FAST TRACK COMMUNICATION

Ferroelectricity in low-symmetry biaxial nematic liquid crystals

To cite this article: Mikhail A Osipov and Maxim V Gorkunov 2010 J. Phys.: Condens. Matter 22 362101

View the article online for updates and enhancements.

Related content
- Molecular models for the SmA-SmC transition in a system of biaxial molecules
  Maxim V Gorkunov and Mikhail A Osipov
- Influence of dipole–dipole correlations on the stability of the biaxial nematic phase in the model bent-core liquid crystal
  Mikhail A Osipov and Grzegorz Pajak
- Ferroelectric liquid crystals
  L M Blinov and L A Beresnev

Recent citations
- Calamitic and antinematic orientational order produced by the generalized Straley lattice model
  Fulvio Bisi et al
- Unified molecular field theory of nematic, smectic-A, and smectic-C phases
  G. Pajk and M. A. Osipov
- Morphological transitions in liquid crystal nanodroplets
  V. Tomar et al
FAST TRACK COMMUNICATION

Ferroelectricity in low-symmetry biaxial nematic liquid crystals

Mikhail A Osipov and Maxim V Gorkunov

1 Department of Mathematics and Statistics, University of Strathclyde, Glasgow G1 1XH, UK
2 A V Shubnikov Institute of Crystallography, Russian Academy of Sciences, 119333 Moscow, Russia

E-mail: m.osipov@strath.ac.uk

Received 20 July 2010
Published 11 August 2010
Online at stacks.iop.org/JPhysCM/22/362101

Abstract

Order parameters and phenomenological theory for both high- and low-symmetry biaxial nematic phases are presented and it is predicted that the chiral low-symmetry biaxial phase must be ferroelectric. This conclusion is based on general symmetry arguments and on the results of the Landau–de Gennes theory. The microscopic mechanism of the ferroelectric ordering in this chiral biaxial phase is illustrated using a simple molecular model based on dispersion interactions between biaxial molecules of low symmetry. Similar to the chiral smectic C* phase, the ferroelectricity in the chiral biaxial nematic phase is improper, i.e., polarization is not a primary order parameter and is not determined by dipolar interactions. Ferroelectric ordering in biaxial nematics may be found, in principle, in materials composed of chiral analogues of the tetrapod molecules which are known to exhibit biaxial phases.

1. Introduction

Conventional nematic liquid crystals are uniaxial anisotropic fluids although they are generally composed of biaxial molecules. In uniaxial nematics, both long and short molecular axes are distributed symmetrically around a unique macroscopic symmetry axis specified by the director $\mathbf{n}$. The symmetry axis is nonpolar and thus $\mathbf{n}$ and $-\mathbf{n}$ are equivalent. If the molecular biaxiality is sufficiently strong, one may expect the corresponding materials to exhibit the biaxial nematic phase in which molecular long and short axes are ordered along the two macroscopic orthogonal directions specified by the primary director $\mathbf{n}$ and the secondary director $\mathbf{m}$. Biaxial nematic materials are very interesting from both the fundamental and the technological points of view. In particular, they have a number of advantages over both conventional nematics and tilted smectics including a possibility of ultra-fast switching of the second director without encountering any problems related to various smectic defects.

The potential existence of the biaxial nematic phase has been supported by computer simulations [1–7] (see also the recent review [8]). In 1980 Yu and Saupe discovered the biaxial nematic phase, but for a lyotropic liquid crystal composed of relatively large micelles [9]. At the same time several compounds have been claimed to form a thermotropic biaxial nematic phase but the experimental evidence has been insufficient.

In recent years biaxial ordering has been found in the nematic phase of bent-core mesogens [10, 11] and in the nematic material composed of tetrapod molecules in which four mesogenic groups are linked by flexible spacers to the central atom [12, 13]. The biaxial phase has been characterized by x-ray scattering [14], conoscopy and deuterium NMR [15, 16], polarized infrared spectroscopy [12] and polarized Raman scattering [17]. Several biaxial order parameters have been determined for both bent-core nematics [17] and tetrapod materials [12].

The first molecular theory of biaxial nematics was proposed by Fraser [18] and Straley [19] and then developed by other authors [20–22]. Straley has also proposed a general quadrupolar model interaction potential for biaxial molecules which is composed of second rank molecular tensors. This potential has been widely used in the recent molecular theories [23–26]. At the same time, little attention has been paid so far to a relationship between the symmetry of
constituent biaxial molecules and the macroscopic symmetry of the biaxial nematic phase. The existing theories are based on the assumption that the biaxial phase is characterized by the $D_{2h}$ point symmetry group, i.e., it possesses three mutually orthogonal mirror planes. The Straley model interaction potential also possesses the same symmetry.

It should be noted, however, that at present there is no direct evidence regarding a particular symmetry of the biaxial phases. It has been proposed recently that a low-symmetry biaxial phase may also exist [27]. In such a phase, characterized by the $C_{2h}$ symmetry, there is only one mirror plane and the $C_2$ symmetry axis perpendicular to it. One may speculate that this phase may, in principle, be exhibited by tetrapodal materials, because in its main conformation the tetrapod molecule also possess the $C_{2h}$ symmetry. In a recent paper we have proposed a more general model potential for low-symmetry biaxial molecules and have estimated the coupling constants numerically using a simple model of a flat tetrapod-like molecule with four mesogenic groups [28]. We have also proposed an additional tensor order parameter which is defined only for nematic phases composed of molecules of the $C_{2h}$ symmetry or lower.

The primary aim of this paper is to show that the low-symmetry biaxial nematic phase must be ferroelectric provided that the constituent molecules are chiral. As discussed in detail below, in the chiral low-symmetry biaxial phase the only mirror plane disappears and the symmetry axis becomes polar. As a result, the spontaneous polarization should appear in the direction of this axis. This is rather similar to the appearance of the spontaneous polarization in the smectic C* phase which has the same point symmetry. In chiral smectics the polarization is induced by the tilt of the director with respect to the smectic layer normal, while in chiral biaxial nematics the corresponding mechanism is different because there are no layers.

The paper is arranged as follows. In section 2 we discuss all tensor order parameters of the low-symmetry biaxial nematic phase and propose the primary scalar order parameter of the transition into this phase. General symmetry reasons for the appearance of the spontaneous polarization in the chiral biaxial phase are considered in section 3. In section 4 we present the Landau–de Gennes theory of the ferroelectric biaxial nematic phase, discuss general mechanisms of ferroelectric ordering in such a phase and obtain simple expressions for the spontaneous polarization. In section 5 we illustrate the appearance of the spontaneous polarization using a simple molecular model. Finally, in section 6 we present our conclusions.

2. Order parameters of the low-symmetry biaxial phase

To describe the orientation of a rigid biaxial molecule one can introduce the unit vectors $\mathbf{a}$ and $\mathbf{b}$ in the direction of the primary (‘long’) and secondary (‘short’) molecular axes, respectively. The third molecular axis is then specified by the unit vector $\mathbf{c}$ which is orthogonal to both $\mathbf{a}$ and $\mathbf{b}$.

In the conventional approach [19], one introduces the molecular tensors $\mathbf{Q} = \mathbf{a} \otimes \mathbf{a} - \mathbf{b} \otimes \mathbf{b} - \mathbf{c} \otimes \mathbf{c}$. Statistical averages of these molecular tensors are used to describe the biaxial nematic ordering by two orientational tensor order parameters

$$Q_{ij} = \langle Q_{n}^{ij} \rangle = S(n_i n_j - \delta_{ij}/3) + \frac{1}{2} P (m_i m_j - \delta_{ij}/3),$$

$$B_{ij} = \langle B_{n}^{ij} \rangle = D(n_i n_j - \delta_{ij}/3) + C (m_i m_j - \delta_{ij}/3),$$

where $\langle \cdot \cdot \cdot \rangle$ denotes the statistical average and the unit vectors $\mathbf{n}$, $\mathbf{m}$ and $\mathbf{h}$ are three directors of the biaxial phase. The scalar order parameters $S$, $P$, $D$ and $C$ are expressed as the averages

$$S = \langle P_2(\cos \gamma) \rangle,$$

$$P = \langle \sin^2 \gamma \cos 2\phi \rangle,$$

$$D = \frac{1}{2} \langle \sin^2 \gamma \cos 2\psi \rangle,$$

$$C = \frac{1}{2} \langle \cos 2\phi \cos 2\psi(1 + \cos^2 \gamma) - 2 \cos \gamma \sin 2\phi \sin 2\psi \rangle,$$

where $\gamma$, $\phi$ and $\psi$ are the corresponding angles. The angle $\gamma$ is the polar angle between the primary axis $\mathbf{a}$ and the primary director $\mathbf{n}$, the angle $\phi$ is the azimuthal angle which specifies the orientation of the projection of the axis $\mathbf{b}$ on the $(\mathbf{m}, \mathbf{h})$ plane, and $\psi$ specifies the angle between the short axis $\mathbf{b}$ and the $(\mathbf{a}, \mathbf{n})$ plane.

It should be noted, however, that equations (1) and (2) are simultaneously valid only in the high-symmetry biaxial nematic phase characterized by the $D_{2h}$ symmetry. Such a phase possesses three mutually orthogonal mirror planes which uniquely specify the orientation of the three directors $\mathbf{n}$, $\mathbf{m}$ and $\mathbf{h}$ which are normal to these planes.

Recently it has been suggested [27, 28] that a low-symmetry biaxial nematic phase may also exist. This lower-symmetry phase is characterized by the $C_{2h}$ symmetry, i.e. it possess only one mirror plane and the two-fold symmetry axis perpendicular to that plane. In this low-symmetry phase the tensors $\mathbf{Q}$ and $\mathbf{B}$ have only one common principal axis (say, $\mathbf{h}$) which is parallel to the $C_{2h}$ symmetry axis. The other two directors $\mathbf{n}$ and $\mathbf{m}$ lie in the mirror plane, but their particular orientation is not specified by any symmetry reasons and thus they may be different for different tensors.

The two tensor order parameters $\mathbf{Q}$ and $\mathbf{B}$, however, are generally insufficient for the description of the low-symmetry biaxial phase. Indeed, let us consider the system with perfect orientational order at low temperatures (the so called ‘ground state’ when all the molecules are oriented identically). In the ground state, all long molecular axes $\mathbf{a}$ are parallel to the director $\mathbf{n}$ and the short axes $\mathbf{b}$ are parallel, say, to the director $\mathbf{m}$. As a result, the tensor order parameter $\mathbf{Q}$ appears to be uniaxial with $P = 0$ and $S = 1$, while the tensor $\mathbf{B}$ has $D = 0$ and $C = 1$, i.e., is biaxial and one of its principal axes is parallel to the director $\mathbf{n}$, which is also the principal axis of $\mathbf{Q}$. As a result, this ground state corresponds to the biaxial phase of the $D_{2h}$ symmetry. It is unlikely that the low-symmetry biaxial phase may still occur at intermediate temperatures, and this example indicates that the lower-symmetry phase should appear in materials composed of molecules of lower symmetry, which are to be characterized by additional ordering tensors.
Indeed, the molecular tensors $Q^M$ and $B^M$ are invariant under independent sign inversions of the molecular axes $a$, $b$, and $c$. Thus they are invariant under all point symmetry transformations of the biaxial molecules of the $D_{2h}$ symmetry. At the same time, for molecules of lower symmetry it is possible to define additional molecular tensors. It has been shown recently [28, 30] that for the molecules of $C_{2h}$ symmetry with the symmetry axis $c$ it is possible to introduce the third independent molecular tensor $a \otimes b$, which is invariant under all symmetry transformations of such a molecule and which is orthogonal to both the invariants $Q^M$ and $B^M$ used in the conventional theories. This additional molecular tensor can be separated into symmetric and antisymmetric microscopic tensors $\Gamma^M = a \otimes b + b \otimes a$ and $\Omega^M = a \otimes b - b \otimes a$, which give rise to the additional symmetric and antisymmetric tensor order parameters $\Gamma_{ij} = \langle a_i b_j + b_j a_i \rangle$ and $\Omega_{ij} = \langle a_i b_j - b_j a_i \rangle$ respectively. The latter can be generally expressed in terms of the macroscopic pseudovector $M_i = \epsilon_{ijk} \Omega_{jk}$, where $\epsilon_{ijk}$ is the absolute antisymmetric $Levy-Civita$ tensor. One can also directly write this pseudovector as the average: $M = (a \times b)$.

Now let us consider the low-symmetry biaxial nematic phase of the $C_{2h}$ symmetry, with the unit vector $h$ in the direction of the symmetry axis of the phase. In this phase the primary nematic tensor $Q$ can also be diagonalized and expressed in the form of equation (1) with $n$, $m$ and $h$ being the principal axes of $Q$.

At the same time in the low-symmetry phase, the additional tensor order parameter $\Gamma$ is generally not diagonal in the same frame and should be expressed as:

$$\Gamma_{ij} = G(n_i n_j - \frac{1}{3} \delta_{ij}) + H(m_i m_j - h_i h_j) + V(n_i m_j + n_j m_i),$$

$$(7)$$

where $G$, $H$ and $V$ are the scalar order parameters expressed as the following statistical averages:

$$G = -\frac{1}{2} \langle \sin 2\gamma \cos \psi \rangle,$$

$$(8)$$

$$H = \frac{1}{2} \langle \sin 2\gamma \cos 2\phi \cos \psi - \sin \gamma \sin 2\phi \sin \psi \rangle,$$

$$(9)$$

$$V = 2 \langle \cos 2\gamma \cos \phi \cos \psi - \cos \gamma \sin \phi \sin \psi \rangle.$$  

$$(10)$$

The non-diagonal form of the tensor $\Gamma$ follows from the fact that in the low-symmetry $C_{2h}$ phase there is only a single symmetry axis $h$, which has to be the main axis of all tensor order parameters. The other two main axes of a tensor should lie in the symmetry plane, but they can be directed arbitrarily and independently for each tensor.

As a simpler argument one can also consider again the limiting case of perfect orientational order. In this case $a$ is parallel to $n$ and $b$ is parallel to $m$, and the tensor $\Gamma_{ij} = n_i m_j + m_i n_j$, $i.e.$, it contains only off-diagonal components. This tensor can be also diagonalized, but its principal axes are rotated by the angle of $\pi/4$ with respect to the main axes of the tensor order parameter $Q$.

For $V = 0$, the tensor order parameter $\Gamma$ takes the form of the tensor $Q$ which corresponds to the high-symmetry biaxial nematic phase. Therefore, the presence of the scalar order parameter $V$ reduces the symmetry of the phase from $D_{2h}$ to $C_{2h}$ and one may consider it as the order parameter of the low-symmetry biaxial phase. One also notes that the parameters $G$ and $H$ vanish in the limit $S \to 1$.

In the low-symmetry biaxial phase the axes of the tensor $B$ may also be rotated with respect to those of the tensor $Q$. However, as discussed above, this rotation vanishes in the limit of perfect orientational order, and thus it is expected to be generally small in the low-temperature biaxial phase. In this paper we will neglect it for simplicity and assume that the principal axes of $B$ coincide with those of $Q$.

Finally the pseudovector order parameter $M$ is also nonzero in the low-symmetry biaxial phase. The symmetry of the phase indicates that $M$ should be parallel to the $C_2$ symmetry axis, i.e. it should be in the direction of the main axis $h$ of the $Q$ tensor:

$$M = M(n \times m)$$

$$(11)$$

where the scalar order parameter $M$ reads

$$M = |\cos \phi \cos \psi - \cos \gamma \sin \phi \sin \psi|.$$  

$$(12)$$

As a result, in this description, the $C_{2h}$ biaxial nematic phase is characterized by eight scalar order parameters, where only the parameters $V$ and $M$ vanish in the high-symmetry $D_{2h}$ phase. Furthermore, the parameters $D$, $G$ and $H$ can be neglected in the first approximation if the temperature interval of the $C_{2h}$ biaxial phase is far from the nematic–isotropic transition and the nematic order parameter $S$ is sufficiently large.

3. Spontaneous polarization in the low-symmetry biaxial phase

Now we are going to show that if the low-symmetry biaxial nematic phase is chiral, it must be ferroelectric, i.e. possessing the spontaneous polarization $P_s$.

Let us consider a simple model of a chiral biaxial molecule composed of a flat rigid core which possesses the $C_{2h}$ symmetry and a transverse permanent dipole $d$ perpendicular to the molecular plane. One notes that the transverse dipole makes the molecule chiral as it violates the otherwise present mirror plane of the molecule. Then the macroscopic polarization in the biaxial nematic phase can be written in the form:

$$P_s = \rho(d) = \rho d(\mathbf{c}) = \rho d\Delta((a \times b)),$$

$$(13)$$

where $\rho$ is the molecular number density and $\Delta = \{a \times b\} \cdot \mathbf{c}$ is the molecular unit pseudoscalar which specifies the handedness of the molecular coordinate system. Here we have taken into account that the unit vector $\mathbf{c}$ can be expressed in terms of the unit vectors $a$ and $b$ as $\mathbf{c} = \Delta(a \times b)$. Note that $\mathbf{c}$ is a conventional polar vector which is expressed as a product of the pseudovector $(a \times b)$ and the pseudoscalar $\Delta$.

Now the spontaneous polarization can be rewritten as:

$$P_s = \rho d\Delta(a \times b) = \rho d\Delta M.$$  

$$(14)$$

Thus the spontaneous polarization $P$ in the chiral low-symmetry biaxial nematic phase appears to be proportional to
the pseudovector order parameter $\mathbf{M}$ and the pseudoscalar $\Delta$ which characterizes molecular chirality.

The existence of the spontaneous polarization in the chiral biaxial phase can also be interpreted using general symmetry arguments. Let us start from the high-symmetry $D_{2h}$ biaxial phase and show that in this phase both $\mathbf{M}$ and $\mathbf{P}$ vanish identically. Firstly one notes that the $D_{2h}$ symmetry group is nonpolar and therefore a nonzero macroscopic polarization $\mathbf{P}$ is inconsistent with the symmetry of the corresponding phase. One notes also that $\mathbf{M}$ is a pseudovector and thus it changes sign under the inversion with respect to a plane parallel to it. The $D_{2h}$ phase possesses three mutually orthogonal mirror planes which define the orthogonal frame, and the pseudovector order parameter $\mathbf{M}$ must be invariant under all symmetry transformations of this phase. On the other hand, any component of $\mathbf{M}$ in this frame must change sign under the inversion with respect to the corresponding plane, and therefore all components of $\mathbf{M}$ must vanish.

In contrast, in the $C_{2h}$ biaxial phase the nonzero order parameter $\mathbf{M}$ may exist in the direction perpendicular to the mirror plane because it is invariant under the reflection with respect to this plane. At the same time the macroscopic polarization must vanish because the $C_{2h}$ symmetry group is nonpolar. Now, in the chiral phase the only mirror plane disappears and the two-fold symmetry axis, which was perpendicular to the plane, becomes polar. Then, according to the Curie principle, macroscopic polarization may appear along the symmetry axis, i.e. in the direction of the order parameter $\mathbf{M}$.

One notes that this symmetry argument is similar to the one originally used by Meyer [29] to justify the existence of the spontaneous polarization in the chiral smectic C* phase. In chiral smectic liquid crystals the polarization is induced by the tilt of the director with respect to the smectic layer normal, while in the chiral biaxial nematics the polarization is induced by the rotation of the primary axes of the tensor order parameter $\Gamma$ with respect to the axes of the primary nematic tensor $\mathbf{Q}$.

4. Free energy expansion in the chiral biaxial nematic phase

Let us develop the phenomenological theory of a phase transition into the low-symmetry biaxial nematic phase. The first possible scenario is a direct transition from the ordinary uniaxial nematic to the low-symmetry biaxial nematic phase. Another possibility includes a more complex phase sequence: with decreasing temperature the LC undergoes a transition from the uniaxial nematic phase to the orthogonal biaxial nematic phase and then into the low-symmetry biaxial phase.

In the uniaxial nematic phase all three scalar order parameters: $S$, $D$, and $G$ are generally nonzero. Accordingly, all three tensor order parameters $\mathbf{Q}$, $\mathbf{B}$ and $\mathbf{\Gamma}$ are present, but all of them are proportional to the same tensor $\mathbf{n} \otimes \mathbf{n} - 1/3$. The orthogonal biaxial nematic phase is characterized by another three order parameters $\mathbf{P}$, $\mathbf{C}$ and $H$, which vanish at the biaxial–uniaxial transition point. In the low-symmetry biaxial nematic phase there exists the additional scalar order parameter $V$, which is the primary order parameter of the transition between the two biaxial nematic phases. Finally, the low-symmetry biaxial phase is characterized by the pseudovector $\mathbf{M}$, which is directly related to the spontaneous polarization $\mathbf{P}$, in the chiral phase according to equation (14).

As discussed in [28], the order parameter $H$ is expected to be small and can be neglected in the first approximation. Then the free energy difference between the uniaxial nematic and the low-symmetry biaxial nematic phases can be expanded in powers of the ordering tensors $\mathbf{V} = \mathbf{V}(\mathbf{n} \otimes \mathbf{m} + \mathbf{m} \otimes \mathbf{n})$, $\mathbf{C} = \mathbf{C}((\mathbf{m} \otimes \mathbf{m} - \mathbf{h} \otimes \mathbf{h})$ and $\mathbf{T} = \mathbf{T}(\mathbf{m} \otimes \mathbf{m} - \mathbf{h} \otimes \mathbf{h})$. In the chiral phase the expansion in powers of the spontaneous polarization $\mathbf{P}$ should also be performed.

As usual in the Landau–de Gennes approach, the coefficients in the expansion of the free energy in powers of the tensorial order parameters are generally tensors which have the symmetry of the high-temperature phase. In our case the high-temperature phase is the uniaxial nematic one, and its symmetry is characterized by the tensor $\mathbf{n} \otimes \mathbf{n}$. Thus the expansion of the free energy difference between the uniaxial and biaxial nematic phases should contain all scalar invariants composed of the ordering tensors $\mathbf{V}$, $\mathbf{T}$, $\mathbf{C}$, polarization vector $\mathbf{P}$, and the nematic tensor $\mathbf{n} \otimes \mathbf{n}$.

It can readily be shown that in a non-chiral nematic phase the invariants, which are odd in $\mathbf{V}$, are not allowed. This has a simple symmetry explanation. Indeed, the free energies of the states with $+\mathbf{V}$ and $-\mathbf{V}$ are the same because the opposite signs of $\mathbf{V}$ correspond to the opposite directions of rotation of the axes of the tensor $\mathbf{\Gamma}$ with respect to those of the tensor $\mathbf{Q}$. Thus the free energy of a non-chiral LC must be even in $\mathbf{V}$.

Then, the general expansion of the free energy of a non-chiral LC near the transition from uniaxial to the low-symmetry biaxial nematic to the fourth order in $\mathbf{V}$, $\mathbf{P}$ and $\mathbf{C}$ can be presented in the form:

$$F_{\text{BN}} - F_{\text{UN}} \approx F_{B0} + A_4 (\mathbf{V} \cdot \mathbf{V}) + A_2 (\mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V})$$

$$+ ((\mathbf{V} \cdot \mathbf{V}) \cdot \mathbf{G}) + \frac{1}{2} B_4 (\mathbf{V} \cdot \mathbf{V})^2 + \frac{1}{2} B_2 (\mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V})^2$$

$$+ \frac{1}{2} B_3 ((\mathbf{V} \cdot \mathbf{V}) \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V}) + \frac{1}{2} B_1 (\mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V} \cdot \mathbf{V}$$,

where

$$\mathbf{G} = \kappa_1 \mathbf{T} + \kappa_2 \mathbf{C} + \kappa_{11} (\mathbf{T} \cdot \mathbf{T}) + \kappa_{22} (\mathbf{C} \cdot \mathbf{C}) + \kappa_{12} (\mathbf{T} \cdot \mathbf{C})$$

(16)

Here $F_{B0}$ is a sum of all invariants which depend only on the order parameters $\mathbf{P}$ and $\mathbf{C}$. We do not present them explicitly because we are focusing on the order parameter $\mathbf{V}$ which induces spontaneous polarization in the chiral biaxial phase.

Substituting the expressions for $\mathbf{V}$, $\mathbf{T}$ and $\mathbf{C}$ one can readily reduce this to the standard form of the free energy expansion near the second order transition:

$$F_{\text{B_2}} \approx F_0 + AV^2 + \frac{1}{2} BV^4$$

(17)

with $A = 2A_4 + A_2 + \kappa_1 P + \kappa_2 C + \kappa_{12} P^2 + \kappa_{22} C^2 + \kappa_{12} PC$ and $B = 4B_4 + 2B_2 + B_1$. This free energy expansion indicates that the transition is generally of the second order unless the coefficient $B$ in the fourth order term turns negative. The transition into the low-symmetry biaxial phase occurs when
A = 0. One notes that the temperature variation of $\Delta$ is mainly determined by the biaxial order parameters $C$ and $P$, but may also be affected by the temperature variation of $S$.

The free energy expansion in the chiral biaxial phase contains also the leading scalar term which describes a linear coupling between $V$ and the spontaneous polarization parallel to the $C_2$ symmetry axis:

$$\mu V P_s \cdot [(n \times V) \cdot n] = \mu V (P_s \cdot [n \times m]),$$  \hspace{1cm} (18)

where $(n \times V)_{ij} = \epsilon_{ijkl} n_k V_{lj}$. In principle, one should also take into consideration the linear coupling terms between $P_s$, $V$ and the ordering tensors $T$ and $C$. The corresponding invariants have the general form $[(\mu_1 P + \mu_2 C)(P_s \cdot [(m \times V) \cdot m])]$ taking into account that $(h \cdot V) = 0$. However, after substitution of the explicit expression for $V$, this term reduces to the general form above, i.e. it simply gives a contribution $\mu_1 P + \mu_2 C$ to the coefficient $\mu$.

One notes that the combination $[(n \times V) \cdot n] = [n \times m]$ is a pseudovector which does not change sign under space inversion. At the same time, the polarization $P_s$ is a polar vector and thus the product $P_s \cdot [(n \times V) \cdot n]$ is a pseudoscalar. On the other hand, the free energy is a scalar and thus the coefficient $\mu$ must also be a pseudoscalar. Such a pseudoscalar material parameter may exist only if at least a part of the LC molecules are chiral, and it vanishes identically in a non-chiral LC.

Adding also the electrostatic energy $1/2 P_s \cdot \chi^{-1} \cdot P_s$, where $\chi$ is the dielectric susceptibility tensor in the uniaxial phase, we arrive at the free energy of the chiral low-symmetry biaxial nematic:

$$F_{ch} \approx F_0 + AV^2 + \frac{1}{2} BV^4 + \mu V P_s + \frac{1}{2} \chi_1 P_s^2,$$  \hspace{1cm} (19)

where $\chi_1$ is the transverse dielectric susceptibility.

Minimizing the free energy with respect to $P_s$ one obtains the explicit expression for the spontaneous polarization:

$$P_s = -\chi_1 V \mu (n \times m).$$  \hspace{1cm} (20)

According to equation (20), ferroelectricity is only possible in the low-symmetry biaxial nematic phase characterized by the ‘off-diagonal’ order parameter $V$ and the molecular chirality which determines the pseudoscalar $\mu$. Thus the chiral low-symmetry biaxial nematic phase should be ferroelectric, i.e. possess spontaneous polarization in the direction of the two-fold symmetry axis of the phase. The absolute value of the polarization is proportional to the order parameter $V$, which vanishes in the high-symmetry biaxial nematic phase. One notes that the phenomenological theory presented here is very similar to that for the chiral smectic C* phase, which has the same $C_2$ point symmetry. In the smectic C* phase, the spontaneous polarization is also parallel to the $C_2$ symmetry axis and is proportional to the tilt angle $\theta$ which vanishes in the high-temperature smectic A* phase.

In section 5 we consider a simple molecular model which enables one to illustrate the appearance of the spontaneous polarization in the low-symmetry biaxial phase on the microscopic level.

## 5. Simple dispersion interaction model

In this section we obtain an approximate expression for the spontaneous polarization of the low-symmetry biaxial phase using the simple model of a rigid chiral biaxial molecule with the main axis of the polarization tensor slightly tilted with respect to the primary molecular axis within the molecular plane and with the transverse molecular dipole perpendicular to that plane. The primary axis of such a molecule is determined by the molecular inertia tensor and aligns along the director. One notes that the biaxiality of such a molecule is mainly determined by the angle between the axis of the polarization tensor and the primary molecular axis. The chirality of the molecule is determined by the transverse permanent dipole, which removes the only mirror plane.

Now let us consider the simple dispersion interaction potential between such molecules:

$$V(1, 2) = -J(r_{12}) P_2 (a_1 \cdot a_2) - J_0 \alpha_{ij}^{(1)} T_{ik} (r_{12}) \alpha_{kl}^{(2)} T_{lj} (r_{12}),$$  \hspace{1cm} (21)

where $T(r) = r^{-3}(1 - 3u \otimes u)$ is the dipole–dipole propagator, and $u$ is the unit vector along the intermolecular vector: $u = r/r$.

The first term in equation (21) is the standard Maier–Saupe model interaction potential, which is also assumed to be uniaxial to reduce the number of model parameters. This part of the interaction potential may be determined by the isotropic dispersion attraction modulated by short-range anisotropic repulsion.

For simplicity, we assume that the molecular polarizability $\alpha_{ij}$ is uniaxial:

$$\alpha_{ij} = \alpha_0 \delta_{ij} + \Delta \alpha (l_i l_j - \delta_{ij}/3),$$  \hspace{1cm} (22)

and only the second traceless anisotropic term contributes to the potential (21). Here $\Delta \alpha$ is the polarizability anisotropy, and $l$ is the principal axis of the molecular polarizability, which is assumed to make an angle $\beta$ with respect to the molecular primary axis $a$:

$$l = a \cos \beta + b \sin \beta.$$  \hspace{1cm} (23)

One notes that the interaction potential (21) possesses the $C_{2h}$ symmetry. Indeed the unit vectors $a$ and $l$ deform the ‘molecular plane’ and the potential is only invariant under reflection with respect to this plane.

One can also introduce the corresponding microscopic tensor $L^M = I \otimes I - 1/3$, which can be presented as a linear combination of the microscopic tensors $Q^M$, $B^M$, and $C^M$ introduced before:

$$L^M = Q^M P_2 (\cos \beta) + \frac{1}{2} B^M \sin^2 \beta + \frac{1}{8} C^M \sin 2\beta.$$  \hspace{1cm} (24)

Accordingly, its average $L = \langle L^M \rangle$ can be expressed as:

$$\langle L_{ij} \rangle = L_1 n_i n_j - \delta_{ij}/3 + L_2 (m_i m_j - h_i h_j) + \frac{V}{2} \sin 2\beta (n_i m_j + n_j m_i),$$  \hspace{1cm} (25)

where the parameters $L_1$ and $L_2$ are expressed as linear combinations of the scalar order parameters $S, D, G, P, C$.
and $H$

$$L_1 = P_2(\cos \beta)S + \frac{1}{2} \sin^2 \beta D + \frac{1}{2} \sin 2\beta G, \quad (26)$$

$$L_2 = \frac{1}{2} P_2(\cos \beta)P + \frac{1}{2} \sin^2 \beta C + \frac{1}{2} \sin 2\beta H. \quad (27)$$

In the mean-field approximation, the one-particle orientational distribution function is given by the following expression:

$$f_i(\mathbf{a}, \mathbf{b}) = \frac{1}{Z} \exp \left[ - \frac{U_{\text{MF}}(\mathbf{a}, \mathbf{b})}{k_B T} \right], \quad (28)$$

where $U_{\text{MF}}(\mathbf{a}, \mathbf{b})$ is the mean-field potential generally defined as:

$$U_{\text{MF}}(\mathbf{a}, \mathbf{b}) = \int f_i(\mathbf{a}', \mathbf{b}') U_{\text{eff}}(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}') \, d\mathbf{a}' \, d\mathbf{b}'. \quad (29)$$

Here $U_{\text{eff}}$ is the effective interaction potential averaged over all intermolecular vectors $\mathbf{r}$:

$$U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{b}_1, \mathbf{b}_2) = \rho \int V(1, 2) \, d\mathbf{r}. \quad (30)$$

Taking into account that

$$\int T_{ij}(\mathbf{r}) \, d^2\mathbf{u}_{12} = 0 \quad (31)$$

and

$$\int T_{ij}(\mathbf{r}) T_{kl}(\mathbf{r}) \, d^2\mathbf{u}_{12} = \frac{4\pi}{15}\rho \left( 4\delta_{ij}\delta_{kl} + 9\delta_{ik}\delta_{jl} + 9\delta_{il}\delta_{jk} \right) \quad (32)$$

one obtains

$$U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{b}_1, \mathbf{b}_2) = -\bar{J} Q_1^M : Q_2^M - \bar{J}_d L_1^M : L_2^M, \quad (33)$$

where

$$\bar{J} = \frac{3\rho}{2} \int_R J(r) r^2 \, dr, \quad \bar{J}_d = \frac{8\pi \rho (\Delta \alpha)^2}{5R^2} J_d, \quad (34)$$

and $R$ is the effective radius of the molecular hard core.

Substituting the effective potential (33) into equation (29) and noticing that the averaging reduces to substituting the molecular tensors of the second molecule by their averages (1) and (25), one obtains the following mean-field potential

$$U_{\text{MF}}(\mathbf{a}, \mathbf{b}) = -\bar{J}[\frac{1}{2} P_2(\cos \beta) P_2(\mathbf{a} \cdot \mathbf{n}) + \frac{1}{2} \sin^2 \beta(\mathbf{b} \cdot \mathbf{n})^2 - (\mathbf{c} \cdot \mathbf{n})^2] + \sin 2\beta(\mathbf{a} \cdot \mathbf{n})(\mathbf{b} \cdot \mathbf{n})$$

$$= \bar{J}_d L_1^M \times \bar{J}_{\text{eff}} L_2^M$$

$$+ \frac{1}{2} \sin^2 \beta[(\mathbf{b} \cdot \mathbf{m})(\mathbf{b} \cdot \mathbf{n}) - (\mathbf{a} \cdot \mathbf{h})(\mathbf{b} \cdot \mathbf{h})]$$

$$= \bar{J}_d L_1^M \times \bar{J}_{\text{eff}} L_2^M$$

Indeed, according to the general equation (14) the polarization can be written in the form

$$P_s = \rho \bar{J}_d \sin^2 \beta V(\mathbf{a} \times \mathbf{b})(\mathbf{b} \cdot \mathbf{m}) \quad (30)$$

where the orientational distribution function $f_1$ is given by (28) with the mean-field potential (35).

One notes that in the uniaxial and high-symmetry biaxial nematic phases the polarization vanishes identically, because in these phases $V = 0$ and the mean-field potential is invariant under the sign inversion of $\mathbf{a}$ or $\mathbf{b}$. At the same time, the product $\mathbf{a} \times \mathbf{b}$ changes sign under such an inversion and, therefore, the average $\langle \mathbf{a} \times \mathbf{b} \rangle = 0$. Thus the polarization may only be nonzero in the low-symmetry biaxial phase. We evaluate the polarization in the vicinity of the transition into the low-symmetry biaxial phase when the order parameter $V$ is nonzero but small. Substituting the mean-field potential (35) into equation (30) and expanding the exponent in powers of $V$ to the first order one obtains

$$P_s \approx \frac{\bar{J}_d \rho \Delta \alpha}{2k_B T} V \sin^2 \beta V(\mathbf{a} \times \mathbf{b})(\mathbf{b} \cdot \mathbf{m})$$

$$= \frac{\bar{J}_d \rho \Delta \alpha}{4k_B T} \sin^2 \beta V(1 + C)(\mathbf{a} \times \mathbf{b})(\mathbf{b} \cdot \mathbf{m}), \quad (31)$$

where we have taken into account that $\delta_{ij} = a_i a_j + b_i b_j + c_i c_j$ and hence in this limit $B_{ij} = 2(b_i b_j) - n_i n_j - \delta_{ij}$ and $(b_i b_j) = 1/2[C(m_i m_j - h_i h_j) + 1 + n_i n_j]$. The order parameter $C$ here is defined at $V = 0$.

This spontaneous polarization, calculated using a molecular model, has exactly the same general form as the equation (20) obtained using the Landau–de Gennes theory. At the same time, the magnitude of the polarization is now approximately expressed in terms of the parameters of the present model.

6. Conclusions

In this paper we have considered the order parameters of both high-and low-symmetry biaxial nematic phases and have shown that the low-symmetry phase must be ferroelectric. The high-symmetry biaxial nematic phase is characterized by the D_{2h} symmetry and possesses three mutually orthogonal mirror planes. This phase is described by the two conventional tensor order parameters $Q$ and $B$ which are widely used in the existing
theory. One notes that the primary axes of these tensors are parallel (see equations (1) and (2)) as determined by the orthogonal symmetry of the phase.

It has been shown recently [28, 30] that biaxial molecules of the C_{2h} point symmetry group with the symmetry axis e are characterized by the additional molecular invariant a_i b_j, where the unit vectors a and b are in the direction of the long and short molecular axis, respectively. The statistical average of the symmetric part gives rise to the additional tensor order parameter \( \Gamma_{ij} = (a_i b_j + b_i a_j) \), while the average of the antisymmetric part yields the pseudovector order parameter \( \mathbf{M} = (a \times b) \). In the high-symmetry biaxial phase \( \mathbf{M} = 0 \), while the tensor \( \Gamma \) has the same mathematical form as \( \mathbf{Q} \) and \( \mathbf{B} \). As a result, the high-symmetry phase is characterized by six scalar order parameters \( S, P, D, C, G \) and \( H \), although the parameters \( G \) and \( H \) are considered to be less important [28].

The low-symmetry biaxial phase, which is characterized by the \( C_{2v} \) symmetry, possesses only one mirror plane and the \( C_2 \) symmetry axis perpendicular to it. As shown in section 2, in this phase the primary axes of the tensor order parameter \( \Gamma \) are no longer parallel to those of the nematic tensor \( \mathbf{Q} \). It follows from the symmetry that the two tensors still have one common primary axis \( \mathbf{h} \) which is parallel to the symmetry axis of the phase. The other two axes of the tensor \( \Gamma \) deviate from the axes of \( \mathbf{Q} \) (i.e. from the directors \( \mathbf{n} \) and \( \mathbf{m} \)) within the mirror plane. This deviation is specified by the new scalar order parameter \( V \), which is the primary order parameter of the transition from the high-symmetry to the low-symmetry biaxial phase. Landau–de Gennes theory presented in this paper indicates that this transition is generally of the second order.

One notes that at present there is no direct evidence of the actual symmetry of biaxial nematic phases exhibited by different materials. However, it is reasonable to assume that the low-symmetry biaxial phase is more likely to be found in liquid crystals composed of molecules of the \( C_{2h} \) symmetry similar to tetrapods [12, 13, 16].

As discussed in detail in section 3, the chiral low-symmetry biaxial nematic phase must be ferroelectric for general symmetry reasons. Indeed, in the chiral phase the mirror plane disappears and the \( C_2 \) symmetry axis becomes polar. Thus one expects that according to the Curie principle the spontaneous polarization must appear in the chiral biaxial nematic phase in the direction of the symmetry axis. This is similar to the ferroelectric smectic C* phase in which the spontaneous polarization is also parallel to the polar \( C_2 \) axis normal to the tilt plane. At the same time, the mechanism of ferroelectric ordering in the biaxial nematic phase is different.

In the chiral smectic C* phase, the polarization is induced by the tilt of the director with respect to the smectic layer normal which defines the reference frame in the high-temperature smectic A phase. In contrast, in chiral nematics the high-temperature phase is the uniaxial nematic one, and the polarization in the low-symmetry biaxial nematic phase is induced by the rotation of the axes of the tensor order parameter \( \Gamma \) with respect to the primary nematic director \( \mathbf{n} \). In both cases the ferroelectricity can be called pseudo-proper, i.e. polarization is not the primary order parameter but is induced by another order parameter with which it is linearly coupled. From the microscopic point of view this means that the ferroelectric ordering is not directly determined by dipolar interactions.

It has been shown in section 3 that in a system of planar molecules, which also possess transverse dipoles, the spontaneous polarization is rigorously proportional to the pseudovector order parameter \( \mathbf{M} \) with a pseudoscalar coefficient which specifies molecular chirality. One notes that the pseudovector \( \mathbf{M} \) is nonpolar itself, and exists also in the non-chiral low-symmetry biaxial phase, as it is invariant under symmetry transformations of the \( C_{2h} \) group. At the same time the polarization is nonzero only if the molecules are chiral.

A general expression for the spontaneous polarization in the chiral biaxial phase is obtained in section 4. The polarization is parallel to the \( C_2 \) axis and its magnitude is proportional to the order parameter \( V \). The microscopic mechanism of the ferroelectric ordering in chiral biaxial nematics has also been illustrated using a simple molecular model based on dispersion interaction between biaxial molecules. The \( C_{2h} \) symmetry of the molecules is determined by the relative tilt of the maximum polarizability axis from the long molecular axis \( \mathbf{a} \). An explicit expression for the polarization has been obtained in the case of large \( S \) and small \( V \).

We believe that the ferroelectric biaxial nematic phase deserves further investigation because in such a phase the secondary director can be easily switched by an external electric field due to the linear coupling between the spontaneous polarization and the field. Thus, such materials are very promising from the application point of view, and an effort should be made to synthesize chiral molecules of the corresponding structure which may form biaxial nematic phases.