

# Statistical Theory of Biaxial Nematic and Cholesteric Phases

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A statistical theory of biaxial nematic and cholesteric phases is presented. It is derived in the thermodynamic limit at small density and small distortions. The considered phases are composed of short rigid biaxial or less symmetric molecules. The expressions for various macroscopic parameters involve the one-particle distribution function and the potential energy of two-body short-range interactions. The cholesteric phase is regarded as a distorted form of the nematic phase. Exemplary calculations are shown for several systems of molecules interacting via Corner-type potential based on the Lennard-Jones 12-6 functional dependence. The temperature dependence of the order parameters, the elastic constants, the phase twists, the dielectric susceptibilities, and the flexoelectric coefficients are obtained. The flow properties and defects in nematics are also discussed.

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## 1. Introduction

The liquid crystalline state of matter is found between solids and liquids. There are numerous different types of liquid crystalline phases, but here we will focus on the nematic state. Nematic liquid crystals are characterized by anisotropic positional short-range order and orientational long-range order [1]. In the biaxial nematic ( $N_B$ ) phase the mesogenic molecules tend to be parallel to selected axes, labelled by the unit orthogonal vectors ( $\mathbf{L}, \mathbf{M}, \mathbf{N}$ ). In the uniaxial nematic ( $N_U$ ) phase only the  $\mathbf{N}$  vector survives. Generally, two uniaxial phases are distinguished: prolate ( $N_{U+}$ ) and oblate ( $N_{U-}$ ), formed by rod-like and disk-like molecules, respectively. The uniaxial nematic phase has the  $D_{\infty h}$  point group symmetry and any second-rank tensorial property has two different principal components. The biaxial nematic phase has the  $D_{2h}$  point group symmetry and the corresponding second-rank tensorial property has three different principal components.

Most nematogenic molecules are intrinsically biaxial but they give rise to uniaxial phases as a consequence of the rotational disorder around the long molecular axis. However, this rotational disorder can be hampered by interactions favouring the molecules to stick parallel to one another. The first idea to assess the macroscopic effects of molecular biaxiality was of Freiser [2, 3]. Later, liquid crystals phases formed by biaxial molecules have been studied using molecular field treatments [4–9], the Landau-de Gennes theory [10–13], computer simulations of lattice models [14–17], an SU(3) representation [18, 19]. It was shown that single-component models consisting of biaxial molecules and interacting by properly chosen continuous potentials, can produce a biaxial phase. The transition between biaxial and uniaxial

phases is usually second order, and a direct transition between isotropic and biaxial nematic phases is also predicted. Similar results were obtained from the analytical study of single-component systems consisting of biaxial molecules interacting via hard-core potentials [20–25], and confirmed by simulation results [26–28].

On the experimental side, a biaxial nematic phase was discovered in a lyotropic system in 1980 [29]. In 1991 phase biaxiality was reported for side-chain polymers [30]. In 1992 biaxial defects were observed in a biaxial thermotropic polymer [31]. The existence of stable biaxial phases in thermotropic low molecular weight systems was not certain for many years [32–34]. The first convincing thermotropic biaxial nematic phase was jointly reported in 2004 by Kumar, Samulski and coworkers [35–37] from bent-core mesogens based on a mesogenic oxadiazole core with lateral substituents. In the same year 2004, a novel class of biaxial phases based on organosiloxane tetrapodes was found by Mehl and coworkers [38–40].

We would like to note that bent-core molecules have  $C_{2v}$  symmetry and their phases and phase transitions were studied by Lubensky and Radzihovsky [41]. Among many possible phases, the orientationally ordered but optically isotropic tetrahedral nematic  $T$  phase is described ( $T_d$  symmetry). Tetrahedral symmetry in nematogenic molecules was studied by Fel [42, 43] and a third-rank order parameter was introduced. Recently it was shown within the extended Straley model that the following transition sequence is possible on decreasing temperature: the second-order transition from the isotropic to the tetrahedral phase and the first-order transition from the tetrahedral to the biaxial nematic phase [44]. A detailed symmetry classification of unconventional nematic phases has been carried out by Mettout [45]. Structures and properties of liquid crystalline phases formed by bent-core molecules were reviewed by Takezoe and Takanishi [46].

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There is another system in which a biaxial nematic phase could occur: a mixture of rod-like and plate-like molecules of comparable size and in comparable amounts [47]. Unfortunately, it has been found by theory and experiment that these mixtures tend to phase separate [48–50]. In order to avoid demixing the rods and discs must have an attractive potential, such that they would be attracted more to one another than to each other. Alternatively, the rod-like and the disk-like components should be linked together covalently, either at the terminal end or in a lateral position of the rod [51]. Recent synthetic [52] and computer simulation [53] results have renewed optimism for the achievement of the first biaxial rod-plate thermotropic nematic mixture.

Biaxial materials could offer significant advantages over conventional nematic liquid crystals in display applications by leading to improved response times and to better viewing characteristics. First confirmations of the speed advantage of biaxial nematics have been obtained both experimentally [54] and from computer simulations [55]. However, a number of fundamental material-related issues have to be successfully addressed before biaxial nematics can be applied in competitive display applications: engineering of room-temperature low mass materials, controlling of optical axes alignment, selective addressability of optical axes by applied electric field, and many others [56].

In this paper we present a statistical theory of biaxial nematic and cholesteric phases. The cholesteric phase is regarded as a distorted form of the nematic phase. In Sect. 2 the description of the orientational order is presented. In Sect. 3 different potentials used for biaxial systems are described. In Sect. 4 a statistical theory of the nematic phase is showed. In Sect. 5 static distortions of the nematic phase are analysed. Sections 6 and 7 deal with electric field effects, namely dielectric anisotropy and the flexoelectric effect. Section 8 is devoted to chiral biaxial nematics. In Sect. 9 viscous properties and defects of the nematic phases are briefly described.

## 2. Orientational order

The long-range orientational order is the defining characteristic of a liquid crystal. It is responsible for the anisotropy in the properties of the nematic phase. It is important to understand the orientational order and tools describing it. Here we introduce the definitions of the orientational distribution function and order parameters.

### 2.1. Orientational distribution function

Let us assume that molecules are rigid blocks of  $D_{2h}$  symmetry. The orientation of a molecule is described by the three Euler angles  $R = (\phi, \theta, \psi)$  or by the three orthonormal vectors  $(\mathbf{l}, \mathbf{m}, \mathbf{n})$ . In a space-fixed reference frame  $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$  they can be written as

$$\begin{aligned} \mathbf{l} &= l_\alpha \mathbf{e}_\alpha = R_{1\alpha} \mathbf{e}_\alpha, & \mathbf{m} &= m_\alpha \mathbf{e}_\alpha = R_{2\alpha} \mathbf{e}_\alpha, \\ \mathbf{n} &= n_\alpha \mathbf{e}_\alpha = R_{3\alpha} \mathbf{e}_\alpha. \end{aligned} \quad (1)$$

The most complete description of the orientational order in the homogeneous phase is provided by the orientational distribution function,  $f(R)$ , which gives the probability density of finding a molecule at a given orientation. By definition the distribution function is normalized, that is,

$$\int dR f(R) = \int d\phi d\theta \sin \theta d\psi f(\phi, \theta, \psi) = 1. \quad (2)$$

The distribution function can be expanded in a complete basis set of functions spanning the relevant orientational space

$$f(R) = \sum_{j\mu\nu} f_{\mu\nu}^{(j)} F_{\mu\nu}^{(j)}(R), \quad (3)$$

where  $F_{\mu\nu}^{(j)}$  are defined in Ref. [57]. The definition and the main properties of the functions  $F_{\mu\nu}^{(j)}$  are recalled in Appendix A.

Four different cases can be distinguished, depending on the molecule and phase symmetry.

(i) Uniaxial molecules in uniaxial phases.  $F_{00}^{(j)}(R) = P_j(\cos \theta)$  are used,  $j$  is even,  $P_j$  are the Legendre polynomials.

(ii) Biaxial molecules in uniaxial phases.  $F_{0\nu}^{(j)}$  are used,  $j$  is even.

(iii) Uniaxial molecules in biaxial phases.  $F_{\mu 0}^{(j)}$  are used,  $j$  is even. Here the second macroscopic axis must have an external cause, an external field for example, because no molecular interaction in a system of uniaxial molecules can produce a macroscopic ordering that is less symmetric than the molecules themselves.

(iv) Biaxial molecules in biaxial phases.  $F_{\mu\nu}^{(j)}$  are used,  $j$  can be even or odd.

The expansion coefficients  $f_{\mu\nu}^{(j)}$  can be identified by using the orthogonality of the functions  $F_{\mu\nu}^{(j)}$

$$f_{\mu\nu}^{(j)} = \langle F_{\mu\nu}^{(j)} \rangle \frac{2j+1}{8\pi^2}, \quad (4)$$

where the angular brackets denote an ensemble average over the orientations of the molecules. For any function  $A(R)$ , this average is defined by

$$\langle A \rangle = \int dR f(R) A(R). \quad (5)$$

The expansion (3) does not converge rapidly partly because of the growth of the numerical factors. An alternative expansion of the orientational distribution function has generally a better convergence

$$\ln f(R) = \sum_{j\mu\nu} S_{\mu\nu}^{(j)} F_{\mu\nu}^{(j)}(R). \quad (6)$$

In the case of the Corner potential energy of interaction the expansion (6) can be finite. We note that for non-rigid molecules the orientational distribution function should depend also on a set of torsional angles which describe the conformational state.

In practice the alignment is characterised not through the complete distribution function  $f$  but by some numerical parameters — order parameters. They should be zero in the less ordered phase and nonzero in the more ordered phase. In the case of the nematic phase the most important are the averages  $\langle F_{\mu\nu}^{(2)} \rangle$ . The parameters  $\langle F_{00}^{(2)} \rangle$  and  $\langle F_{02}^{(2)} \rangle$  are nonzero in both uniaxial and biaxial nematic phases. The parameters  $\langle F_{20}^{(2)} \rangle$  and  $\langle F_{22}^{(2)} \rangle$  are zero in the uniaxial phase and nonzero in the biaxial phase. In the limit of the perfect uniaxial order ( $\langle F_{00}^{(2)} \rangle = 1$ ,  $\langle F_{22}^{(2)} \rangle = 0$ ) or biaxial order ( $\langle F_{00}^{(2)} \rangle = \langle F_{22}^{(2)} \rangle = 1$ ) the parameters  $\langle F_{02}^{(2)} \rangle$  and  $\langle F_{20}^{(2)} \rangle$  vanish. Note that in the case of the tetrahedral phase the order parameter  $\langle F_{22}^{(3)} \rangle$  should be taken into account. The order parameters  $\langle F_{00}^{(4)} \rangle$  and  $\langle F_{44}^{(4)} \rangle$  were computed in the Monte Carlo simulations of hard tetragonal parallelepipeds [58] in order to identify the cubic (parquet) phase.

### 2.2. Order parameter tensor

The ordering of the phase can be also described by a symmetric traceless second-rank tensor  $Q$  of the form [12]

$$Q_{\alpha\beta} = \frac{3}{2}x(N_\alpha N_\beta - \frac{1}{3}\delta_{\alpha\beta}) - \frac{1}{2}y(L_\alpha L_\beta - M_\alpha M_\beta), \quad (7)$$

where  $\mathbf{L}$ ,  $\mathbf{M}$ , and  $\mathbf{N}$  are the orthogonal eigenvectors of  $Q$  corresponding to the eigenvalues  $-(x+y)/2$ ,  $-(x-y)/2$ , and  $x$ , respectively. Three different phases can occur: isotropic ( $x = y = 0$ ), uniaxial nematic ( $x \neq 0$ ,  $y = 0$ ), and biaxial nematic ( $x \neq 0$ ,  $y \neq 0$ ). The order parameter tensor can be constructed by means of the anisotropic part of the diamagnetic susceptibility or, in some cases, by means of other macroscopic response functions [1]. In the absence of electric and magnetic fields the bulk free energy for the isotropic and the nematic phases in the Landau-de Gennes theory has the form [13]

$$F(Q) = F[\text{Tr}(Q^2), \text{Tr}(Q^3)]. \quad (8)$$

It is possible to construct order parameters in relation to specific molecular models. These order parameters will be called microscopic. For rigid biaxial molecules the order tensors can be defined [27]:

$$Q_{\alpha\beta}^l = \frac{1}{2}(3\langle l_\alpha l_\beta \rangle - \delta_{\alpha\beta}), \quad (9)$$

$$Q_{\alpha\beta}^{mm} = \frac{1}{2}(3\langle m_\alpha m_\beta \rangle - \delta_{\alpha\beta}), \quad (10)$$

$$Q_{\alpha\beta}^{nn} = \frac{1}{2}(3\langle n_\alpha n_\beta \rangle - \delta_{\alpha\beta}). \quad (11)$$

The order tensors are used to determine the principal axes of the system and the order parameters in computer simulations [16]. We can express the eigenvalues of the order tensors by means of the order parameters (see Table I).

On the other hand, the order parameters can be calculated from the eigenvalues of the order tensors in several ways

$$\langle F_{00}^{(2)} \rangle = Q_{zz}^{nn} = -Q_{zz}^l - Q_{zz}^{mm}, \quad (12)$$

TABLE I

Expansion coefficients of the order tensors eigenvalues over the four order parameters  $\langle F_{\mu\nu}^{(2)} \rangle$ .

$Q_{\alpha\beta}^{ij}$	$\langle F_{00}^{(2)} \rangle$	$\langle F_{02}^{(2)} \rangle$	$\langle F_{20}^{(2)} \rangle$	$\langle F_{22}^{(2)} \rangle$
$Q_{xx}^l$	1/4	$-\sqrt{3}/4$	$-\sqrt{3}/4$	3/4
$Q_{yy}^l$	1/4	$-\sqrt{3}/4$	$\sqrt{3}/4$	-3/4
$Q_{zz}^l$	-1/2	$\sqrt{3}/2$	0	0
$Q_{xx}^{mm}$	1/4	$\sqrt{3}/4$	$-\sqrt{3}/4$	-3/4
$Q_{yy}^{mm}$	1/4	$\sqrt{3}/4$	$\sqrt{3}/4$	3/4
$Q_{zz}^{mm}$	-1/2	$-\sqrt{3}/2$	0	0
$Q_{xx}^{nn}$	-1/2	0	$\sqrt{3}/2$	0
$Q_{yy}^{nn}$	-1/2	0	$-\sqrt{3}/2$	0
$Q_{zz}^{nn}$	1	0	0	0

$$\begin{aligned} \sqrt{3}\langle F_{02}^{(2)} \rangle &= Q_{zz}^l - Q_{zz}^{mm} \\ &= Q_{xx}^{mm} + Q_{yy}^{mm} - Q_{xx}^l - Q_{yy}^l, \end{aligned} \quad (13)$$

$$\begin{aligned} \sqrt{3}\langle F_{20}^{(2)} \rangle &= Q_{xx}^{nn} - Q_{yy}^{nn} \\ &= Q_{yy}^l + Q_{yy}^{mm} - Q_{xx}^l - Q_{xx}^{mm}, \end{aligned} \quad (14)$$

$$\langle F_{22}^{(2)} \rangle = \frac{1}{3}(Q_{xx}^l - Q_{yy}^l - Q_{xx}^{mm} + Q_{yy}^{mm}). \quad (15)$$

The procedure of assigning the eigenvalues should satisfy the following conditions: (a)  $\langle F_{00}^{(2)} \rangle > 0$ ; (b) the same order parameters must have the same values in all the ways they are computed; (c) for each configuration at one temperature the order parameters must be as close as possible to the mean value of the order parameters of the previous temperature [16].

### 3. Model potentials

Statistical theories of nematic liquid crystals span between two extreme approaches. The first approach starts from Onsager's paper [59], where the ordering isotropic-nematic transition was found by assuming that nematogenic molecules can be represented as elongated hard cylinders only interacting by excluded volume. The Onsager theory is fully entropic and athermal, the number density is a control parameter. Anisotropic, short-range, repulsive interactions are taken into account only. The theory is exact in the limit of infinitely long molecules at low concentrations. Although the theory gave rather poor predictions for the I-N transition, the statistical mechanics of simple fluids suggest that anisotropic hard-body interactions need to be understood before theories of softer interactions become predictive. A review of early computer simulations of hard-core molecules can be found in the paper by Frenkel [60].

The second approach is a mean-field description of thermotropic liquid crystals by Maier and Saupe (MS) [61]. Here the temperature is the control parameter and the theory is entirely formulated in terms of anisotropic long-range attractive interactions. The MS

theory is exact only when the molecular interactions are infinitely long-range. Let us present extensions of the two approaches to biaxial molecules.

### 3.1. Hard core interactions

In hard-core interactions, the excluded volume between two molecules is proportional to the second virial coefficient in the functional expansion of the configurational free energy. That is why many efforts have been made to find the excluded volume for bodies with biaxial symmetry. Two technical approaches have been followed to achieve this. The former relies on convex-body coordinate systems [62] and takes biaxial ellipsoids as prototypes for biaxial molecules. The excluded volume between biaxial ellipsoids was first computed by Tijpto-Margo and Evans [63], and then recast in a different form.

In a second approach, biaxial bodies are obtained by Minkowski addition of a sphere and another, suitably chosen body. Mulder [21] first applied this technique to compute the excluded volume between two identical spheroplatelets and his results were generalized by Taylor [64] to the case of unequal spheroplatelets. In 2005 Mulder [65] computed the excluded volume for an important class of convex bodies, the spherozonotopes. By applying Mulder's results, Rosso and Virga [66] computed the quadrupolar projection of the excluded volume between two spherocuboids.

The equation of state of gases may be expressed in the form of the virial expansion

$$\frac{pV}{Nk_{\text{B}}T} = 1 + B_2 \frac{N}{V} + B_3 \frac{N^2}{V^2} + \dots, \quad (16)$$

where  $p$  is the pressure,  $V$  is the volume,  $k_{\text{B}}$  is the Boltzmann constant, and  $T$  is the temperature. The coefficients  $B_n$ , which are functions of the temperature, are called the virial coefficients. These coefficients have been given in terms of the interactions between molecules. In the case of hard ellipsoids it is possible to calculate  $B_2$  exactly (elliptic integrals) by the formula  $B_2 = R_e S_e + V_e$ , where  $R_e$ ,  $S_e$ , and  $V_e$  are the mean radius of curvature, surface and volume of the hard ellipsoid, respectively [67]. The first five virial coefficients were evaluated numerically by Vega [68] and the proposed isotropic phase equation of state was checked by means of the Monte Carlo simulations [69]. The first seven virial coefficients for isotropic fluids of hard uniaxial convex bodies were calculated in Ref. [70], where the radius of convergence was also estimated.

### 3.2. Anisotropic attractive interactions

The extension of the MS theory for biaxial molecules was first proposed by Freiser [2, 3] and next by Straley [5]. The Straley model builds a mean-field theory upon the most general quadrupolar effective interaction compatible with the  $D_{2h}$  symmetry

$$V(R_1, R_2) = v_{00}^{(0)} + \sum_{\mu\nu} v_{\mu\nu}^{(2)} F_{\mu\nu}^{(2)}(R_2^{-1}R_1), \quad (17)$$

where  $v_{\mu\nu}^{(2)} = v_{\nu\mu}^{(2)}$  due to particle interchange symmetry.

The phase diagram obtained for a fixed choice of length-to-width ratio of the platelets showed a direct isotropic-to-biaxial transition at an isolated Landau point. However, it was realized [71] that the Straley potential could lead to a different phase diagram, also exhibiting a tricritical point in the uniaxial-to-biaxial transition line and a direct isotropic-to-biaxial transition. The proper form of the potential energy is

$$V(R_1, R_2) = v_{00}^{(2)} F_{00}^{(2)}(R_2^{-1}R_1) + v_{22}^{(2)} F_{22}^{(2)}(R_2^{-1}R_1), \quad (18)$$

and it was called the minimum coupling model capable of producing biaxial ordering [72]. Actually, there is another tricritical point in the same model, but along the line of the direct isotropic-to-biaxial transition [73]. A special case of the Straley potential was introduced by Luckhurst et al. [6]

$$V(R_1, R_2) = -\epsilon \left[ F_{00}^{(2)}(R_2^{-1}R_1) + \lambda F_{02}^{(2)}(R_2^{-1}R_1) + \lambda F_{20}^{(2)}(R_2^{-1}R_1) + \lambda^2 F_{22}^{(2)}(R_2^{-1}R_1) \right]. \quad (19)$$

The model was compared with the Monte Carlo simulations [14, 16]. Simulation results suggest that the potential of the form

$$V(R_1, R_2) = v_{00}^{(2)} F_{00}^{(2)}(R_2^{-1}R_1) + v_{02}^{(2)} \left[ F_{02}^{(2)}(R_2^{-1}R_1) + F_{20}^{(2)}(R_2^{-1}R_1) \right] \quad (20)$$

entails the absence of biaxial order [14].

### 3.3. Gay-Berne (GB) models

In 1972 Berne and Pechukas proposed simple analytical forms for the orientational dependence of the potential between two molecules which they derived from a Gaussian overlap model [74]. Next the model was modified to mimic a linear site-site potential [75]. The first generalization of a Gaussian overlap model for biaxial molecules was that of Ayton and Patey [76]. By reducing the thickness of a hard uniaxial 1:1:3 ellipsoid (lacking in a nematic phase), first a uniaxial nematic phase and then biaxial nematic phase were found.

The interactions between unlike biaxial particles were described by Berardi et al. [77, 78]

$$\Phi(R_1, R_2, \mathbf{u}) = 4\epsilon_0 \epsilon(R_1, R_2, \mathbf{u}) \times [w^{12}(R_1, R_2, \mathbf{u}) - w^6(R_1, R_2, \mathbf{u})], \quad (21)$$

where  $w(R_1, R_2, \mathbf{u}) = \sigma_0 / [u - \sigma(R_1, R_2, \mathbf{u}) + \sigma_0]$ ,  $\sigma(R_1, R_2, \mathbf{u})$  is the anisotropic contact distance,  $\epsilon(R_1, R_2, \mathbf{u})$  is the anisotropic interaction term,  $\sigma_0$  and  $\epsilon_0$  are empirical parameters. A similar generalization of the GB potential to non-homogeneous biaxial interactions is that of Cleaver et al. [79].

### 3.4. Corner potential energy

The Corner potential energy [80] has the form  $\Phi_{12}(u/\sigma)$ , where  $u$  is the distance between molecules and  $\sigma$  depends on the molecule orientation  $R_1$  and  $R_2$ , and on the vector  $\Delta$ . For  $\sigma$  it is possible to write the general

expansion proposed by Blum and Torruella [81] which is evidently invariant under rotations and translations. It involves the 3- $j$  Wigner symbols and the standard rotation matrix elements. In the case of the chiral biaxial molecules the lowest order terms of the expansion are

$$\begin{aligned}
 \sigma &= \sigma_0 + \sigma_1 [(\boldsymbol{\Delta} \cdot \mathbf{n}_1)^2 + (\boldsymbol{\Delta} \cdot \mathbf{n}_2)^2] + \sigma_2 (\mathbf{n}_1 \cdot \mathbf{n}_2)^2 \\
 &+ \sigma_3 [(\boldsymbol{\Delta} \cdot \mathbf{l}_1)^2 + (\boldsymbol{\Delta} \cdot \mathbf{l}_2)^2] + \sigma_4 (\mathbf{l}_1 \cdot \mathbf{l}_2)^2 \\
 &+ \sigma_5 [(\mathbf{l}_1 \cdot \mathbf{n}_2)^2 + (\mathbf{l}_2 \cdot \mathbf{n}_1)^2] \\
 &+ \sigma_6 [(\mathbf{n}_1 \cdot \mathbf{n}_2)(\mathbf{n}_1 \times \mathbf{n}_2) \cdot \boldsymbol{\Delta}] \\
 &+ \sigma_7 [(\mathbf{l}_1 \cdot \mathbf{n}_2)(\mathbf{l}_1 \times \mathbf{n}_2) \cdot \boldsymbol{\Delta} \\
 &- (\mathbf{m}_1 \cdot \mathbf{n}_2)(\mathbf{m}_1 \times \mathbf{n}_2) \cdot \boldsymbol{\Delta} + (\mathbf{n}_1 \cdot \mathbf{l}_2)(\mathbf{n}_1 \times \mathbf{l}_2) \cdot \boldsymbol{\Delta} \\
 &- (\mathbf{n}_1 \cdot \mathbf{m}_2)(\mathbf{n}_1 \times \mathbf{m}_2) \cdot \boldsymbol{\Delta}] \\
 &+ \sigma_8 [(\mathbf{l}_1 \cdot \mathbf{l}_2)(\mathbf{l}_1 \times \mathbf{l}_2) \cdot \boldsymbol{\Delta} \\
 &+ (\mathbf{m}_1 \cdot \mathbf{m}_2)(\mathbf{m}_1 \times \mathbf{m}_2) \cdot \boldsymbol{\Delta} \\
 &- (\mathbf{l}_1 \cdot \mathbf{m}_2)(\mathbf{l}_1 \times \mathbf{m}_2) \cdot \boldsymbol{\Delta} \\
 &- (\mathbf{m}_1 \cdot \mathbf{l}_2)(\mathbf{m}_1 \times \mathbf{l}_2) \cdot \boldsymbol{\Delta}]. \tag{22}
 \end{aligned}$$

The meaning of the expansion coefficients  $\sigma_i$  is explained in Table II. The potential energy of the form  $\Phi_{12}(u/\sigma)$  allows us to close the temperature dependence of many physical quantities inside the functions  $B_s(T)$  defined in Appendix B. In the case of wedge-shaped molecules or banana-shaped molecules other terms in  $\sigma$  are necessary (see the description of the flexoelectric effect). Let us note that  $\sigma_0$  determines the length scale, whereas  $\epsilon$  determines the energy scale. It is convenient to define the kernel

$$\begin{aligned}
 K(R_1, R_2) &= \int d\boldsymbol{\Delta} (\sigma/\sigma_0)^3 \\
 &= \sum_j \sum_{\mu\nu} K_{\mu\nu}^{(j)} F_{\mu\nu}^{(j)}(R_2^{-1}R_1), \tag{23}
 \end{aligned}$$

where the following symmetries can be identified: (i)  $K(R_2, R_1) = K(R_1, R_2)$  or  $K_{\mu\nu}^{(j)} = K_{\nu\mu}^{(j)}$ ; (ii)  $K(RR_1, RR_2) = K(R_1, R_2)$  for any rotation  $R$ . The molecule volume is approximated by

$$V_{\text{mol}} = K_{00}^{(0)} \sigma_0^3 / 24. \tag{24}$$

The Corner potential is connected with the so-called Parsons-Lee decoupling approximation which leads to

TABLE II  
The meaning of the expansion coefficients  $\sigma_i$ .

$\sigma_i$	Description
$\sigma_0$	isotropic
$\sigma_1, \sigma_2$	achiral uniaxial nematic
$\sigma_3, \sigma_4, \sigma_5$	achiral biaxial nematic
$\sigma_6$	chiral uniaxial nematic
$\sigma_7, \sigma_8$	chiral biaxial nematic

the good description of hard and soft repulsive nematogens [82, 83]. In the case of soft interactions an effective molecule volume should be taken into account due to the interpenetration of the compressible molecular core [84].

#### 4. Statistical theory of the phase

In this section the free energy of the system, based on the statistical mechanics, is presented. The free energy depends on the one particle distribution function which describes the state of the molecule alignment.

##### 4.1. The free energy of the phase

We assume that the molecules interact via two-body short-range forces that depend on the distance between the molecules and their orientations;  $\Phi_{12}$  gives the potential energy of interactions. The free energy for our system can be derived in the thermodynamic limit ( $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \text{const}$ ) from the Born-Bogoliubov-Green-Kirkwood-Yvon hierarchy [57] or as the cluster expansion [85]. The total free energy  $F$  consists of the entropy term and the interaction term, namely,

$$F = F_{\text{ent}} + F_{\text{int}}, \tag{25}$$

where

$$\beta F_{\text{ent}} = \int d\mathbf{r} dR G(\mathbf{r}, R) [\ln(G(\mathbf{r}, R)\Lambda) - 1], \tag{26}$$

$$\begin{aligned}
 \beta F_{\text{int}} &= -\frac{1}{2} \int d\mathbf{r}_1 dR_1 d\mathbf{r}_2 dR_2 \\
 &\times G(\mathbf{r}_1, R_1) G(\mathbf{r}_2, R_2) f_{12}. \tag{27}
 \end{aligned}$$

Here  $G$  is the one particle distribution function with the normalization

$$\int d\mathbf{r} dR G(\mathbf{r}, R) = N, \tag{28}$$

$f_{12} = \exp(-\beta\Phi_{12}) - 1$  is the Mayer function,  $\beta = 1/(k_B T)$ ,  $\Lambda$  is related to the ideal gas properties. The equilibrium distribution  $G$  minimizing the free energy (25) satisfies the following equation:

$$\ln(G(\mathbf{r}_1, R_1)\Lambda) - \int d\mathbf{r}_2 dR_2 G(\mathbf{r}_2, R_2) f_{12} = \text{const}. \tag{29}$$

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

$$\int dR f(R) = 1. \tag{30}$$

##### 4.2. Exemplary calculations

Let us define a dimensionless parameter

$$\lambda = B_2(T) \sigma_0^3 (N/V). \tag{31}$$

The set of coefficients  $S_{\mu\nu}^{(j)}$  (6) is derived from the equations

$$S_{\mu\nu}^{(j)} = \sum_{\rho} \lambda K_{\rho\nu}^{(j)} \langle F_{\mu\rho}^{(j)} \rangle \quad \text{for } j > 0, \quad (32)$$

$$\langle F_{00}^{(0)} \rangle = 1 \quad \text{the normalization condition.} \quad (33)$$

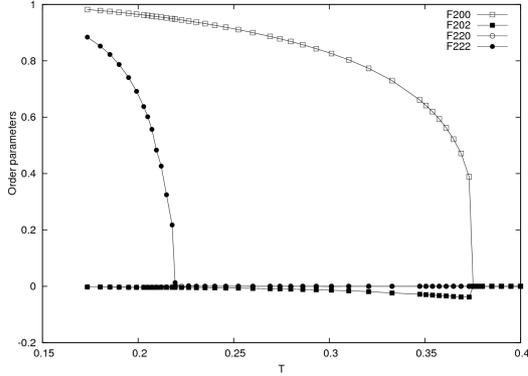


Fig. 1. Temperature dependence of the order parameters  $\langle F_{\mu\nu}^{(2)} \rangle$ .  $T$  is the dimensionless temperature.

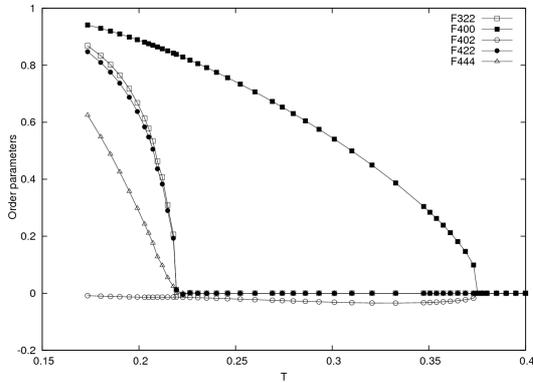


Fig. 2. Temperature dependence of the order parameters  $\langle F_{22}^{(3)} \rangle$  and  $\langle F_{\mu\nu}^{(4)} \rangle$ .  $T$  is the dimensionless temperature.

We used the Lennard–Jones 12-6 potential energy,  $\sigma_1/\sigma_0 = 0.5$ ,  $\sigma_2/\sigma_0 = 0.1$ , and  $\sigma_3/\sigma_0 = -0.4$ , packing  $NV_{\text{mol}}/V = 0.1$ . We were looking for the orientationally stable, the lowest energy solution. On decreasing the temperature we meet the first-order transition to the uniaxial nematic phase at  $T = 0.374$  and the second-order transition to the biaxial nematic phase at  $T = 0.220$ . The temperature dependence of the order parameters is presented in Figs. 1 and 2. Temperatures are expressed in  $\epsilon/k_B$ . Let us note that in the uniaxial nematic phase the most significant are  $\langle F_{00}^{(2)} \rangle$  and  $\langle F_{00}^{(4)} \rangle$ , whereas in the biaxial nematic phase we should add  $\langle F_{22}^{(2)} \rangle$ ,  $\langle F_{22}^{(3)} \rangle$ ,  $\langle F_{22}^{(4)} \rangle$ , and  $\langle F_{44}^{(4)} \rangle$ .

### 5. Static distortions of the nematic phase

In the ideal biaxial nematic phase, the molecules are (on average) aligned along common directions

( $\mathbf{L}, \mathbf{M}, \mathbf{N}$ ). In the absence of external fields the orientation of the directions is arbitrary, which is a consequence of the fact that the nematic phase arise from the spontaneous breaking of the continuous rotational symmetry. In most practical circumstances the ideal conformation will not be compatible with the constraints that are imposed by limiting surfaces of the sample and by external fields acting on the molecules [1]. There will be some deformation of the alignment and the order parameter tensor  $Q(\mathbf{r})$  will vary from point to point. Generally, both eigenvectors and eigenvalues of  $Q$  depend on  $\mathbf{r}$ . But in the hydrodynamic limit the eigenvalues are nearly constant and only the directors depend on position [86]. The inhomogeneity of the director field results in a distortion (elastic) free energy. In a continuum approach this energy is obtained as an expansion about an undistorted reference state with respect to gradients of the tensor order parameter  $Q$  [87–89] or gradients of the directors [90]. There are many equivalent forms of the biaxial elastic free energy and it is possible to transform one to another after making use of relations that follow from constraints imposed by the orthonormality of the directors.

The elastic constants are material constants that determine the change in the elastic free energy of a nematic phase. The phenomenological theory of the elastic constants and viscosity coefficients of biaxial liquid crystals was developed for the first time by Saupe [91]. The density-functional formalism for the elastic constants was used by Singh et al. [92]. Kini and Chandrasekhar [93] discussed the feasibility of determining some of the biaxial elastic constants by studying the effects of external magnetic and electric fields applied in different sample geometries. They showed that at certain conditions a Fredericksz transition should occur above a critical value of the field.

The elastic constants influence almost all phenomena observed in liquid crystals: light scattering, defect shapes, long-wavelength fluctuations, etc. They play a crucial role in almost all applications of liquid crystalline materials, especially in display devices. On the other hand, they provide valuable information regarding the nature and importance of various anisotropies of the intermolecular potentials and of the spatial and angular correlation functions.

#### 5.1. Distortion free energy

Let us call  $F_d$  the free energy due to the distortion of the local frame ( $\mathbf{L}, \mathbf{M}, \mathbf{N}$ ). A general form of its density  $f_d(\mathbf{r})$  was derived in [90] in the case of small distortions. When a considered phase has a  $D_2$  symmetry group (the biaxial cholesteric phase) we get

$$\begin{aligned} f_d = & K_{11}D_{11} + K_{22}D_{22} + K_{33}D_{33} + \frac{1}{2}K_{1111}(D_{11})^2 \\ & + \frac{1}{2}K_{1212}(D_{12})^2 + \frac{1}{2}K_{1313}(D_{13})^2 + \frac{1}{2}K_{2121}(D_{21})^2 \\ & + \frac{1}{2}K_{2222}(D_{22})^2 + \frac{1}{2}K_{2323}(D_{23})^2 + \frac{1}{2}K_{3131}(D_{31})^2 \\ & + \frac{1}{2}K_{3232}(D_{32})^2 + \frac{1}{2}K_{3333}(D_{33})^2 + K_{1122}D_{11}D_{22} \end{aligned}$$

$$\begin{aligned}
 &+ K_{1133}D_{11}D_{33} + K_{2233}D_{22}D_{33} + K_{1221}D_{12}D_{21} \\
 &+ K_{1331}D_{13}D_{31} + K_{2332}D_{23}D_{32} \\
 &+ L_{123}\partial_\alpha(L_\alpha D_{23} + M_\alpha D_{13}) \\
 &+ L_{231}\partial_\alpha(M_\alpha D_{31} + N_\alpha D_{21}) \\
 &+ L_{312}\partial_\alpha(N_\alpha D_{12} + L_\alpha D_{32}), \tag{34}
 \end{aligned}$$

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

$$\begin{aligned}
 D_{11} &= L_\alpha M_\beta \partial_\alpha N_\beta, & D_{12} &= L_\alpha N_\beta \partial_\alpha L_\beta, \\
 D_{13} &= L_\alpha L_\beta \partial_\alpha M_\beta, & D_{21} &= M_\alpha M_\beta \partial_\alpha N_\beta, \\
 D_{22} &= M_\alpha N_\beta \partial_\alpha L_\beta, & D_{23} &= M_\alpha L_\beta \partial_\alpha M_\beta, \\
 D_{31} &= N_\alpha M_\beta \partial_\alpha N_\beta, & D_{32} &= N_\alpha N_\beta \partial_\alpha L_\beta, \\
 D_{33} &= N_\alpha L_\beta \partial_\alpha M_\beta. \tag{35}
 \end{aligned}$$

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

$$\begin{aligned}
 \partial_\alpha(L_\beta \partial_\beta L_\alpha - L_\alpha \partial_\beta L_\beta) &= 2(D_{23}D_{32} - D_{22}D_{33}), \tag{36} \\
 \partial_\alpha(M_\beta \partial_\beta M_\alpha - M_\alpha \partial_\beta M_\beta) &= 2(D_{31}D_{13} - D_{11}D_{33}), \\
 \partial_\alpha(N_\beta \partial_\beta N_\alpha - N_\alpha \partial_\beta N_\beta) &= 2(D_{12}D_{21} - D_{11}D_{22}). \tag{37}
 \end{aligned}$$

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

In the case of the uniaxial cholesteric phase the distortion free-energy density has the form

$$\begin{aligned}
 f_d &= K_0 \mathbf{N} \cdot (\nabla \times \mathbf{N}) + \frac{1}{2} K_1 (\nabla \cdot \mathbf{N})^2 \\
 &+ \frac{1}{2} K_2 [\mathbf{N} \cdot (\nabla \times \mathbf{N})]^2 + \frac{1}{2} K_3 [\mathbf{N} \times (\nabla \times \mathbf{N})]^2 \\
 &+ \frac{1}{2} K_4 \nabla \cdot [(\mathbf{N} \cdot \nabla) \mathbf{N} - \mathbf{N} (\nabla \cdot \mathbf{N})] \\
 &+ \frac{1}{2} K_5 \nabla \cdot [(\mathbf{N} \cdot \nabla) \mathbf{N} + \mathbf{N} (\nabla \cdot \mathbf{N})]. \tag{39}
 \end{aligned}$$

Therefore, we have 4 bulk (from  $K_0$  to  $K_3$ ) and 2 surface terms ( $K_4$  and  $K_5$ ).

### 5.2. Basic deformations of the biaxial nematic phase

Three basic types of deformations appear in the continuum theory of uniaxial nematic liquid crystals: splay, twist, and bend. They extract from the distortion free energy terms with  $K_1$ ,  $K_2$ , and  $K_3$ , respectively. Basic deformations of biaxial nematic liquid crystals were defined by Kapanowski [94] and only nine deformations extract one constant from the distortion free energy. These deformations are collected in Table III together with deformation parameters  $q_i$  ( $i = 1, \dots, 9$ ).

For the sake of future reference, we will write the spatial dependence of the vectors ( $\mathbf{L}$ ,  $\mathbf{M}$ ,  $\mathbf{N}$ ). In the case of twists, which are important for the theory of chiral phases, we have

$$\mathbf{L}(\mathbf{r}) = [1, q_3 z, -q_2 y],$$

TABLE III

Basic deformations of the biaxial nematic phase. The corresponding elastic constants and the FE coefficients are given, the values for the uniaxial nematic phase are in parentheses.

Parameter	Deformation	Elastic constant	FE coefficient
$q_1$	$\mathbf{M}$ twist, $\mathbf{N}$ twist	$K_{1111}$ ( $K_2$ )	none
$q_2$	$\mathbf{L}$ twist, $\mathbf{N}$ twist	$K_{2222}$ ( $K_2$ )	none
$q_3$	$\mathbf{L}$ twist, $\mathbf{M}$ twist	$K_{3333}$ (0)	none
$q_4$	$\mathbf{N}$ splay, $\mathbf{L}$ bend	$K_{1212}$ ( $K_1$ )	$a_4$ ( $e_1$ )
$q_5$	$\mathbf{M}$ splay, $\mathbf{L}$ bend	$K_{1313}$ (0)	$a_5$ (0)
$q_6$	$\mathbf{N}$ splay, $\mathbf{M}$ bend	$K_{2121}$ ( $K_1$ )	$a_6$ ( $e_1$ )
$q_7$	$\mathbf{L}$ splay, $\mathbf{M}$ bend	$K_{2323}$ (0)	$a_7$ (0)
$q_8$	$\mathbf{M}$ splay, $\mathbf{N}$ bend	$K_{3131}$ ( $K_3$ )	$a_8$ ( $-e_3$ )
$q_9$	$\mathbf{L}$ splay, $\mathbf{N}$ bend	$K_{3232}$ ( $K_3$ )	$a_9$ ( $-e_3$ )

$$\mathbf{M}(\mathbf{r}) = [-q_3 z, 1, q_1 x],$$

$$\mathbf{N}(\mathbf{r}) = [q_2 y, -q_1 x, 1]. \tag{40}$$

Splays and bends will be used in the description of the flexoelectric effect

$$\mathbf{L}(\mathbf{r}) = [1, q_7 y - q_5 x, q_9 z - q_4 x],$$

$$\mathbf{M}(\mathbf{r}) = [q_5 x - q_7 y, 1, q_8 z - q_6 y],$$

$$\mathbf{N}(\mathbf{r}) = [q_4 x - q_9 z, q_6 y - q_8 z, 1]. \tag{41}$$

### 5.3. Elastic constants

In the homogeneous biaxial nematic phase composed of  $C_{2v}$  or  $D_{2h}$  molecules the distribution function has the form [94]

$$G_0(R) = G_0(\mathbf{l} \cdot \mathbf{L}, \mathbf{l} \cdot \mathbf{N}, \mathbf{n} \cdot \mathbf{L}, \mathbf{n} \cdot \mathbf{N}). \tag{42}$$

In order to derive expressions for the elastic constants it is enough to assume that, in the deformed phase, the phase orientation depends on the position but the magnitude of the alignment is constant,

$$G_0(\mathbf{r}, R) = G_0[\mathbf{l} \cdot \mathbf{L}(\mathbf{r}), \mathbf{l} \cdot \mathbf{N}(\mathbf{r}), \mathbf{n} \cdot \mathbf{L}(\mathbf{r}), \mathbf{n} \cdot \mathbf{N}(\mathbf{r})]. \tag{43}$$

Let us denote the derivatives

$$U_\alpha = \partial_1 G_0 l_\alpha + \partial_3 G_0 n_\alpha, \quad W_\alpha = \partial_2 G_0 l_\alpha + \partial_4 G_0 n_\alpha. \tag{44}$$

The twist elastic constants are

$$\beta K_{1111} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_x^2 W_{1y} W_{2y}, \tag{45}$$

$$\begin{aligned}
 \beta K_{2222} &= \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_y^2 (U_{1z} - W_{1x}) \\
 &\times (U_{2z} - W_{2x}), \tag{46}
 \end{aligned}$$

$$\beta K_{3333} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_z^2 U_{1y} U_{2y}. \tag{47}$$

The splay-bend elastic constants have the form

$$\begin{aligned}
 \beta K_{1212} &= \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_x^2 (U_{1z} - W_{1x}) \\
 &\times (U_{2z} - W_{2x}), \tag{48}
 \end{aligned}$$

$$\beta K_{1313} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_x^2 U_{1y} U_{2y}, \quad (49)$$

$$\beta K_{2121} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_y^2 W_{1y} W_{2y}, \quad (50)$$

$$\beta K_{2323} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_y^2 U_{1y} U_{2y}, \quad (51)$$

$$\beta K_{3131} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_z^2 W_{1y} W_{2y}, \quad (52)$$

$$\beta K_{3232} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_z^2 (U_{1z} - W_{1x}) \times (U_{2z} - W_{2x}). \quad (53)$$

Other constants are connected with more complicated deformations

$$\beta K_{1122} = \frac{1}{4} \int dR_1 dR_2 d\mathbf{u} f_{12} u_x u_y \times [(U_{1z} - W_{1x})W_{2y} + W_{1y}(U_{2z} - W_{2x})], \quad (54)$$

$$\beta K_{1133} = \frac{1}{4} \int dR_1 dR_2 d\mathbf{u} f_{12} u_x u_z \times [-U_{1y}W_{2y} - W_{1y}U_{2y}], \quad (55)$$

$$\beta K_{2233} = \frac{1}{4} \int dR_1 dR_2 d\mathbf{u} f_{12} u_y u_z \times [-U_{1y}(U_{2z} - W_{2x}) - (U_{1z} - W_{1x})U_{2y}], \quad (56)$$

$$K_{1221} = K_{1122}, \quad K_{1331} = K_{1133}, \quad K_{2332} = K_{2233}, \quad (57)$$

$$L_{123} = L_{231} = L_{312} = 0. \quad (58)$$

In the case of the uniaxial nematic phase  $U_\alpha = 0$  and we get several equivalent expressions for elastic constants  $K_1$ ,  $K_2$ , and  $K_3$ ,

$$K_1 = K_{1212} = K_{2121}, \quad K_2 = K_{1111} = K_{2222}, \quad (59)$$

$$K_3 = K_{3131} = K_{3232}, \quad (60)$$

$$K_4 = \frac{1}{2}(K_1 + K_2), \quad K_5 = 0.$$

#### 5.4. Exemplary calculations

Let us define

$$\eta = k_B T B_4(T) \sigma_0^5 (N/V)^2. \quad (61)$$

The elastic constants can be written as finite sums of the form

$$K_{ijkl} = \eta \sum_{[I][J]} \langle F^{[I]} \rangle \langle F^{[J]} \rangle A_{ijkl}^{[I][J]}, \quad (62)$$

where the coefficients  $A_{ijkl}^{[I][J]}$  depend on  $\sigma_i$  only.

The parameters of the model system from Sect. 4 were used to calculate the temperature dependence of the elastic constants shown in Figs. 3 and 4. The elastic constants are expressed in  $\epsilon/\sigma_0$ . If we assume the molecular length  $\sigma_0 = 1$  nm and the interaction energy  $\epsilon = 0.1$  eV, then we can estimate the values of the elastic constants  $\epsilon/\sigma_0 = 16$  pN and the temperature  $\epsilon/k_B = 1160$  K. In

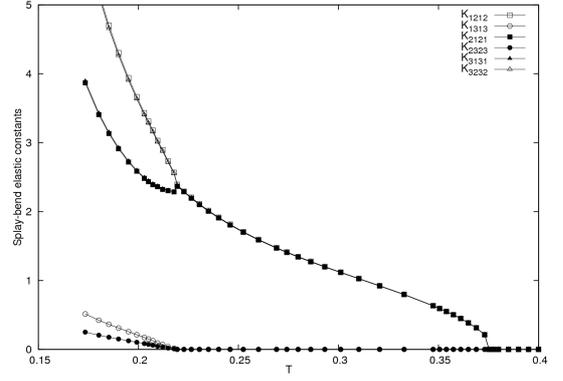


Fig. 3. Temperature dependence of the splay-bend elastic constants expressed in  $\epsilon/\sigma_0$ .  $T$  is the dimensionless temperature.

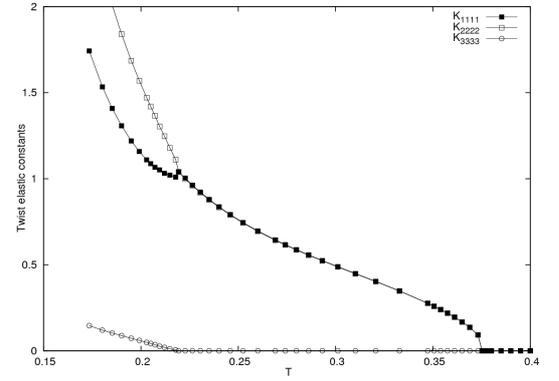


Fig. 4. Temperature dependence of the twist elastic constants expressed in  $\epsilon/\sigma_0$ .  $T$  is the dimensionless temperature.

the uniaxial nematic phase three independent bulk constants are present:  $K_1$ ,  $K_2$ , and  $K_3$ . In the biaxial nematic phase  $K_1$  splits into  $K_{1212} > K_{2121}$ ,  $K_2$  splits into  $K_{2222} > K_{1111}$ , and  $K_3$  splits into  $K_{3232} > K_{3131}$ . The new twist elastic constant is  $K_{3333} > 0$  and the new splay-bend elastic constants are  $K_{1313} > K_{2323} > 0$ . Other new constants are positive  $K_{1133}$ ,  $K_{2233}$  and negative  $K_{1122}$ . The elastic constants in display applications provide the restoring mechanism when the applied electric field is switched off. The small biaxial elastic constants signal possible difficulties with the restoring mechanism for biaxial modes.

## 6. Dielectric anisotropy

A static electric field imposed on a nematic is connected with at least two different processes: namely, the dielectric constant anisotropy and the flexoelectric effect. In this section we will focus on the dielectric constant and in the next section we will describe the flexoelectric effect.

### 6.1. Theory of the dielectric susceptibility

The dielectric permittivity ( $\epsilon$ ) and the susceptibility ( $\chi = \epsilon - 1$ ) are tensors with three different values along

the different axes, at least in the most general case. The purpose of the dielectric theory is to relate them to the molecular properties, i.e., to the polarizability  $\alpha$  and the dipole moment  $\mu$ .

The dielectric susceptibility is defined as:

$$\epsilon_0 \chi_{\lambda\sigma} = \frac{\partial P_\lambda}{\partial E_\sigma}, \quad (63)$$

where  $E$  is the electric field and  $P = P^{\text{ind}} + P^{\text{dip}}$  is the total electric polarization which can be divided into the part due to the molecular polarizability and the part due to the dipole moment. According to the theory of polar nematic liquid crystals by Maier and Meier (MM) [95], the susceptibility can be calculated from the equation

$$\chi_{\lambda\lambda} = \frac{N}{V} h F \sum_i \langle R_{i\lambda}^2 \rangle (\alpha_i + \mu_i^2 \beta F / \epsilon_0), \quad (64)$$

where  $h$  and  $F$  are the factors introduced by Onsager and can be written as

$$h = \frac{3\tilde{\chi} + 3}{2\tilde{\chi} + 3}, \quad (65)$$

$$F = \frac{1}{1 - \tilde{\alpha}\epsilon_0 f}, \quad (66)$$

$$\epsilon_0 f = \frac{2\tilde{\chi}}{2\tilde{\chi} + 3} \left( \frac{3N}{V} \right), \quad (67)$$

$\alpha_i$  and  $\mu_i$  are the components of the molecule polarizability and the molecule dipole moment, respectively. In the expressions for  $h$ ,  $F$ , and  $f$  the averaged susceptibility  $\tilde{\chi}$  and the polarizability  $\tilde{\alpha}$  were used, i.e. the anisotropy was neglected. Apart from that, the molecule under consideration was contained in a *spheroidal* cavity. It is unrealistic for liquid crystals and that is why the generalized Clausius–Mossotti (GCM) approach was proposed by Kapanowski and Wietecha [96, 97]. We note that Maier and Meier took into account the polarization of the surroundings by the permanent and induced dipole moment. This leads to the presence of the reaction field. In the case of small density, small dipoles or non-polar molecules, the reaction field is small and can be neglected.

Let us assume that the selected molecule is in a non-spherical cavity of molecular dimensions and surrounded by the anisotropic polarized continuum. Then the internal electric field acting on the molecule depends on the external electric field, the polarization and the shape factors  $\Omega_i$ . Exemplary formulae for different cavities are given in Appendix B. The susceptibilities have the form

$$\chi_{\lambda\lambda} = \frac{(N/V) \sum_i \langle R_{i\lambda}^2 \rangle (\alpha_i + \mu_i^2 \beta / \epsilon_0)}{1 - (N/V) \sum_i \langle R_{i\lambda}^2 \rangle \Omega_i (\alpha_i + \mu_i^2 \beta / \epsilon_0)}. \quad (68)$$

We have to add that both expressions for the susceptibility (64) and (68) have some limitations. Firstly, the polarizability of a molecule is represented by an anisotropic point polarizability, whereas in reality the polarizability of a molecule will be distributed over its whole volume. Secondly, the local Lorentz field approximation is not

valid for dense fluids because the field from the molecules inside the cavity (the near field) cannot be neglected (the Mossotti catastrophe). In the case of isotropic polar liquids the Kirkwood–Fröhlich theory provides in principle a framework in which short ranged dipole–dipole interactions can be explicitly evaluated. The theory has been extended to liquid crystals by Bordewijk [98]. Corresponding expressions for the biaxial nematic phase can be found in Ref. [99].

## 6.2. Exemplary calculations

In order to calculate the susceptibilities, we have to provide data on the polarizability and the dipole moment. The ordering of the phase is described by the model from Sect. 4, where the molecules are similar to ellipsoids with three different axes  $2a \times 2b \times 2c$  and  $a : b : c$  is  $1 : 2 : 5$ . The elements of the polarizability tensor  $\alpha$  are estimated from the model described in [96]

$$\alpha_1 = 3V_{\text{mol}}, \quad \alpha_2 = 4V_{\text{mol}}, \quad \alpha_3 = 5.567V_{\text{mol}}. \quad (69)$$

The temperature dependence of the susceptibilities calculated from Eq. (64) for non-polar molecules is shown in Fig. 5. In the uniaxial nematic phase we have  $\chi_{zz} > \chi_{yy} = \chi_{xx}$ . At the transition to the biaxial nematic phase the lower susceptibility branch splits into two independent  $\chi_{yy} > \chi_{xx}$ . For the considered system the reaction field is important as the susceptibilities calculated from Eq. (68) are twice smaller.

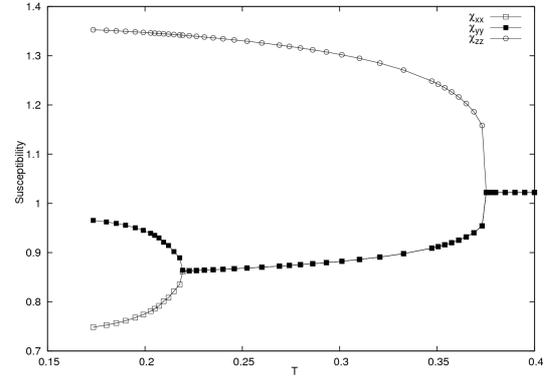


Fig. 5. Temperature dependence of the susceptibilities.  $T$  is the dimensionless temperature.

## 7. Flexoelectric effect

In a deformed uniaxial nematic liquid crystal, there should appear in many cases a spontaneous dielectric polarization described by Meyer [100]:

$$P_\alpha = e_1 N_\alpha \partial_\beta N_\beta + e_3 N_\beta \partial_\beta N_\alpha, \quad (70)$$

where  $e_1$  and  $e_3$  are the splay and the bend flexoelectric (FE) coefficients, respectively. The appearance of spontaneous polarization in liquid crystals as a result of orientational deformations is referred to as the flexoelectric effect. The inverse effect is also possible: when an

electric field is applied on the nematic phase, the alignment may become distorted, since a suitable distortion will imply a polarization parallel to the electric field.

The FE effect can influence electro-optical properties, defect formation, and structural instability. That is why different techniques have been suggested to observe possible mechanisms producing the FE polarization: measurements of the polarisations or the surface charges induced by an imposed distortion, pyroelectric-effect-based techniques, a technique inspired by the flexoelectric-optic effect [101].

### 7.1. Flexoelectric polarization in the biaxial nematic phase

A statistical theory for the dipole FE polarization in the uniaxial nematic phase was derived by Kapanowski [102] in the thermodynamic limit at small distortions and a small density. The theory was applied to two systems with polar wedge-shaped and banana-shaped molecules [103]. In the case of the biaxial nematic phase the FE polarization has the form [104]

$$P_\alpha = s_{11}L_\alpha\partial_\beta L_\beta + b_{11}L_\beta\partial_\beta L_\alpha + s_{22}M_\alpha\partial_\beta M_\beta + b_{22}M_\beta\partial_\beta M_\alpha + s_{33}N_\alpha\partial_\beta N_\beta + b_{33}N_\beta\partial_\beta N_\alpha, \quad (71)$$

where the parameters  $s_{ii}$  and  $b_{ii}$  ( $i = 1, 2, 3$ ) are not unique because if we add any constant to all of them, the polarization will not change. The physical FE coefficients  $a_i$  ( $i = 4, \dots, 9$ ) are connected with the proper basic deformations of the phase (see Table III). The FE polarization calculated for splay and bend deformations (41) gives

$$P_x = q_7(s_{11} - b_{22}) + q_9(s_{11} - b_{33}) = q_7a_7 + q_9a_9, \quad (72)$$

$$P_y = q_5(s_{22} - b_{11}) + q_8(s_{22} - b_{33}) = q_5a_5 + q_8a_8, \quad (73)$$

$$P_z = q_4(s_{33} - b_{11}) + q_6(s_{33} - b_{22}) = q_4a_4 + q_6a_6. \quad (74)$$

The physical coefficients satisfy the identity

$$a_4 - a_5 - a_6 + a_7 + a_8 - a_9 = 0. \quad (75)$$

### 7.2. Flexoelectric coefficients

The molecule electric dipole moment is defined as

$$\mu_\alpha(R) = \mu_1l_\alpha + \mu_2m_\alpha + \mu_3n_\alpha, \quad \alpha = x, y, z. \quad (76)$$

The microscopic expressions for the physical FE coefficients are

$$a_4 = \int \mathbf{d}\mathbf{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_z(R_1) (-u_x) \times (U_{2z} - W_{2x}), \quad (77)$$

$$a_5 = \int \mathbf{d}\mathbf{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_y(R_1) (-u_x) U_{2y}, \quad (78)$$

$$a_6 = \int \mathbf{d}\mathbf{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_z(R_1) u_y W_{2y}, \quad (79)$$

$$a_7 = \int \mathbf{d}\mathbf{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_x(R_1) u_y U_{2y}, \quad (80)$$

$$a_8 = \int \mathbf{d}\mathbf{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_y(R_1) (-u_z) W_{2y}, \quad (81)$$

$$a_9 = \int \mathbf{d}\mathbf{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_x(R_1) u_z (U_{2z} - W_{2x}). \quad (82)$$

In the case of the uniaxial nematic phase composed of wedge-shaped molecules ( $\mathbf{n}$  is the long molecule axis)  $U_\alpha = 0$  and the Meyer two FE coefficients are recovered

$$e_1 = a_4 = a_6, \quad e_3 = -a_8 = -a_9. \quad (83)$$

The expressions (83) are valid for  $C_{2v}$  molecules, whereas very often simpler expressions for  $C_{\infty v}$  molecules are present in the literature. We also note that the polarization in a deformed liquid crystal can be produced as a result of a gradient in the average density of the molecule quadrupole moments [105]. Such a polarization does not need asymmetry in molecular shape.

### 7.3. Exemplary calculations

In order to describe  $C_2$  molecules we write  $\sigma$  of the form ( $\mathbf{n}$  is the symmetry axis)

$$\begin{aligned} \sigma = & \sigma_0 + \sigma_1 [(\mathbf{\Delta} \cdot \mathbf{n}_1)^2 + (\mathbf{\Delta} \cdot \mathbf{n}_2)^2] + \sigma_2 (\mathbf{n}_1 \cdot \mathbf{n}_2)^2 \\ & + \sigma_3 [(\mathbf{\Delta} \cdot \mathbf{l}_1)^2 + (\mathbf{\Delta} \cdot \mathbf{l}_2)^2] + \sigma_4 (\mathbf{l}_1 \cdot \mathbf{l}_2)^2 \\ & + \sigma_5 [(\mathbf{l}_1 \cdot \mathbf{n}_2)^2 + (\mathbf{l}_2 \cdot \mathbf{n}_1)^2] + \sigma_6 (\mathbf{n}_1 \cdot \mathbf{n}_2) \\ & + \sigma_7 (\mathbf{\Delta} \cdot \mathbf{n}_1 - \mathbf{\Delta} \cdot \mathbf{n}_2) + \sigma_8 [(\mathbf{n}_1 \times \mathbf{n}_2) \cdot \mathbf{\Delta}], \end{aligned} \quad (84)$$

where the terms with  $\sigma_6, \sigma_7$  (achiral) and  $\sigma_8$  (chiral) are the lowest order terms compatible with the  $C_2$  symmetry. Analytical calculations suggest that the most important for the FE effect is the  $\sigma_7$  term. Let us define

$$\zeta = \mu_3 B_3(T) \sigma_0^4 (N/V)^2. \quad (85)$$

The FE coefficients can be written as finite sums of the form

$$a_i = \zeta \sum_{[I][J]} \langle F^{[I]} \rangle \langle F^{[J]} \rangle A_i^{[I][J]}, \quad (86)$$

where the coefficients  $A_i^{[I][J]}$  depend on  $\sigma_i$  only.

We used the Lennard-Jones 12-6 potential energy,  $\sigma_1/\sigma_0 = 0.5$ ,  $\sigma_2/\sigma_0 = 0.1$ ,  $\sigma_3/\sigma_0 = -0.4$ ,  $\sigma_7/\sigma_0 = 0.1$ ,  $\sigma_4 = \sigma_5 = \sigma_6 = \sigma_8 = 0$ , packing  $NV_{\text{mol}}/V = 0.1$ . The molecules are similar to cones pointing down. The temperature dependence of the FE coefficients is shown in Fig. 6. The FE coefficients are expressed in  $\mu_3/\sigma_0^2$ , temperatures in  $\epsilon/k_B$ . On decreasing the temperature we meet the first-order transition from the isotropic phase to the uniaxial nematic phase at  $T = 0.373$  and the second-order transition to the biaxial nematic phase at  $T = 0.220$ . The splay FE coefficient  $e_1$  splits into  $a_4 > a_6 > 0$  whereas the bend FE coefficient  $-e_3$  splits into  $0 > a_8 > a_9$ . The coefficients  $a_5$  and  $a_7$  are small and negative. If we assume the molecular length  $\sigma_0 = 1$  nm

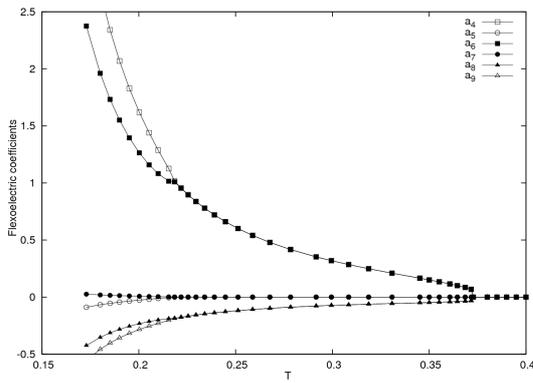


Fig. 6. Temperature dependence of the FE coefficients expressed in  $\mu_3/\sigma_0^2$ .  $T$  is the dimensionless temperature.

and the electric dipole moment  $\mu = 1$  D, then we can estimate the values of the FE coefficients  $\mu/\sigma_0^2 = 3.3$  pC/m.

## 8. Chiral biaxial nematics

An object is chiral if its image in a plane mirror cannot be brought to coincide with itself. A chiral molecule induces chiral interactions that produce intermolecular torques of a given sign and can give rise to equilibrium chiral structures [106]. The effective chiral interactions can arise from classical or quantum interactions [107]. In liquid crystal physics, chiral interactions lead to many different phases, such as cholesteric phases, blue phases or some smectic phases. The (uniaxial) cholesteric phase is characterized by a helical arrangement of the director field  $\mathbf{N}$  along a common pitch axis

$$\mathbf{N}(\mathbf{r}) = [0, -\sin(q_0x), \cos(q_0x)], \quad (87)$$

where  $q_0 = K_0/K_2$ ,  $P = 2\pi/|q_0|$  is the cholesteric pitch and the distortion free-energy density is  $f_d = -K_0^2/2K_2$ . The sign of  $K_0$  distinguishes between right- and left-handed helices. It is interesting that dimensional analysis does not predict the pitch correctly; the cholesteric phase possesses an additional mesoscopic length scale.

Chiral thermotropic mesogens are used in optoelectronic applications due to the unique rheological, electrical, and optical properties. Chiral lyotropic mesogens are also common; for example, DNA, the rod-like *fd*-virus, or polypeptides. In these systems, the cholesteric pitch is very sensitive to concentration, temperature, pressure, as well as to the solvent conditions. The temperature dependence types for the pitch of the helix can be falling, rising, and inverting. The first of these types is most often found in pure cholesterics, the second is rather rare [108, 109], and the third is observed in mixtures of right-handed and left-handed cholesterics [110]. Theoretical attempts to predict the behavior of the cholesteric pitch are challenging owing to the complexity of the chiral interaction and the inhomogeneous and anisotropic nature of the phase [111, 112]. Early models of the uniaxial cholesteric phase were discussed in [113], where a gener-

alized van der Waals theory of lyotropic cholesterics was presented. The influence of fluctuations on the phase diagram of chiral nematic liquid crystals was studied by Englert et al. [114, 115]. The analysis of all five helicity modes was done by Longa et al. [116].

There is a connection between chirality and biaxiality. In 1974 Priest and Lubensky [117] recognized that cholesteric liquid crystals must have some slight biaxial order because of the difference between the directions along and perpendicular to the helical axis. A connection between the phase biaxiality and the stability of various chiral liquid crystalline phases was studied in [118] using the extended de Gennes–Ginzburg–Landau theory. Issaenko and Harris [119] showed that an accurate evaluation of the intermolecular dispersion forces contributing to chiral ordering requires consideration of biaxial correlations between molecules. In 1989 Krolin et al. [120] measured the chirality-induced biaxiality in lyotropic liquid crystals. Recently, Dhakal and Selinger [121] investigated the statistical mechanics of chirality and biaxiality in liquid crystals through a variety of theoretical approaches. Their calculations show that the twist acts as a field on the biaxial order, and conversely, the biaxial order increases the twist (reduces the pitch). In this paper, only one twist is taken into account in the biaxial cholesteric phase. Some experiments with lyotropic liquid crystals suggest [122, 120] that the biaxial cholesteric phase chooses its chiral axis along the axis associated to the smallest eigenvalue of the order parameter tensor  $Q_{\alpha\beta}$ . It seems that in real experiments boundary conditions can be an important factor determining the phase configuration. We will show how three twists can minimize the distortion free energy.

### 8.1. Chiral elastic constants

The statistical theory of biaxial cholesteric liquid crystals was derived by Kapanowski [123] in the limit of small twists. The cholesteric phase was regarded as a distorted form of the nematic phase. Microscopic expressions for the chiral elastic constants of the biaxial cholesteric phase are as follows:

$$\beta K_{11} = -\frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_x G_0(R_1) W_{2y}, \quad (88)$$

$$\beta K_{22} = -\frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_y G_0(R_1) (U_{2z} - W_{2x}), \quad (89)$$

$$\beta K_{33} = \frac{1}{2} \int dR_1 dR_2 d\mathbf{u} f_{12} u_z G_0(R_1) U_{2y}. \quad (90)$$

In the case of the uniaxial cholesteric phase  $U_\alpha = 0$  and we get

$$K_{11} = K_{22} = K_0, \quad K_{33} = 0. \quad (91)$$

### 8.2. The equilibrium distortion in the chiral biaxial phase

The equilibrium distortion of the biaxial cholesteric phase is composed of three twists with respect to the

orthogonal axes. In the limit of small distortions the vectors  $(\mathbf{L}, \mathbf{M}, \mathbf{N})$  have the form (40). Minimizing the distortion free-energy density  $f_d$  we get the equilibrium twists  $q_1$ ,  $q_2$ , and  $q_3$  [123]. It is important that a global minimum of  $f_d$  exists only if the matrix

$$\begin{bmatrix} K_{1111} & K_{1122} & K_{1133} \\ K_{1122} & K_{2222} & K_{2233} \\ K_{1133} & K_{2233} & K_{3333} \end{bmatrix} \quad (92)$$

is positive definite. In the opposite case there is no stable biaxial cholesteric (and nematic) phase. In the limit of the uniaxial cholesteric phase the stability condition has a simple form

$$K_1 < 3K_2. \quad (93)$$

As far as we know the condition (93) is satisfied in almost all theories and experiments. The equality  $K_1 = 3K_2$  appears in some theories with hard molecules [124, 125]. Recently, the elastic constants and orientational viscosities of bent-core nematic liquid crystals have been determined [126] and the unusual anisotropies of these parameters have been discussed in terms of short-range, smectic-C correlations among molecules. The relation (93) was not satisfied and the viscosity ratios also contrasted with ordinary calamitics.

Now we would like to explain a certain ambiguous situation concerning the pitch at the transition from the biaxial nematic to the uniaxial nematic phase. If the twists  $q_1$ ,  $q_2$ , and  $q_3$  (40) are applied to the biaxial nematic phase and we move to the uniaxial nematic phase, the distortion free energy will be transformed to the form

$$f_d = -K_0(q_1 + q_2) + \frac{1}{2}K_2(q_1 + q_2)^2 - K_4q_1q_2. \quad (94)$$

The  $q_3$  twist is not present because it is undefined in the uniaxial nematic phase but there is a surface term with  $K_4$  in Eq. (94). The  $K_4$  term is present because  $K_{1122} = K_2 - K_4$  at the transition. In the thermodynamic limit surface terms are negligible and as the result the equilibrium twist  $q_0 = q_1 + q_2 = K_0/K_2$  is obtained. As a side effect, there is a discontinuity in the pitch at the transition.

### 8.3. Exemplary calculations

Let us define

$$\xi = k_B T B_3(T) \sigma_0^4 (N/V)^2. \quad (95)$$

The chiral elastic constants can be written as finite sums of the form

$$K_{ii} = \xi \sum_{[I][J]} \langle F^{[I]} \rangle \langle F^{[J]} \rangle A_{ii}^{[I][J]}, \quad (96)$$

where the coefficients  $A_{ii}^{[I][J]}$  depend on  $\sigma_i$  only.

We used the Lennard-Jones 12-6 potential energy,  $\sigma$  of the form (22) with  $\sigma_1/\sigma_0 = 0.5$ ,  $\sigma_2/\sigma_0 = 0.1$ ,  $\sigma_3/\sigma_0 = -0.4$ ,  $\sigma_6/\sigma_0 = 0.01$ ,  $\sigma_7/\sigma_0 = \sigma_8/\sigma_0 = 0.001$ , packing  $NV_{\text{mol}}/V = 0.1$ . The achiral elastic constants are expressed in  $\epsilon/\sigma_0$ , the chiral elastic constants in  $\epsilon/\sigma_0^2$ , the twist parameters  $q_i$  in  $1/\sigma_0$ , temperatures in  $\epsilon/k_B$ .

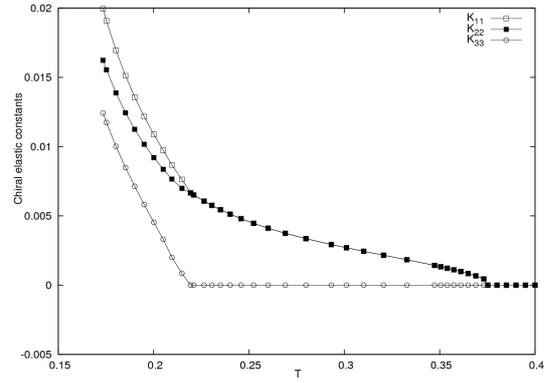


Fig. 7. Temperature dependence of the chiral elastic constants expressed in  $\epsilon/\sigma_0^2$ .  $T$  is the dimensionless temperature.

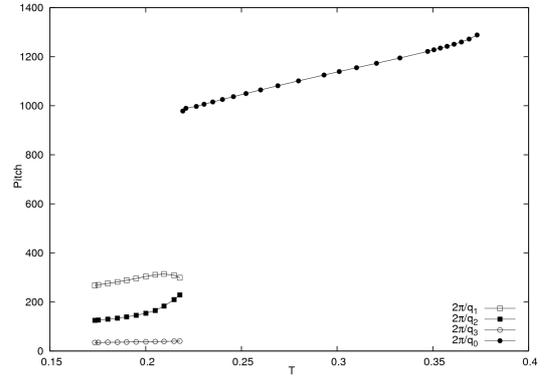


Fig. 8. Temperature dependence of the pitches expressed in  $\sigma_0$ .  $T$  is the dimensionless temperature.

The temperature dependence of the achiral elastic constants is similar to shown in Figs. 3 and 4. The temperature dependence of the chiral elastic constants is shown in Fig. 7. The temperature dependence of the pitches is shown in Fig. 8. In the uniaxial cholesteric phase there is one chiral elastic constant  $K_0$ . On decreasing the temperature,  $K_0$  splits into  $K_{11} > K_{22}$  and  $K_{33}$  becomes nonzero. The twist parameters satisfy the inequalities  $q_1 < q_2 < q_3$  and all are greater than  $q_0$ . We would like to add that relatively small changes of chiral parameters  $\sigma_6$ ,  $\sigma_7$ , and  $\sigma_8$  can change the described picture qualitatively. Generally, the pitches in the biaxial cholesteric phase are smaller than in the uniaxial cholesteric phase. It is in accordance with other approaches to the description of the biaxial cholesteric phase [121]. If we assume the molecular length  $\sigma_0 = 1$  nm and the interaction energy  $\epsilon = 0.1$  eV, then we can estimate the values of the chiral elastic constants  $\epsilon/\sigma_0^2 = 0.16$  N/m.

## 9. Other physical properties of nematics

In this section we would like to describe briefly two physical properties of biaxial nematics where the theory is well developed and interesting.

### 9.1. Viscous properties

Let us consider a nematic film between two parallel glass plates. If the plates slide parallel to each other, the molecules will flow, just as an ordinary fluid. However, due to the coupling between orientation and flow the nematodynamics is more difficult to study than the hydrodynamics of isotropic liquids. The theory relates the viscous stress tensor  $\sigma_{\alpha\beta}$  to viscosity coefficients, the velocity gradient tensor and the directors. A complete set of viscosity coefficients for the uniaxial nematic consists of five elements [127]: three Mięslowicz coefficients  $\eta_1$ ,  $\eta_2$ , and  $\eta_3$ , the coefficient  $\eta_{12}$ , and the rotational viscosity coefficient  $\gamma_1$ . Theoretical treatments of the viscous properties often use different sets of coefficients and the most common is a set of five  $\alpha_i$  introduced by Leslie [128, 129].

The most complete formulation of the viscosity theory for biaxial liquid crystals was given by Leslie et al. in Ref. [130], where twelve independent viscosity coefficient were identified (three rotational viscosities and nine effective shearing viscosities). The method of calculation of the Leslie viscosity coefficients was given by Fiałkowski for the case of ellipsoids with three different principal axes [131, 132]. The derived formulae were expressed in terms of order parameters, temperature, number density, and diffusion constants.

### 9.2. Defects

A nematic liquid crystal can be regarded as an ordered medium, where a region of space is described by a function  $\psi$  that assigns to every point of the region of an order parameter [133]. The possible values of the order parameter constitute a space known as the order parameter space  $M$ , manifold of internal states or a space of degeneracy [134]. The region of space is usually three-dimensional space, though two-dimensional regions can be used for films. Distortions of  $\psi$  can contain singularities, where  $\psi$  is not defined. For a three-dimensional medium, the singular regions might be either zero-dimensional (points), one-dimensional (lines), or two-dimensional (walls). These are defects. Whenever an inhomogeneous state cannot be eliminated by continuous variations of the order parameter, it is called a topological defect. If the inhomogeneous state does not contain singularities, but nevertheless is not deformable continuously into a homogeneous state, one says that the system contains a topological configuration or soliton [135]. Defects are local breakings of symmetry in an ordered medium. Dislocations break translational symmetries. Disclinations break rotational symmetries and are basic defects in liquid crystals [136].

An adequate description of defects in ordered media requires the theory of homotopy, which is part of algebraic topology [137]. Then it is possible to classify the defects types, to find the laws of decay, merger and crossing of defect, to trace out their behaviour during phase transitions, and so on. The key point is the concept of topological invariant or topological charge which is inherent

in every defect. The stability of the defect is guaranteed by the conservation of its topological charge. Topologically stable wall, line, and point defects are described by elements of the homotopy groups  $\pi_0(M)$ ,  $\pi_1(M)$ , and  $\pi_2(M)$ , respectively. The situation becomes more complex when we wish to study surface defects, namely defects that arise on a surface bonding the body [138].

The order parameter space for uniaxial nematics is the surface of unit sphere, where opposite points are identified. This space is known as the real projective plane  $M = RP^2$ .  $M$  can be expressed as the coset space  $M = SO(3)/D_\infty$ . The important results are  $\pi_0(M) = Z_2$ ,  $\pi_1(M) = Z_2$ ,  $\pi_2(M) = Z$ .

The order parameters space for biaxial nematics is the full proper three-dimensional rotation group  $SO(3)$ , provided the appropriate discrete sets of points are identified (proper point group  $D_2$ ). Thus  $M = SO(3)/D_2$  but it turns out that the natural representation is  $M = SU(2)/H$ , where  $H$  is the quaternion group. Here  $\pi_1(M) = H$  and there are five types of line defects because there are five classes of conjugated elements in  $H$ . The groups  $\pi_0(M)$  and  $\pi_2(M)$  are trivial.

The structures, energies, and interactions of defects in many liquid crystalline phases were presented by Chandrasekhar and Ranganath [139]. In 1997 Biscari and Peroli studied the topological properties of manifolds which describe uniaxial and biaxial nematics in order to compare and classify all types of bulk and surface defects in nematics [138]. The manifold of the traceless order tensor  $Q$  consists of three disjoint subsets with different symmetries (isotropic, uniaxial, and biaxial distributions). The surfaces induce in the order tensor the additional symmetry which is important for surface defects. Information about the nature of surface defects come from the structure of the relative homotopy groups.

## 10. Conclusions

In this paper the statistical theory of biaxial nematic and cholesteric phases was presented. It was derived in the thermodynamic limit at small density and small distortions. The microscopic expressions for many macroscopic parameters were shown: for the elastic constants, the dielectric susceptibilities, the FE coefficients, and the phase twists. The expressions involve the one-particle distribution function and the potential energy of two-body short-range interactions. In addition flow properties and defects of biaxial nematics were briefly discussed. Exemplary calculations were shown for several systems of molecules interacting via Corner-type potential based on the Lennard–Jones 12-6 functional dependence. Estimates for all parameters were given as the direct comparison between the theory and the experiment is in many cases difficult at present.

The presented theory can be generalized in many directions. It is desirable to go beyond the low density limit where the Mayer function  $f_{12}$  is replaced with a better approximation of the direct correlation function. It is

known that to understand the thermodynamic properties of dense fluids, the repulsive forces must be treated to all orders whereas attractive forces can be treated by a perturbation theory [140]. Let us consider the convex peg model [140, 141], where molecules are envisioned to have a hard biaxial core embedded in a spherically symmetric square well. Then the interaction term in the free energy (27) can be written as

$$\begin{aligned} \beta F_{\text{int}} = & \frac{N^2}{2V} \int dR_1 dR_2 f(R_1) f(R_2) \\ & \times \left\{ V_{\text{excl}}(R_1, R_2) \left[ \frac{4 - 3\rho}{4(1 - \rho)^2} + e^{\beta\epsilon} - 1 \right] \right. \\ & \left. + (1 - e^{\beta\epsilon}) V_{\text{sw}} \right\}, \end{aligned} \quad (97)$$

where  $\rho = NV_{\text{mol}}/V$ ,  $V_{\text{excl}}(R_1, R_2)$  is the excluded volume of the hard core, and  $V_{\text{sw}} = (4/3)\pi\sigma_{\text{sw}}^3$  is the excluded volume of the spherical square well. Hard core interactions are mapped into the dense hard sphere system using a Carnahan–Starling approximation. If we consider the Corner square well potential energy (104), then by means of similar assumptions we derive

$$\begin{aligned} \beta F_{\text{int}} = & \frac{N^2}{2V} \int dR_1 dR_2 f(R_1) f(R_2) K(R_1, R_2) (\sigma_0^3/3) \\ & \times \left[ \frac{4 - 3\rho}{4(1 - \rho)^2} - 3B_2(T) - 1 \right]. \end{aligned} \quad (98)$$

The theory can be generalized to the case of many component liquid crystalline mixtures. In fact, mixtures are essential for technological applications of liquid crystals because various combinations of physical properties are required [51]. The design and synthesis of materials exhibiting the biaxial nematic phase with desired properties constitute one of the major challenges in liquid crystal science.

### Appendix A Invariants

We list the main properties of the functions  $F_{\mu\nu}^{(j)}$ , which describe biaxial and uniaxial molecules in biaxial and uniaxial phases [94].

(i) The definition of the functions  $F_{\mu\nu}^{(j)}$ :

$$\begin{aligned} F_{\mu\nu}^{(j)}(R) = & \left( \frac{1}{\sqrt{2}} \right)^{2+\delta_{\mu 0}+\delta_{\nu 0}} \\ & \times \sum_{\rho, \sigma = \pm 1} (-1)^{j(\sigma-\rho)/2} D_{\rho \times \mu, \sigma \times \nu}^{(j)}(R), \end{aligned} \quad (99)$$

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

(ii) The functions  $F_{\mu\nu}^{(j)}$  are real.

(iii) For the inverse rotation  $F_{\mu\nu}^{(j)}(R^{-1}) = F_{\nu\mu}^{(j)}(R)$ . For the zero rotation  $F_{\mu\nu}^{(j)}(0) = \delta_{\mu\nu}$ .

(iv) The orthogonality relations have the form

$$\int dR F_{\mu\nu}^{(j)}(R) F_{\rho\sigma}^{(k)}(R) = \delta_{jk} \delta_{\mu\rho} \delta_{\nu\sigma} 8\pi^2 / (2j + 1). \quad (100)$$

(v) The invariants can be labelled by the indicator  $[I]$ , where  $I$  runs from 1 by 1 to infinity. For two indicators  $[I] = (j, \mu, \nu)$  and  $[J] = (k, \rho, \sigma)$  we can write that  $[I] < [J]$  only when  $j < k$ , or when  $j = k$  and  $\mu < \rho$ , or when  $j = k$ ,  $\mu = \rho$ , and  $\nu < \sigma$ .

### Appendix B Corner potential energy

We list some examples for the dependence of the Corner potential energy  $\Phi_{12}$  on  $u/\sigma$ , together with the functions  $B_s(T)$  defined as  $[\beta = 1/(k_B T)]$ :

$$B_s(T) = \int_0^\infty dx x^s f_{12}(x) = \int_0^\infty dx x^s [\exp(-\beta\Phi_{12}(x)) - 1]. \quad (101)$$

(i) The soft-core potential energy ( $m \geq s + 2$ ):

$$\Phi_{12}(u/\sigma) = \epsilon(\sigma/u)^m, \quad (102)$$

$$B_s(T) = \frac{-1}{s+1} \Gamma\left(\frac{m-s-1}{m}\right) (\beta\epsilon)^{(s+1)/m}. \quad (103)$$

(ii) The square-well potential energy

$$\Phi_{12}(u/\sigma) = \begin{cases} +\infty & \text{for } (u/\sigma) < 1, \\ -\epsilon & \text{for } 1 < (u/\sigma) < R_{\text{sw}}, \\ 0 & \text{for } (u/\sigma) > R_{\text{sw}}, \end{cases} \quad (104)$$

$$B_s(T) = \frac{1}{s+1} \{[\exp(\beta\epsilon) - 1](R_{\text{sw}}^{s+1} - 1) - 1\}. \quad (105)$$

(iii) The soft-well potential energy ( $m \geq s + 2$ )

$$\Phi_{12}(u/\sigma) = \begin{cases} +\infty & \text{for } (u/\sigma) < 1, \\ -\epsilon(\sigma/u)^m & \text{for } (u/\sigma) > 1, \end{cases} \quad (106)$$

$$B_s(T) = \frac{-1}{s+1} {}_1F_1\left(-\frac{s+1}{m}, 1 - \frac{s+1}{m}, \beta\epsilon\right). \quad (107)$$

(iv) The Lennard–Jones  $m$ – $n$  potential energy ( $m > n > s + 1$ ):

$$\Phi_{12}(u/\sigma) = 4\epsilon[(\sigma/u)^m - (\sigma/u)^n], \quad (108)$$

$$\begin{aligned} B_s(T) = & \frac{-1}{s+1} \sum_{p=0}^{\infty} \frac{1}{p!} (4\beta\epsilon)^{[p(m-n)+s+1]/m} \\ & \times \Gamma\left(\frac{pn+m-s-1}{m}\right) \\ & + \frac{1}{s+1} \sum_{p=0}^{\infty} \frac{1}{p!} \frac{n}{m} (4\beta\epsilon)^{[p(m-n)+m-n+s+1]/m} \\ & \times \Gamma\left(\frac{pn+n-s-1}{m}\right). \end{aligned} \quad (109)$$

### Appendix C Shape factors for biaxial molecules

We list shape factors for model biaxial molecules with the  $D_{2h}$  symmetry. The reference point, where we calculate the electric field, is always placed in the molecule mass center.

(i) Ellipsoids with the axes  $2a \times 2b \times 2c$ :

$$\Omega_1 = J(1 - a^2/b^2, 1 - a^2/c^2), \quad (110)$$

$$\Omega_2 = J(1 - b^2/a^2, 1 - b^2/c^2), \quad (111)$$

$$\Omega_3 = J(1 - c^2/a^2, 1 - c^2/b^2), \quad (112)$$

where the function  $J(x, y)$  is defined for  $x < 1$  and  $y < 1$  as

$$J(x, y) = \int_0^1 \frac{dt t^2}{\sqrt{(1 - xt^2)(1 - yt^2)}}. \quad (113)$$

(ii) Platelets of dimensions  $a \times b \times c$ :

$$\Omega_1 = F_p(a, b, c), \quad \Omega_2 = F_p(b, a, c),$$

$$\Omega_3 = F_p(c, a, b), \quad (114)$$

$$F_p(x, y, z) = F_p(x, z, y) = \frac{2}{\pi} \arcsin \left( \frac{yz}{\sqrt{(x^2 + y^2)(x^2 + z^2)}} \right). \quad (115)$$

Let us note that  $\Omega_1 + \Omega_2 + \Omega_3 = 1$ .

(iii) Spherocuboids [65] obtained by the Minkowski addition of a parallelepiped with sides of length  $a$ ,  $b$ , and  $c$ , and a sphere of radius  $R$ . As a special case one can obtain platelets, spheroplatelets or spherocylinders. A spherocuboid can be bounded by the box of dimensions  $(a + 2R) \times (b + 2R) \times (c + 2R)$ .

$$\Omega_1 = F_p(a + 2R, b, c) + F_s(a, b, c) + F_c(a, b, c) + F_c(a, c, b), \quad (116)$$

$$\Omega_2 = F_p(b + 2R, a, c) + F_s(b, a, c) + F_c(b, a, c) + F_c(b, c, a), \quad (117)$$

$$\Omega_3 = F_p(c + 2R, a, b) + F_s(c, a, b) + F_c(c, a, b) + F_c(c, b, a), \quad (118)$$

$$F_s(x, y, z) = \int_0^{\pi/2} d\phi \times \int_0^{\pi/2} d\theta \frac{8R^2(x + 2R \cos \theta) \sin \theta \cos \theta}{\pi \xi_s^3}, \quad (119)$$

$$\xi_s^2 = (x + 2R \cos \theta)^2 + (y + 2R \sin \theta \sin \phi)^2 + (z + 2R \sin \theta \cos \phi)^2, \quad (120)$$

$$F_c(x, y, z) = \int_0^{\pi/2} d\theta \frac{4R \cos \theta (x + 2R \cos \theta) z}{\pi \xi_c^2 \sqrt{z^2 + \xi_c^2}}, \quad (121)$$

$$\xi_c^2 = (x + 2R \cos \theta)^2 + (y + 2R \sin \theta)^2, \quad (122)$$

$$F_s(0, 0, 0) = 1/3 \quad \text{like for spheres}, \quad (123)$$

$$F_c(0, 0, z) = \frac{z}{2\sqrt{z^2 + 4R^2}} \quad \text{like for cylinders}. \quad (124)$$

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