of small distorsions. It has the form

$$f_\mathrm{d}(\boldsymbol{r}) = k_{ij}D_{ij} + \frac{1}{2}K_{ijkl}D_{ij}D_{kl} + \frac{1}{2}L_{ijk}S_{ijk}, \tag{4}$$

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

$$D_{ij} = \frac{1}{2}\epsilon_{jkl}R_{i\alpha}R_{k\beta}\partial_\alpha R_{l\beta}, \tag{5}$$

$$S_{ijk} = S_{jik} = \partial_\alpha(R_{i\alpha}D_{jk} + R_{j\alpha}D_{ik}), \tag{6}$$

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

$$K_{ijkl} = K_{klij},\ L_{ijk} = L_{jik}. \tag{7}$$

In general, the linear first order terms with $k_{ij}$ give 6 bulk and 3 surface terms; the quadratic first order terms with $K_{ijkl}$ give 39 bulk and 6 surface terms; the terms with $L_{ijk}$ give 18 surface terms. The total number of bulk and surface terms is 45 and 27, respectively.

When a considered phase has a $D_{2h}$ symmetry group, the distorsion free-energy density has the form

$$
\begin{aligned}
f_{\mathrm{d}} = {} & \frac{1}{2}K_{1111}(D_{11})^2 + \frac{1}{2}K_{1212}(D_{12})^2 + \frac{1}{2}K_{1313}(D_{13})^2 \\
& + \frac{1}{2}K_{2121}(D_{21})^2 + \frac{1}{2}K_{2222}(D_{22})^2 + \frac{1}{2}K_{2323}(D_{23})^2 \\
& + \frac{1}{2}K_{3131}(D_{31})^2 + \frac{1}{2}K_{3232}(D_{32})^2 + \frac{1}{2}K_{3333}(D_{33})^2 \\
& + K_{1122}D_{11}D_{22} + K_{1133}D_{11}D_{33} + K_{2233}D_{22}D_{33} \\
& + K_{1221}D_{12}D_{21} + K_{1331}D_{13}D_{31} + K_{2332}D_{23}D_{32} \\
& + L_{123}S_{123} + L_{231}S_{231} + L_{312}S_{312}. \qquad (8)
\end{aligned}
$$

The terms with $K_{ijkl}$ give 12 bulk and 3 surface terms, whereas the terms with $L_{ijk}$ give 3 surface terms. The total numbers of bulk and surface terms are 12 and 6, respectively.

When a considered phase possesses a $D_{\infty h}$ symmetry group, the number of elastic constants is smaller. Let the $z$ axis be oriented along the axis of symmetry. Then the distorsion free-energy density has the form

$$
\begin{aligned}
f_{\mathrm{d}} = {} & \frac{1}{2}K_1(\nabla \cdot \boldsymbol{N})^2 + \frac{1}{2}K_2[\boldsymbol{N} \cdot (\nabla \times \boldsymbol{N})]^2 \\
& + \frac{1}{2}K_3[\boldsymbol{N} \times (\nabla \times \boldsymbol{N})]^2 \\
& + \frac{1}{2}K_4\nabla \cdot [(\boldsymbol{N} \cdot \nabla)\boldsymbol{N} - \boldsymbol{N}(\nabla \cdot \boldsymbol{N})] \\
& + \frac{1}{2}K_5\nabla \cdot [(\boldsymbol{N} \cdot \nabla)\boldsymbol{N} + \boldsymbol{N}(\nabla \cdot \boldsymbol{N})].
\end{aligned} \qquad (9)
$$

Therefore, in case of an uniaxial phase we have 3 bulk ($K_1$, $K_2$ and $K_3$) and 2 surface terms ($K_4$ and $K_5$). One can calculate the distorsion free energy from its density (8) or (9) by

$$
F_{\mathrm{d}} = \int \mathrm{d}\boldsymbol{r} f_{\mathrm{d}}. \qquad (10)
$$

Note that we can not reject surface terms in (8) or (9) although we assume the thermodynamic limit. This will be explained in Sect. 5.

### 2.3. Basic Deformations

Splay, twist, and bend are known as the three basic types of deformations in the continuum theory of uniaxial nematics. They describe spatial variations of the director $\boldsymbol{N}(\boldsymbol{r})$ and extract from the distorsion free energy terms with $K_1$, $K_2$ and $K_3$, respectively. In [10] 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 $K_{ijji}$). In the formulas for deformations a parameter $\epsilon$ was used ($1/\epsilon$ is a certain length). Small $\epsilon$ meant a small deformation and a conformation close to the homogeneous one ($\boldsymbol{L}^{(0)}, \boldsymbol{M}^{(0)}, \boldsymbol{N}^{(0)}$). The vectors of the local frame were expanded into a power series with respect to $\epsilon$

$$
\begin{aligned}
\boldsymbol{L} &= \boldsymbol{L}^{(0)} + \epsilon\, \boldsymbol{L}^{(1)} + \epsilon^2 \boldsymbol{L}^{(2)} + \ldots, \\
\boldsymbol{M} &= \boldsymbol{M}^{(0)} + \epsilon\, \boldsymbol{M}^{(1)} + \epsilon^2 \boldsymbol{M}^{(2)} + \ldots, \qquad (11) \\
\boldsymbol{N} &= \boldsymbol{N}^{(0)} + \epsilon\, \boldsymbol{N}^{(1)} + \epsilon^2 \boldsymbol{N}^{(2)} + \ldots .
\end{aligned}
$$

It appeared that the most important terms in (11) were those linear in $\epsilon$. They were sufficient to calculate the distorsion free enery up to the second order in $\epsilon$ and to calculate the elastic constants of biaxial nematic liquid crystals. For the sake of completeness we list the terms linear in $\epsilon$ from (11) for all groups of deformations. The first group is, for $K_{1111}$,

$$
\boldsymbol{L}^{(1)} = (0,0,0),\ \boldsymbol{M}^{(1)} = (0,0,x),\ \boldsymbol{N}^{(1)} = (0,-x,0), \qquad (12)
$$

for $K_{2222}$,

$$
\boldsymbol{L}^{(1)} = (0,0,-y),\ \boldsymbol{M}^{(1)} = (0,0,0),\ \boldsymbol{N}^{(1)} = (y,0,0), \qquad (13)
$$

and for $K_{3333}$,

$$
\boldsymbol{L}^{(1)} = (0,z,0),\ \boldsymbol{M}^{(1)} = (-z,0,0),\ \boldsymbol{N}^{(1)} = (0,0,0). \qquad (14)
$$

The second group is, for $K_{1212}$,

$$
\boldsymbol{L}^{(1)} = (0,0,-x), \boldsymbol{M}^{(1)} = (0,0,0), \boldsymbol{N}^{(1)} = (x,0,0), \qquad (15)
$$

for $K_{1313}$,

$$
\boldsymbol{L}^{(1)} = (0,-x,0), \boldsymbol{M}^{(1)} = (x,0,0), \boldsymbol{N}^{(1)} = (0,0,0), \qquad (16)
$$

for $K_{2121}$,

$$
\boldsymbol{L}^{(1)} = (0,0,0),\ \boldsymbol{M}^{(1)} = (0,0,-y),\ \boldsymbol{N}^{(1)} = (0,y,0), \qquad (17)
$$

for $K_{2323}$,

$$
\boldsymbol{L}^{(1)} = (0,y,0),\ \boldsymbol{M}^{(1)} = (-y,0,0),\ \boldsymbol{N}^{(1)} = (0,0,0), \qquad (18)
$$

for $K_{3131}$,

$$\boldsymbol{L}^{(1)} = (0,0,0),\ \boldsymbol{M}^{(1)} = (0,0,z),\ \boldsymbol{N}^{(1)} = (0,-z,0), \quad (19)$$

and for $K_{3232}$,

$$\boldsymbol{L}^{(1)} = (0,0,z),\ \boldsymbol{M}^{(1)} = (0,0,0),\ \boldsymbol{N}^{(1)} = (-z,0,0). \quad (20)$$

The third group is, for $L_{123}$,

$$\boldsymbol{L}^{(1)} = (0,x,0),\ \boldsymbol{M}^{(1)} = (-x,0,0),\ \boldsymbol{N}^{(1)} = (0,0,0), \quad (21)$$

for $L_{231}$,

$$\boldsymbol{L}^{(1)} = (0,0,0),\ \boldsymbol{M}^{(1)} = (0,0,y),\ \boldsymbol{N}^{(1)} = (0,-y,0), \quad (22)$$

and for $L_{312}$,

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

The fourth group is, for $K_{1122}$,

$$\boldsymbol{L}^{(1)} = (0,0,-y), \boldsymbol{M}^{(1)} = (0,0,x), \boldsymbol{N}^{(1)} = (y,-x,0), \quad (24)$$

for $K_{1133}$,

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

and for $K_{2233}$,

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

The fifth group is, for $K_{1221}$,

$$\boldsymbol{L}^{(1)} = (0,0,-x), \boldsymbol{M}^{(1)} = (0,0,y), \boldsymbol{N}^{(1)} = (x,-y,0), \quad (27)$$

for $K_{1331}$,

$$\boldsymbol{L}^{(1)} = (0,x,0), \boldsymbol{M}^{(1)} = (-x,0,z), \boldsymbol{N}^{(1)} = (0,-z,0), \quad (28)$$

and for $K_{2332}$,

$$\boldsymbol{L}^{(1)} = (0,y,-z), \boldsymbol{M}^{(1)} = (-y,0,0), \boldsymbol{N}^{(1)} = (z,0,0). \quad (29)$$

## 3. Microscopic Approach

### 3.1. Description of a System

This section is devoted to the microscopic analysis of binary mixtures of uniaxial nematogens which create a homogeneous phase. Let us consider a mixture which consists of two types of rigid uniaxial molecules $A$ and $B$. Orientations are described by two angles $\phi$ and $\theta$ or by a unit vector $\boldsymbol{\Omega}$. We assume a small density approximation, and we take only two-body short-range interactions into account. The potential energies $\Phi_{12}^{IJ}$ depend on a vector of the distance between molecules and orientations of molecules.

The microscopic free energy of the binary mixture has the form [30]

$$\beta F = \sum_{I=A,B} \int \mathrm{d}(1) G_I(1) \left\{ \ln[G_I(1) \Lambda_5^I] - 1 \right\} - \frac{1}{2} \sum_{I,J=A,B} \int \mathrm{d}(1)\mathrm{d}(2) G_I(1) G_J(2) f_{12}^{IJ}, \quad (30)$$

where $G_I(1) = G_I(\boldsymbol{r}_1, \boldsymbol{\Omega}_1)$ $(I = A, B)$ are the one-particle distribution functions with the normalizations

$$\int \mathrm{d}(1) G_I(1) = N_I, \quad (31)$$

$\mathrm{d}(1) = \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{\Omega}_1 = \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\phi_1 \mathrm{d}\theta_1 \sin\theta_1$, $N_I$ denotes the number of molecules $I$ in the volume $V$ $(N_A + N_B = N)$, $f_{12}^{IJ}$ are the Mayer functions $f_{12}^{IJ} = \exp(-\beta\Phi_{12}^{IJ}) - 1$, $\beta = 1/k_B T$, and

$$\Lambda_5^I = \left( \frac{h^2 \beta}{2\pi m_I} \right)^{3/2} \left( \frac{h^2 \beta}{2\pi J_I} \right). \quad (32)$$

The subscript 5 in $\Lambda_5^I$ denotes 5 degrees of freedom of an infinitely thin molecule, although we use this description also for spatially extended uniaxial molecules. $T$ denotes the temperature, $m_I$ is the mass of a molecule $I$, and $J_I$ is a parameter with a dimension of a moment of inertia (for a very prolate molecule it is exactly the moment of inertia with respect to the axis perpendicular to the molecule). Our set of state variables consists of $T$, $V$, $N_A$ and $N_B$. The free energy (30) consists of the ideal terms (with $\Lambda_5^I$) and the excess terms directly related to intermolecular forces. The ideal terms are those of the ideal gas.

The expression (30) was derived systematically for binary mixtures from the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy equations in the thermodynamic limit ($N \to \infty, V \to \infty, N/V = \text{const}$) [30]. Two-particle distribution functions were expressed in terms of 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 (30) satisfy

$$\ln[G_I(1)\Lambda_5^I] - \sum_{J=A,B} \int \mathrm{d}(2) G_J(2) f_{12}^{IJ} = \text{const.} \tag{33}$$

In the homogeneous phase the distribution function $G_I$ does not depend on the position of a molecule and $G_I(1) = G_{0I}(\boldsymbol{\Omega}_1)$. In order to obtain $G_{0I}$ one should solve (33) together with (31).

### 3.2. Distorsion Free Energy

In order to define the microscopic distorsion free energy $F_\mathrm{d}$ one should first identify a homogeneous free energy $F_0$. We would like to divide the total free energy $F$ into a homogeneous free energy $F_0$ and the distorsion free energy $F_\mathrm{d}$. We postulate that

$$\begin{aligned} \beta F_0 = {} & \\ & \sum_{I=A,B} \int \mathrm{d}(1) G_I(1) \left\{ \ln[G_I(1)\Lambda_5^I] - 1 \right\} \\ & - \frac{1}{4} \sum_{I,J=A,B} \int \mathrm{d}(1)\mathrm{d}(2) G_I(\boldsymbol{r}_1, \boldsymbol{\Omega}_1) G_J(\boldsymbol{r}_1, \boldsymbol{\Omega}_2) f_{12}^{IJ} \\ & - \frac{1}{4} \sum_{I,J=A,B} \int \mathrm{d}(1)\mathrm{d}(2) G_I(\boldsymbol{r}_2, \boldsymbol{\Omega}_1) G_J(\boldsymbol{r}_2, \boldsymbol{\Omega}_2) f_{12}^{IJ}. \end{aligned} \tag{34}$$

The definition (34) is equivalent to that by Poniewierski and Stecki [6]. This is a well-founded assumption if we also assume slow variations of the vectors $(\boldsymbol{L}, \boldsymbol{M}, \boldsymbol{N})$. We will also restrict the one-particle distribution functions $G_I$ to the class of $G_{0I}$ functions. This method was succesfully used in the past [5, 31, 32].

Thus, the distorsion free energy can be written as

$$F_\mathrm{d} = F - F_0, \tag{35}$$

were $F$ and $F_0$ are given by (30) and (34), respectively. As we expect, for the homogeneous phase $F_\mathrm{d}$ becomes zero.

In the subsequent sections we will construct the distribution functions for distorted phases and we will derive the microscopic formulas for the elastic constants. Biaxial and uniaxial nematic phases will be considered separately.

### 3.3 Elastic Constants of Biaxial Phases

It was shown in [10, 33] that in the case of a homogeneous biaxial nematic phase composed of uniaxial molecules the one-particle distribution functions $G_I$ depend on two arguments:

$$G_{0I}(\boldsymbol{\Omega}) = G_{0I}(\boldsymbol{\Omega} \cdot \boldsymbol{e}_x, \boldsymbol{\Omega} \cdot \boldsymbol{e}_z), \tag{36}$$

where it is assumed that the vectors $\boldsymbol{e}_\alpha$ of the reference frame coincide with the phase symmetry axes. In the distorted phase we postulate that

$$G_I(\boldsymbol{r}, \boldsymbol{\Omega}) = G_{0I}(Q_1, Q_2), \tag{37}$$

where the relevant arguments are

$$\begin{aligned} Q_1(\boldsymbol{r}, \boldsymbol{\Omega}) &= \boldsymbol{\Omega} \cdot \boldsymbol{L}(\boldsymbol{r}), \\ Q_2(\boldsymbol{r}, \boldsymbol{\Omega}) &= \boldsymbol{\Omega} \cdot \boldsymbol{N}(\boldsymbol{r}). \end{aligned} \tag{38}$$

The local orientation of the phase is described by the vectors $(\boldsymbol{L}, \boldsymbol{M}, \boldsymbol{N})$. We can use the distorsion free-energy density (8) and apply basic deformations described in Section 2. We will follow a procedure similar to one described in [10]. Let us expand the arguments (38) in a power series with respect to $\epsilon$,

$$Q_i = Q_i^{(0)} + \epsilon Q_i^{(1)} + \epsilon^2 Q_i^{(2)} + \cdots, \tag{39}$$

where by means of the expansions (11) we build

$$\begin{aligned} Q_1^{(p)}(\boldsymbol{r}, \boldsymbol{\Omega}) &= \boldsymbol{\Omega} \cdot \boldsymbol{L}^{(p)}(\boldsymbol{r}), \\ Q_2^{(p)}(\boldsymbol{r}, \boldsymbol{\Omega}) &= \boldsymbol{\Omega} \cdot \boldsymbol{N}^{(p)}(\boldsymbol{r}). \end{aligned} \tag{40}$$

The expansion of $G_I$ has the form

$$\begin{aligned} G_I(\boldsymbol{r}, \boldsymbol{\Omega}) = {} & G_{0I}(Q_1^{(0)}, Q_2^{(0)}) \\ & + \epsilon \sum_{i=1,2} \partial_i G_{0I}(Q_1^{(0)}, Q_2^{(0)}) Q_i^{(1)} \\ & + \epsilon^2 \sum_{i=1,2} \partial_i G_{0I}(Q_1^{(0)}, Q_2^{(0)}) Q_i^{(2)} \\ & + \frac{\epsilon^2}{2} \sum_{i,j=1,2} \partial_i \partial_j G_{0I}(Q_1^{(0)}, Q_2^{(0)}) Q_i^{(1)} Q_j^{(1)} \\ & + O(\epsilon^3). \end{aligned} \tag{41}$$

When we substitute the expansion (41) into the distorsion free energy (35) we get

$$\begin{aligned}\beta F_{\mathrm{d}} = \frac{1}{4}\int d(1)d(2)\epsilon^2 \sum_{I,J=A,B} f_{12}^{IJ} \sum_{i,j=1,2} \partial_i G_{0I}(\boldsymbol{\Omega}_1)\partial_j G_{0J}(\boldsymbol{\Omega}_2)\Big[ &-2Q_i^{(1)}(\boldsymbol{r}_1,\boldsymbol{\Omega}_1)Q_j^{(1)}(\boldsymbol{r}_2,\boldsymbol{\Omega}_2) \\ &+ Q_i^{(1)}(\boldsymbol{r}_1,\boldsymbol{\Omega}_1)Q_j^{(1)}(\boldsymbol{r}_1,\boldsymbol{\Omega}_2) + Q_i^{(1)}(\boldsymbol{r}_2,\boldsymbol{\Omega}_1)Q_j^{(1)}(\boldsymbol{r}_2,\boldsymbol{\Omega}_2)\Big] + O(\epsilon^3).\end{aligned} \tag{42}$$

We substitute the basic deformations into the microscopic distorsion free energy (42) and to the phenomenological distorsion free energy (8). By comparison we get the microscopic formulas for the elastic constants. The first group is

$$\beta K_{1111} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1y}^I W_{2y}^J, \tag{43}$$

$$\beta K_{2222} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} (U_{1z}^I - W_{1x}^I)(U_{2z}^J - W_{2x}^J), \tag{44}$$

$$\beta K_{3333} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} U_{1y}^I U_{2y}^J. \tag{45}$$

The second group is

$$\beta K_{1212} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2 d\boldsymbol{u}u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} (U_{1z}^I - W_{1x}^I)(U_{2z}^J - W_{2x}^J), \tag{46}$$

$$\beta K_{1313} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} U_{1y}^I U_{2y}^J, \tag{47}$$

$$\beta K_{2121} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1y}^I W_{2y}^J, \tag{48}$$

$$\beta K_{2323} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} U_{1y}^I U_{2y}^J, \tag{49}$$

$$\beta K_{3131} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} W_{1y}^I W_{2y}^J, \tag{50}$$

$$\beta K_{3232} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} (U_{1z}^I - W_{1x}^I)(U_{2z}^J - W_{2x}^J). \tag{51}$$

The third group is

$$L_{123} = L_{231} = L_{312} = 0. \tag{52}$$

The fourth group is

$$\beta K_{1122} = \frac{1}{4}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_x u_y \sum_{I,J=A,B} f_{12}^{IJ} \big[(U_{1z}^I - W_{1x}^I)W_{2y}^J + W_{1y}^I(U_{2z}^J - W_{2x}^J)\big], \tag{53}$$

$$\beta K_{2233} = \frac{1}{4}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_y u_z \sum_{I,J=A,B} f_{12}^{IJ} \big[-U_{1y}^I(U_{2z}^J - W_{2x}^J) - (U_{1z}^I - W_{1x}^I)U_{2y}^J\big], \tag{54}$$

$$\beta K_{1133} = \frac{1}{4}\int \mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2\mathrm{d}\boldsymbol{u}u_x u_z \sum_{I,J=A,B} f_{12}^{IJ} \big[-U_{1y}^I W_{2y}^J - W_{1y}^I U_{2y}^J\big]. \tag{55}$$

The fifth group is,

$$K_{1221} = K_{1122},\ K_{1331} = K_{1133},\ K_{2332} = K_{2233}. \tag{56}$$

To make the formulas for the elastic constants more compact we write

$$\begin{aligned} U^I_\alpha &= \partial_1 G_{0I}(Q_1^{(0)}, Q_2^{(0)})\Omega_\alpha, \\ W^I_\alpha &= \partial_2 G_{0I}(Q_1^{(0)}, Q_2^{(0)})\Omega_\alpha. \end{aligned} \tag{57}$$

### 3.4. *Elastic Constants of Uniaxial Phases*

In a homogeneous uniaxial phase we have one global symmetry axis which can be oriented along $\boldsymbol{e}_z$. The one-particle distribution functions depend on a one argument, thus

$$\partial_1 G_{0I}(\boldsymbol{\Omega}\cdot\boldsymbol{e}_x, \boldsymbol{\Omega}\cdot\boldsymbol{e}_z) = 0,\ U^I_\alpha = 0. \tag{58}$$

The microscopic expressions for the elastic constants that result from (43) - (56) are

$$\beta K_1 = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{u} u_x^2 \sum_{I,J=A,B} f_{12}^{IJ} W^I_{1x} W^J_{2x}, \tag{59}$$

$$\beta K_2 = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{u} u_y^2 \sum_{I,J=A,B} f_{12}^{IJ} W^I_{1x} W^J_{2x}, \tag{60}$$

$$\beta K_3 = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{u} u_z^2 \sum_{I,J=A,B} f_{12}^{IJ} W^I_{1x} W^J_{2x}, \tag{61}$$

$$K_4 = \frac{1}{2}(K_1 + K_2), \tag{62}$$

$$K_5 = 0. \tag{63}$$

Note that the results (62) - (63) are consistent with the wide discussion on surface elasticity by Yokoyama [34]. These expressions results from (52) and (56) when we change the symmetry of the phase from biaxial to uniaxial.

## 4. 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 interactions because in principle it allows detailed calculations without any additional approximations. On the other hand, it is quite realistic.

### 4.1. *Homogeneous Phases*

In order to simplify calculations for the biaxial phase we assume that the one-particle distribution functions $G_{0I}$ depend only on the angle between the long axis of a molecule, determined by a unit vector $\boldsymbol{\Omega}$, and some symmetry axis, determined by a unit vector $\boldsymbol{e}_I$,

$$G_{0I}(\boldsymbol{\Omega}) = G_{0I}(\boldsymbol{\Omega}\cdot\boldsymbol{e}_I). \tag{64}$$

For the uniaxial phase we will assume that $\boldsymbol{e}_A = \boldsymbol{e}_B$, whereas for the biaxial phase $\boldsymbol{e}_A \cdot \boldsymbol{e}_B = 0$. It is convenient to define dimensionless functions $f_I$

$$G_{I0}(\boldsymbol{\Omega}\cdot\boldsymbol{e}_I) = f_I(\boldsymbol{\Omega}\cdot\boldsymbol{e}_I) N_I / 4\pi V, \tag{65}$$

where the normalization condition is

$$\int \mathrm{d}\boldsymbol{\Omega} f_I(\boldsymbol{\Omega}\cdot\boldsymbol{e}_I)/4\pi = \int_0^1 \mathrm{d}x f_I(x) = 1. \tag{66}$$

The order parameters are defined as

$$\langle P_j \rangle_I = \int_0^1 \mathrm{d}x P_j(x) f_I(x). \tag{67}$$

The functions $f_I$ can be expanded in an infinite series with respect to the Legendre polynomials

$$f_I(x) = \sum_{j-\text{even}} (2j+1)\langle P_j \rangle_I P_j(x). \tag{68}$$

It is useful to describe the nematic ordering of molecules $I$ in a mixture by a symmetric traceless second-rank tensor $\mathbf{S}^I$ with elements [35]

$$\begin{aligned} S^I_{\alpha\beta} &= \langle \Omega_\alpha \Omega_\beta - \frac{1}{3}\delta_{\alpha\beta} \rangle_I \\ &= \frac{1}{4\pi}\int \mathrm{d}\boldsymbol{\Omega} f_I(\boldsymbol{\Omega}\cdot\boldsymbol{e}_I)\Big[\Omega_\alpha\Omega_\beta - \frac{1}{3}\delta_{\alpha\beta}\Big]. \end{aligned} \tag{69}$$

We can show that

$$S^I_{\alpha\beta} = \langle P_2 \rangle_I \Big[(\boldsymbol{e}_\alpha\cdot\boldsymbol{e}_I)(\boldsymbol{e}_\beta\cdot\boldsymbol{e}_I) - \frac{1}{3}(\boldsymbol{e}_\alpha\cdot\boldsymbol{e}_\beta)\Big]. \tag{70}$$

The tensor $\mathbf{S}^I$ is diagonal only if $\boldsymbol{e}_I$ is equal to $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ or $\boldsymbol{e}_z$. Finally, we define an average tensor $\mathbf{S}$ as

$$\mathbf{S} = x_A \mathbf{S}^A + x_B \mathbf{S}^B, \tag{71}$$

where we used concentrations $x_I = N_I/N$. We note that because of our approximation (64), the tensors $\mathbf{S}^I$ are uniaxial (2 different eigenvalues). But the average tensor $\mathbf{S}$ is in general biaxial (3 different eigenvalues) if $\boldsymbol{e}_A \cdot \boldsymbol{e}_B = 0$.

Let us consider the Corner potential energy of the form $\Phi_{12}^{IJ}(u/\sigma^{IJ})$, where $u$ is the distance between molecules $I$ and $J$, $\boldsymbol{u} = u\boldsymbol{\Delta}$, $\sigma^{IJ}$ depends on vectors $\boldsymbol{\Omega}_1$, $\boldsymbol{\Omega}_2$ and $\boldsymbol{\Delta}$. For $\sigma^{IJ}$ one can write the general expansion proposed by Blum and Torruela [36]. It involvs the 3-j Wigner symbols and the standard rotation matrix elements. The same expression was used to describe interactions of biaxial molecules in [33]. In the case of uniaxial molecules, the lowest order terms of the expansion give

$$\begin{aligned}\sigma^{IJ}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \boldsymbol{\Delta}) = \sigma_0^{IJ} + \sigma_{11}^{IJ}(\boldsymbol{\Delta} \cdot \boldsymbol{\Omega}_1)^2 \\ + \sigma_{12}^{IJ}(\boldsymbol{\Delta} \cdot \boldsymbol{\Omega}_2)^2 + \sigma_2^{IJ}(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2)^2.\end{aligned} \tag{72}$$

There are a number of posibilities for the functional dependence of $\Phi_{12}^{IJ}$ on $u/\sigma^{IJ}$, and some of them were given in [10]. We do not have to specify it now, because this dependence will be hidden in a function $B_s(T^*)$ defined as

$$\begin{aligned}B_s(T^*) &= \int_0^\infty \mathrm{d}x\, x^s\, f_{12}(x) \\ &= \int_0^\infty \mathrm{d}x\, x^s \left[\exp(-\beta\Phi_{12}(x)) - 1\right],\end{aligned} \tag{73}$$

where $T^* = 1/\beta\epsilon$ is a dimensionless temperature and $\epsilon$ is a depth of the potential energy (we assume for simplicity that it is the same for both types of molecules).

Thanks to the form of the Corner potential energy one can rewrite (30) and (33) in the form

$$\begin{aligned}\beta F = {} & \\ & \sum_{I=A,B} \int_0^1 \mathrm{d}x N_I f_I(x) \left\{\ln[f_I(x) N_I \Lambda_5^I/4\pi V] - 1\right\} \\ & - \frac{1}{2} \sum_{I,J=A,B} N_I \lambda^{IJ} \sum_{j-\text{even}} K_{jj}^{IJ} \langle P_j\rangle_I \langle P_j\rangle_J P_j(\boldsymbol{e}_I \cdot \boldsymbol{e}_J),\end{aligned} \tag{74}$$

$$\begin{aligned}\ln[f_I(\boldsymbol{\Omega}_1 \cdot \boldsymbol{e}_I)] - \sum_{J=A,B} \lambda^{IJ} \sum_{j-even} K_{jj}^{IJ} \\ \cdot P_j(\boldsymbol{\Omega}_1 \cdot \boldsymbol{e}_I) \langle P_j\rangle_J P_j(\boldsymbol{e}_I \cdot \boldsymbol{e}_J) = \text{const},\end{aligned} \tag{75}$$

where

$$\lambda^{IJ} = (\sigma_0^{IJ})^3 B_2(T^*) 2\pi^2 N_J/4\pi V, \tag{76}$$

$$K^{IJ}(\cos\theta_1, \cos\theta_2) = \frac{1}{\pi^2} \int \mathrm{d}\phi_1 \mathrm{d}\,\boldsymbol{\Delta} (\sigma^{IJ}/\sigma_0^{IJ})^3. \tag{77}$$

As a consequence of the definition (77) we can express the kernel $K^{IJ}$ as a sum with even Legendre polynomials

$$K^{IJ}(x, y) = \sum_{j,k-even} K_{jk}^{IJ} P_j(x) P_k(y), \tag{78}$$

$$\begin{aligned}K_{jk}^{IJ} = {} & (2j+1)(2k+1) \\ & \cdot \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}y K^{IJ}(x, y) P_j(x) P_k(y).\end{aligned} \tag{79}$$

Note that for $\sigma^{IJ}$ given by (72) the kernel is diagonal. Equations (75) imply that $f_I$ should be written as

$$\ln[f_I(x)] = \sum_{j-\text{even}} C_j^I P_j(x). \tag{80}$$

It allows as to transform (75) into a set of equations

$$C_j^I = \sum_{J=A,B} \lambda^{IJ} K_{jj}^{IJ} \langle P_j\rangle_J P_j(\boldsymbol{e}_I \cdot \boldsymbol{e}_J), \tag{81}$$

where $j = 2, 4, 6$ and $I = A, B$. The normalization condition (66) must be also enclosed. In the case of the uniaxial (biaxial) phase we have $\boldsymbol{e}_I \cdot \boldsymbol{e}_J = 1$ ($\boldsymbol{e}_I \cdot \boldsymbol{e}_J = \delta_{IJ}$). The stable solution of (81) which has the lowest free energy will describe a homogeneous phase.

### 4.2. *Elastic Constants for Uniaxial Phases*

We insert the expansion (68) into (59) - (61). It appears that only a finite number of terms gives a nonzero contribution. Thus we get the explicit dependence the elastic constants on the order parameters:

$$K_s = \sum_{I,J=A,B} \sum_{j,k-\text{even}} \eta^{IJ} F_{s,jk}^{IJ} \langle P_j\rangle_I \langle P_k\rangle_J, \tag{82}$$

$$\eta^{IJ} = \epsilon T^* B_4(T^*) (\sigma_0^{IJ})^5 N_I N_J/(4\pi V)^2, \tag{83}$$

$$F^{IJ}_{s,jk} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{\Delta} (\Delta_s)^2 \Omega_{1x}\Omega_{2x}\left(\frac{\sigma^{IJ}}{\sigma^{IJ}_0}\right)^5 \cdot P'_j(\Omega_{1z})P'_k(\Omega_{2z})(2j+1)(2k+1), \tag{84}$$

where $s = 1, 2, 3$. We calculated the coefficients $F^{IJ}_{s,jk}$ analytically. In order to present their structure we list them as an array, where vanishing coefficients are zero

$$\begin{array}{ccccc}
F^{IJ}_{s,2,2} & F^{IJ}_{s,2,4} & 0 & 0 & 0 \\
F^{IJ}_{s,4,2} & F^{IJ}_{s,4,4} & F^{IJ}_{s,4,6} & 0 & 0 \\
0 & F^{IJ}_{s,6,4} & F^{IJ}_{s,6,6} & F^{IJ}_{s,6,8} & 0 \\
0 & 0 & F^{IJ}_{s,8,6} & F^{IJ}_{s,8,8} & F^{IJ}_{s,8,10} \\
0 & 0 & 0 & F^{IJ}_{s,10,8} & F^{IJ}_{s,10,10}.
\end{array} \tag{85}$$

### 4.3. *Elastic Constants for Biaxial Phases*

Let us insert the expansion (68) into (43) - (56). Similarly to the uniaxial case, it appears that a finite number of terms gives a nonzero contribution. The dependence of the elastic constants on the order parameters has the form

$$K_{1111} = \sum_{j,k-\text{even}} \eta^{BB} F^{BB}_{2,jk}\langle P_j\rangle_B \langle P_k\rangle_B, \tag{86}$$

$$\begin{aligned} K_{2222} = \sum_{j,k-\text{even}} \Big[ & \eta^{AA} F^{AA}_{2,jk}\langle P_j\rangle_A\langle P_k\rangle_A \\ & - \eta^{AB} G^{AB}_{2,jk}\langle P_j\rangle_A\langle P_k\rangle_B \\ & - \eta^{BA} G^{BA}_{2,jk}\langle P_j\rangle_B\langle P_k\rangle_A \\ & + \eta^{BB} F^{BB}_{2,jk}\langle P_j\rangle_B\langle P_k\rangle_B \Big], \end{aligned} \tag{87}$$

$$K_{3333} = \sum_{j,k-\text{even}} \eta^{AA} F^{AA}_{2,jk}\langle P_j\rangle_A \langle P_k\rangle_A, \tag{88}$$

$$\begin{aligned} K_{1212} = \sum_{j,k-\text{even}} \Big[ & \eta^{AA} F^{AA}_{3,jk}\langle P_j\rangle_A\langle P_k\rangle_A \\ & - \eta^{AB} G^{AB}_{1,jk}\langle P_j\rangle_A\langle P_k\rangle_B \\ & - \eta^{BA} G^{BA}_{3,jk}\langle P_j\rangle_B\langle P_k\rangle_A \\ & + \eta^{BB} F^{BB}_{1,jk}\langle P_j\rangle_B\langle P_k\rangle_B \Big], \end{aligned} \tag{89}$$

$$K_{1313} = \sum_{j,k-\text{even}} \eta^{AA} F^{AA}_{3,jk}\langle P_j\rangle_A \langle P_k\rangle_A, \tag{90}$$

$$K_{2121} = \sum_{j,k-\text{even}} \eta^{BB} F^{BB}_{1,jk}\langle P_j\rangle_B \langle P_k\rangle_B, \tag{91}$$

$$K_{2323} = \sum_{j,k-\text{even}} \eta^{AA} F^{AA}_{1,jk}\langle P_j\rangle_A \langle P_k\rangle_A, \tag{92}$$

$$K_{3131} = \sum_{j,k-\text{even}} \eta^{BB} F^{BB}_{3,jk}\langle P_j\rangle_B \langle P_k\rangle_B, \tag{93}$$

$$\begin{aligned} K_{3232} = \sum_{j,k-\text{even}} \Big[ & \eta^{AA} F^{AA}_{1,jk}\langle P_j\rangle_A\langle P_k\rangle_A \\ & - \eta^{AB} G^{AB}_{3,jk}\langle P_j\rangle_A\langle P_k\rangle_B \\ & - \eta^{BA} G^{BA}_{1,jk}\langle P_j\rangle_B\langle P_k\rangle_A \\ & + \eta^{BB} F^{BB}_{3,jk}\langle P_j\rangle_B\langle P_k\rangle_B \Big], \end{aligned} \tag{94}$$

$$\begin{aligned} K_{1122} = \frac{1}{2}\sum_{j,k-\text{even}} \Big[ & \eta^{AB} H^{AB}_{3,jk}\langle P_j\rangle_A\langle P_k\rangle_B \\ & + \eta^{BA} H^{BA}_{1,jk}\langle P_j\rangle_B\langle P_k\rangle_A + \eta^{BB} \\ & \cdot (F^{BB}_{2,jk} - F^{BB}_{1,jk})\langle P_j\rangle_B\langle P_k\rangle_B \Big], \end{aligned} \tag{95}$$

$$\begin{aligned} K_{1133} = \frac{1}{2}\sum_{j,k-\text{even}} \Big[ & -\eta^{AB} H^{AB}_{2,jk}\langle P_j\rangle_A\langle P_k\rangle_B \\ & - \eta^{BA} H^{BA}_{2,jk}\langle P_j\rangle_B\langle P_k\rangle_A \Big], \end{aligned} \tag{96}$$

$$\begin{aligned} K_{2233} = \frac{1}{2}\sum_{j,k-\text{even}} \Big[ & \eta^{AA}(F^{AA}_{2,jk} - F^{AA}_{1,jk})\langle P_j\rangle_A\langle P_k\rangle_A \\ & + \eta^{AB} H^{AB}_{1,jk}\langle P_j\rangle_A\langle P_k\rangle_B \\ & + \eta^{BA} H^{BA}_{3,jk}\langle P_j\rangle_B\langle P_k\rangle_A \Big], \end{aligned} \tag{97}$$

where

$$G^{IJ}_{s,jk} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{\Delta} (\Delta_s)^2 \Omega_{1z}\Omega_{2x}(\sigma^{IJ}/\sigma^{IJ}_0)^5 \cdot P'_j(\Omega_{1x})P'_k(\Omega_{2z})(2j+1)(2k+1), \tag{98}$$

$$H^{IJ}_{1,jk} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{\Delta} \Delta_y\Delta_z \Omega_{1y}\Omega_{2x}(\sigma^{IJ}/\sigma^{IJ}_0)^5 \cdot P'_j(\Omega_{1x})P'_k(\Omega_{2z})(2j+1)(2k+1), \tag{99}$$

$$H^{IJ}_{2,jk} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{\Delta} \Delta_x\Delta_z \Omega_{1y}\Omega_{2y}(\sigma^{IJ}/\sigma^{IJ}_0)^5 \cdot P'_j(\Omega_{1x})P'_k(\Omega_{2z})(2j+1)(2k+1), \tag{100}$$

$$H^{IJ}_{3,jk} = \frac{1}{2}\int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2 \mathrm{d}\boldsymbol{\Delta} \Delta_x\Delta_y \Omega_{1z}\Omega_{2y}(\sigma^{IJ}/\sigma^{IJ}_0)^5 \cdot P'_j(\Omega_{1x})P'_k(\Omega_{2z})(2j+1)(2k+1). \tag{101}$$

The structure of the coefficients $G_{s,jk}^{IJ}$ and $H_{s,jk}^{IJ}$ is similar to $F_{s,jk}^{IJ}$*. The coefficients depend only on the parameters $\sigma_i^{IJ}$.

One can notice that some of the biaxial elastic constants depend on the properties only one of the two types of molecules. This is the result of the assumption (64) and in general is not true.

### *4.4. Mixture of Rods and Discs*

It is known that phase diagrams of mixtures can be very complex. The aim of this section is to test predictions of the theory for a model mixture. We considere a mixture of prolate and oblate molecules because it is expected to reveal a biaxial phase. Later we will refer to prolate and oblate molecules as rods and discs, respectively. We apply the square-well potential energy defined as

$$\Phi_{12}(u/\sigma) = \begin{cases} +\infty & \text{for } u/\sigma < 1 \\ -\epsilon & \text{for } 1 < u/\sigma < R_{\mathrm{SW}} \\ 0 & \text{for } u/\sigma > R_{\mathrm{SW}}, \end{cases} \tag{102}$$

$$B_s(T^*) = \frac{1}{s+1}\left\{\left[\exp\left(\frac{1}{T^*}\right) - 1\right](R_{\mathrm{SW}}^{s+1} - 1) - 1\right\}. \tag{103}$$

We have chosen $R_{\mathrm{SW}} = 2$ and $V/N = (10 l_{\mathrm{mol}})^3$, where $l_{\mathrm{mol}}$ denotes some molecular length. Note that $l_{\mathrm{mol}}$ determines the length scale, whereas $\epsilon$ determines the energy scale. The elastic constants will be expressed in $\epsilon/l_{\mathrm{mol}}$. For simplicity reasons we assume that only one (isotropic, uniaxial nematic, or biaxial nematic) phase is present. It corresponds to the solution with the minimum free energy. The possibility of phase separation will not be investigated. The molecular parameters $\sigma_i^{IJ}$ can be connected with the geometry of molecules by means of the excluded volume method described in [33]. In order to get rods and discs we have chosen the following set of these parameters:

$$\begin{aligned} &\sigma_0^{AA} = 4 l_{\mathrm{mol}},\ \sigma_0^{BB} = 10 l_{\mathrm{mol}},\ \sigma_0^{IJ} = \frac{1}{2}(\sigma_0^{II} + \sigma_0^{JJ}), \\ &\sigma_{11}^{AA} = \sigma_{12}^{AA} = 3 l_{\mathrm{mol}},\ \sigma_{11}^{BB} = \sigma_{12}^{BB} = -4 l_{\mathrm{mol}}, \\ &\sigma_{11}^{IJ} = \sigma_{11}^{II},\ \sigma_{12}^{IJ} = \sigma_{11}^{JJ}, \\ &\sigma_2^{IJ} = 0. \end{aligned} \tag{104}$$

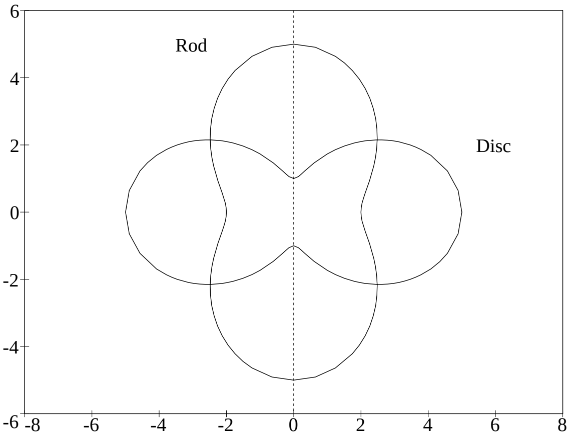

Fig. 1. Cross-sections of the zero equipotential surface of the potential energy for rods and discs (units are equal to $l_{\mathrm{mol}}$). The dashed line denotes the axis of rotary symmetry.

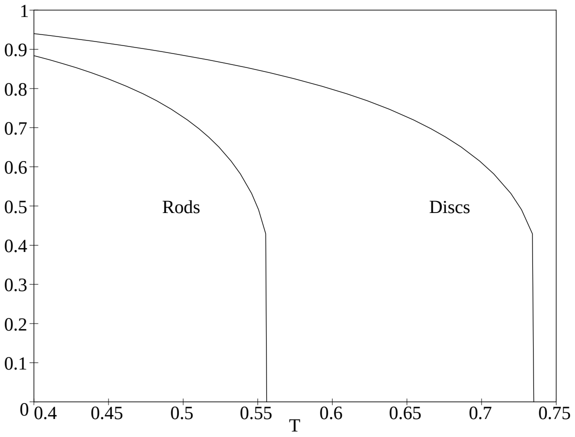

Fig. 2. Temperature dependence of the order parameters $\langle P_2\rangle_A$ (Rods) and $\langle P_2\rangle_B$ (Discs) for the unary systems. $T$ denotes the dimensionless temperature.

The volume of a molecule $I$ one can estimate as

$$\begin{aligned} V_{\mathrm{mol}}^{I} &= \int \mathrm{d}\boldsymbol{\Delta}[\sigma^{II}(\boldsymbol{e}_z, \boldsymbol{e}_z, \boldsymbol{\Delta})]^3/24 \\ &= K^{II}(1,1)(\sigma_0^{II})^3\pi/48 = \sum_j K_{jj}^{II}(\sigma_0^{II})^3\pi/48. \end{aligned} \tag{105}$$

The volumes of the molecules are $V_{\mathrm{mol}}^{A} \approx 145 l_{\mathrm{mol}}^3$ and $V_{\mathrm{mol}}^{B} \approx 267 l_{\mathrm{mol}}^3$. The cross-sections of the zero equipotential surface of the potential energy are shown in Figure 1.

The transition temperatures of unary systems from the isotropic to the uniaxial nematic phase are

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*The electronic version of all coefficients $F_{s,jk}^{IJ}$, $G_{s,jk}^{IJ}$, $H_{s,jk}^{IJ}$ and $K_{jk}^{IJ}$ is available from the authors on request.

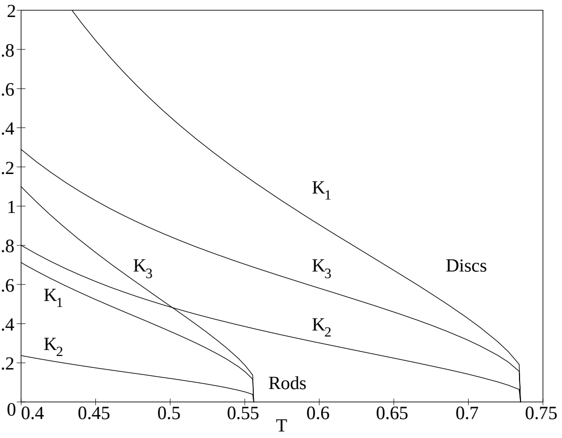

Fig. 3. Temperature dependence of the elastic constants for the unary systems. $T$ denotes the dimensionless temperature.

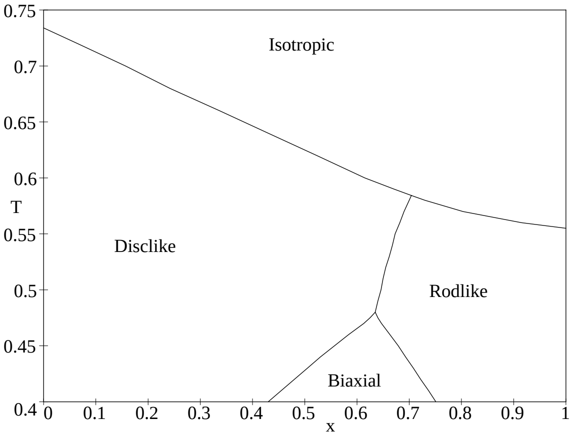

Fig. 4. Phase diagram of the mixture of rods and discs. Four phases are present: isotropic, rodlike uniaxial nematic, disclike uniaxial nematic and biaxial nematic. $T$ denotes the dimensionless temperature and $x = x_A$ is the concentration of rods in the mixture.

$T_A^* = 0.555$ and $T_B^* = 0.734$. The temperature dependence of the order parameters $\langle P_2 \rangle_I$ and the elastic constants for unary systems are shown in Figs. 2 and 3.

On changing the composition of the mixture we were looking for possible uniaxial and biaxial nematic solutions of (81). We checked the stability of all solutions against perturbations of nematic symmetry. The phase diagram of the mixture is shown in Figure 4.

We performed a detailed analysis of the mixture at the temperature $T^* = 0.45$. We have found the

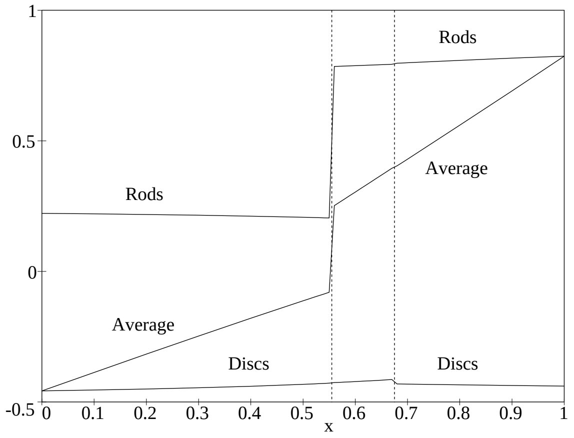

Fig. 5. $(3/2)S_{xx}^A$ (Rods), $(3/2)S_{xx}^B$ (Discs) and $(3/2)S_{xx}$ (Average) vs composition for the mixture of rods and discs at the temperature $T^* = 0.45$ ($x = x_A$ denotes a portion of rods in the mixture).

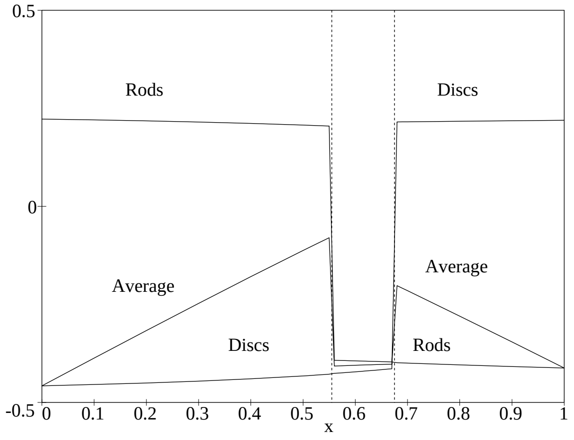

Fig. 6. $(3/2)S_{yy}^A$ (Rods), $(3/2)S_{yy}^B$ (Discs) and $(3/2)S_{yy}$ (Average) vs. composition for the mixture of rods and discs at the temperature $T^* = 0.45$ ($x = x_A$ denotes a portion of rods in the mixture).

following solutions present for all $x_A$:

1. The unstable isotropic solution with $\langle P_2 \rangle_I = 0$ (not physical).

2. The stable rodlike uniaxial nematic solution with $\langle P_2 \rangle_A > 0$ and $\langle P_2 \rangle_B < 0$ (physical for $0.679 < x_A < 1.0$).

3. The stable disclike uniaxial nematic solution with $\langle P_2 \rangle_A < 0$ and $\langle P_2 \rangle_B > 0$. (physical for $0.0 < x_A < 0.557$).

4. The stable (positive) biaxial nematic solution with $\langle P_2 \rangle_I > 0$. (physical for $0.557 < x_A < 0.679$).

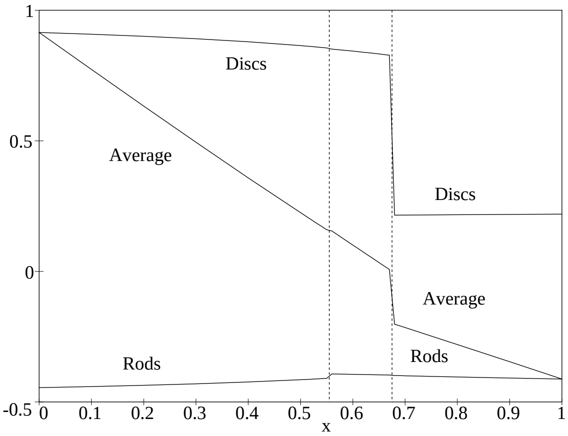

Fig. 7. $(3/2)S^A_{zz}$ (Rods), $(3/2)S^B_{zz}$ (Discs) and $(3/2)S_{zz}$ (Average) vs. composition for the mixture of rods and discs at the temperature $T^* = 0.45$ ($x = x_A$ denotes a portion of rods in the mixture).

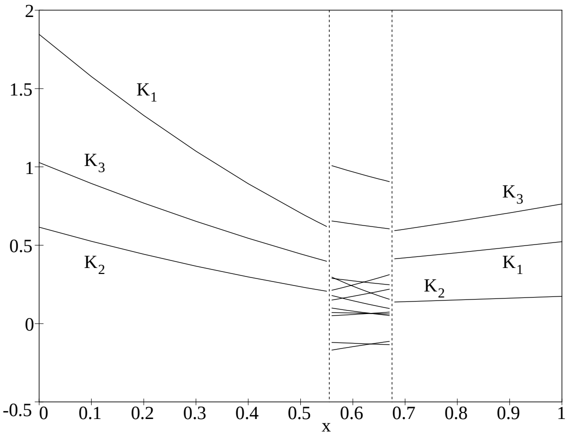

Fig. 8. Elastic constants calculated for the physical solution vs composition for the mixture of rods and discs at the temperature $T^* = 0.45$ ($x = x_A$ denotes a portion of rods in the mixture).

5. The stable (negative) biaxial nematic solution with $\langle P_2 \rangle_I < 0$ (not physical).

In order to get the physical solution we combine solutions with the lowest free energy (see the phase diagram). In Figs. 5 - 7 we present the diagonal elements of the tensor order parameters $\mathbf{S}^I$ and $\mathbf{S}$. In Fig. 8 the elastic constants calculated for the physical solution are shown. In order to understand the connections between the uniaxial and biaxial elastic constants we also plotted in Fig. 9 the elastic constants calculated for the positive biaxial solution.

In Fig. 9 one can notice that the introduction of rods to the unary uniaxial nematic system of discs with $x_A = 0$ (or the introduction of discs to the unary uniaxial nematic system of rods with $x_A = 1$) breakes the uniaxial symmetry. This leads to splittings of the uniaxial elasic constants and a creation of new elastic constants. A similar effect was obtained for unary system of biaxial molecules in [10]. A decrease of temperature induced the breaking of uniaxial symmetry and it caused splittings of uniaxial elastic constants and a creation of new constants. In the case of our mixture the physical picture of Fig. 8 exhibits only a small biaxial “window”, and splitting points are covered by the elastic constants of the uniaxial phases. One can observe only final results of changes. But generally one can not exclude that such splittings will appear for certain mixtures. We add that the concentration dependence of the elastic constants for $T^* = 0.52$ can be found in [37], where also a mixture of rods of different lengths was concerned.

## 5. Conclusions

In this paper we derived the microscopic formulas for the elastic constants of binary mixtures of uniaxial nematic liquid crystals. In order to calculate the values of the elastic constants one needs the potential energy of molecular interactions and the one-particle distribution functions. The theory was developed for rigid molecules interacting via two-body short-range forces. We showed that the Corner potential energy is very useful for calculations. The elastic constants were expressed as a *finite* series in terms of the order parameters. The role of the temperature is more transparent: it determines the order parameters via the function $B_2(T^*)$, (76), and it has a direct influence on the elastic constants via the function $B_4(T^*)$, (83). The Corner potential energy allow us to predict the result of a generalization of the molecular interactions. Let us assume that $\sigma^{IJ}$ is given by a more complex expression than (72), e. g., with higher powers of $(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2)^2$. Then the kernel (77) will be again expressed as a sum (78) but higher number of coefficients $K^{IJ}_{jk}$ will be nonzero. This will lead to more complex one-particle distribution functions $f_I$. They will be described by a higher number of the coefficients $C^I_j$ in (80). Finally, we will get longer series for the elastic constants.

Our theory was applied to a mixture of prolate and oblate uniaxial molecules. The phase diagram and the

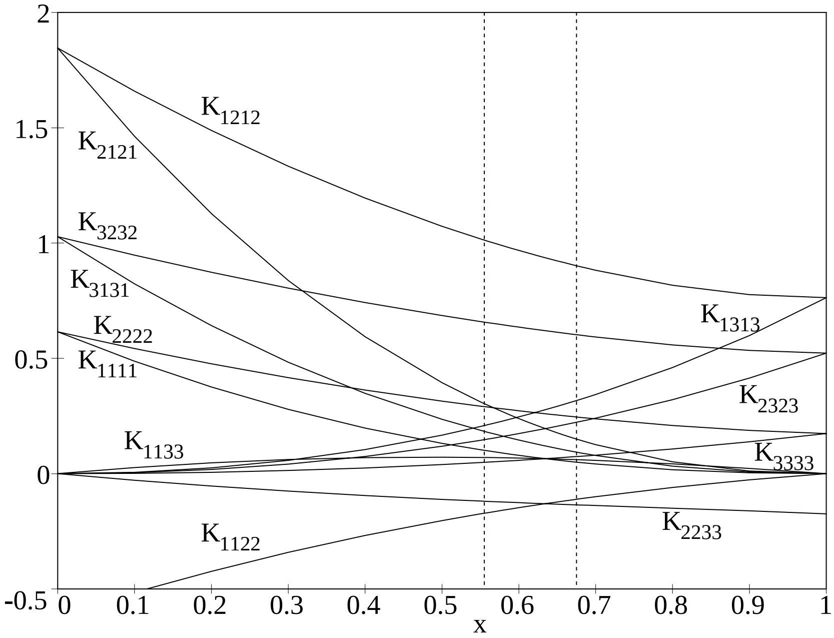

Fig. 9. Elastic constants calculated for the positive biaxial solution vs composition for the mixture of rods and discs at the temperature $T^* = 0.45$ ($x = x_A$ denotes a portion of rods in the mixture). The physical range is for $0.557 < x_A < 0.679$.

concentration dependence of the elastic constants in uniaxial and biaxial nematic phases were obtained. Theoretical predictions for the behaviour of binary mixtures of nematogens are extremely model dependent. Some mean field lattice models [13], extended Onsager theories and mean field van der Waals-type theories [14] have predicted that mixtures of rodlike and disclike nematogens should produce biaxial nematic phases. Conversely, both molecular mean-field theories [16] and MC simulations of mixtures of rods and discs [38] predict that these binary mixtures will separate into two uniaxial phases. The latter prediction is consistent with the lack of experimental evidence for biaxial phases in such mixtures. In our system of rods and discs, from Sect. 4.4 a biaxial phase appears below a certain temperature although a phase separation is not excluded. We note that in our phase diagram all lines of transitions are first order lines. This is non-typical because usually uniaxial-biaxial transitions were reported as second order [13]. But within the Landau theory one can describe both possibilities [35] and it must be decided by the experiment which is true.

Now we would like to explain the relations (52), (56), (62) and (63) for the elastic constants. Firstly, the general expressions (8) and (9) for the phenomenological distorsion free energy include bulk and surface terms that can be identified univocally. Secondly, in order to derive the microscopic distorsion free energy (42) we neglected some surface terms according to the thermodynamic limit. But other surface contributions are still present in a hidden form. Lastly, when we compare the microscopic and phenomenological free energies, those hidden terms will produce consistency relations for the elastic constants.

The theory gives a comfortable starting point for different possible generalizations. It recovers the known expressions in the limit of a unary system and, on the other hand, can be easy extended to the case of three (or more) component mixtures. In order to go beyond a low density approximation one should replace in the free energy the Mayer functions with a better approximation of the direct correlation function $c_2$ (the exact form of $c_2$ is unknown). There exist some solutions for $c_2$ in the case of simple models (see [39]), and they can be incorporated into our theory.

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