Molecular models for the smectic A–smectic C phase transition in a system of biaxial molecules

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Abstract

A molecular theory of the smectic A–smectic C transition in a system of biaxial molecules is developed in the mean-field approximation. The influence of molecular biaxiality on the transition is considered in detail and it is demonstrated how the biaxial order parameters are induced by the tilt. It is shown that the ordering of biaxial molecules of low symmetry in the smectic C phase is generally described by ten independent orientational order parameters, and there exist three different tilt angles which specify the tilt of three ordering tensors. The order parameters are calculated numerically as functions of temperature for two models of biaxial molecules: molecules with two principal axes and molecules with a pair of off-center transverse dipoles. A substantial difference between the three tilt angles is found, which makes impossible a strict definition of a unique director in the smectic C phase. It is also shown that biaxial interactions may lead to an anomalously weak layer contraction in the smectic C phase. Finally, it is demonstrated that the smectic A–smectic C phase transition may be directly driven by biaxial intermolecular interactions. In this case, the tilt of long molecular axes is not a primary order parameter, and its temperature dependence is very different from convention.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Smectic liquid crystals are characterized by both orientational and partial translational order, and exhibit many different phases (see e.g. [1]). The simplest orthogonal smectic phase is the smectic A (SmA) phase where the preferred orientation of the molecular long axes, specified by the director **n**, is perpendicular to the fluid-like smectic layers. The corresponding tilted

phase is the smectic C (SmC) phase where the director is inclined by an angle Θ with respect to the layer normal. Tilted smectic phases attract significant attention because of the application of ferro- and antiferroelectric smectics C* in the new generation of fast electro-optic displays, and because of the rich variety of different phases with unusual 3D structure [2]. Tilting transitions, similar to the SmA–SmC one, are also observed in other soft-matter systems including smectic elastomers [3, 4], lyotropic lamellar phases and Langmuir–Blodgett films [5].

In spite of its apparent simplicity, the nature of the tilt in the SmC phase has been the issue of debate during the past two decades. The simplest picture of the transition corresponds to the collective tilt of nearly parallel molecules with respect to the layer normal. Such a simple tilt, however, can be considered only in the limit of perfect orientational order. More than two decades ago this oversimplified picture was criticized by Goossens [6, 7] who noted that in this case there is no entropy change at the SmA–SmC transition and thus the transition resembles a structural change. At the same time, the simple collective tilt of molecules can be considered as a limiting case of a more realistic SmA–SmC transition which may occur in the system of uniaxial molecules with partial orientational disorder.

It has been shown by several authors that there exist a number of common intermolecular interactions which promote tilt in a smectic phase, including the induction interaction between the molecular dipole and the polarizability of a neighboring molecule [8] and the electrostatic interaction between longitudinal molecular quadrupoles [9]. In the case of partial disorder the transition occurs at a particular temperature T_c [10]. Recently a detailed study of the SmA–SmC phase transition in a system of uniaxial molecules has been undertaken by the present authors using a complete set of orientational order parameters [11]. It has been shown that the 'uniaxial model' can be used to describe smectics C with both low and high tilt, and even to reproduce a constant or very weakly temperature dependent layer spacing in the SmC phase [11, 12].

On the other hand, real mesogenic molecules are essentially biaxial, and the biaxiality is expected to play a significant role in the SmC phase. Recently some of the biaxial order parameters of the SmC phase have been measured experimentally for a number of smectic materials [13–15], and it has been found that the biaxial parameters may reach the values of 0.2–0.3. Thus there exists a significant ordering of short molecular axes in the SmC phase, and therefore the molecular biaxiality should be taken into account in the corresponding molecular theory. Moreover, it has long been known that at least in principle the SmA–SmC phase transition may be caused by biaxial molecular interactions. In fact, the first molecular model for the SmC phase proposed by Wulf [16] was based on a model interaction potential between biaxial molecules of 'zig-zag' shape. Later Goossens defined a biaxial order parameter which is linearly coupled to the tilt and showed using a particular model, that the tilt may be caused by the biaxial ordering . It has also been shown that the SmC phase may be stabilized by steric interactions between oblique cylinders [17] and between flexible zig-zag molecules in the two-dimensional system [18].

The existing molecular theory of the biaxial SmC phase is incomplete as it is based on few particular models and does not employ the complete set of orientational order parameters. The known models enable one to determine the SmA–SmC transition temperature, but the biaxial order parameters have not been calculated before.

In this paper, we show that the number of orientational order parameters of the SmC phase depends on the molecular symmetry. We derive the explicit expressions for six order parameters in the case of biaxial molecules of the D_{2h} symmetry (simplest biaxial molecules) and ten order parameters for the molecules having the more realistic C_{2h} symmetry. Within two particular model biaxial interactions, coupling of two molecular principal axes and dipolar

interaction, we calculate numerically all biaxial order parameters and study in detail the effect of biaxiality on the SmA–SmC transition.

The paper is arranged as follows. In section 2 we present the analysis of all order parameters allowed by the symmetry of the molecules. Section 3 describes the effects of weak biaxiality on the tilting transition in the case when molecular biaxiality is determined by the presence of the second principal molecular axis inclined with respect to the main one. Next, in section 4 we study this also in the system of molecules with uniaxial cores and a pair of transverse dipoles and pay special attention to the pronounced reduction of smectic layer contraction due to biaxiality. In section 5 the so-called primary-biaxial SmA–SmC transition promoted by the ordering of short molecular axes is investigated. Finally, the summary and general conclusions are presented in section 6.

2. Order parameters of the biaxial smectic C phase

2.1. Smectic C phase composed of uniaxial molecules

It is well known that orientation of a uniaxial molecule in a nonpolar phase can be sufficiently characterized by the symmetric second rank tensor $Q_{ij}^M = a_i a_j - (1/3)\delta_{ij}$ with $\mathbf{a}$ being the unit vector of molecular axis. The corresponding tensor order parameter $Q_{ij} = \langle a_i a_j - (1/3)\delta_{ij}\rangle$ is the ensemble average of the microscopic tensor $\mathbf{Q}^M$. In the biaxial SmC phase, the tensor order parameter can be expressed in the following general form:

$$Q_{ij} = S\left(n_i n_j - \tfrac{1}{3}\delta_{ij}\right) + \tfrac{1}{2}P(m_i m_j - h_i h_j), \tag{1}$$

where S is the nematic order parameter and P is the biaxial order parameter which characterizes the biaxial ordering of long molecular axes. Here the mutually orthogonal unit vectors $\mathbf{n}$, $\mathbf{m}$ and $\mathbf{h}$ are the primary axes of the tensor order parameter $\mathbf{Q}$. The unit vector $\mathbf{n}$ is called the director, and in the SmC phase it is tilted from the smectic layer normal by the tilt angle Θ_Q. The unit vector $\mathbf{h}$ is parallel to the C_2 axis of the SmC phase which is normal to the tilt plane, and the third primary axis $\mathbf{m}$ lies within the tilt plane.

In equation (1) the tensor order parameter is expressed in the diagonal frame. On the other hand, the tensor $\mathbf{Q}$ can also be expressed in the non-diagonal frame based on the unit vectors $\mathbf{k}$, $\mathbf{h}$ and $\mathbf{t}$, where $\mathbf{k}$ is the smectic layer normal and $\mathbf{t}\perp\mathbf{k}$ specifies the direction of the tilt:

$$Q_{ij} = S_k\left(k_i k_j - \tfrac{1}{3}\delta_{ij}\right) + \tfrac{1}{2}P_k(t_i t_j - h_i h_j) + \tfrac{1}{2}V_Q(k_i t_j + t_i k_j). \tag{2}$$

Introducing the polar angle γ and azimuthal angle φ of the long molecular axis so that

$$\mathbf{a} = \mathbf{k}\cos\gamma + \mathbf{t}\sin\gamma\cos\varphi + \mathbf{h}\sin\gamma\sin\varphi, \tag{3}$$

we can present the uniaxial order parameter as $S_k = \langle P_2(\cos\gamma)\rangle$ and see that it describes the nematic ordering with respect to the layer normal $\mathbf{k}$. Similarly, the biaxial order parameter $P_k = \langle \sin^2\gamma\cos 2\varphi\rangle$ describes the biaxial ordering of long molecular axes in the layer plane, and $V_Q = \langle \sin 2\gamma\cos\varphi\rangle$ is the tilt order parameter, which is nonzero only in a tilted smectic phase.

The advantage of using the order parameters S_k, P_k and V_Q instead of the traditional parameters S, P and the tilt angle Θ_Q is determined by the fact that the parameters S_k, P_k, V_Q are all explicitly expressed as statistical averages of the corresponding microscopic quantities. In particular, in contrast to the tilt angle Θ_Q, which can be determined only after evaluation and diagonalization of the whole tensor $\mathbf{Q}$, the tilt order parameter V_Q can be evaluated directly using some experimental techniques, computer simulations or an analytical theory without knowing the orientation of the director.

Diagonalization of the tensor (2) enables one to establish the exact relationships between the order parameters S, P, Θ_Q and S_k, P_k, V_Q [12]:

$$\tan 2\Theta_Q = \frac{V_Q}{S_k - 0.5P_k}, \tag{4}$$

$$S = \frac{1}{4}S_k + \frac{3}{8}P_k + \frac{3V_Q}{4\sin 2\Theta_Q}, \tag{5}$$

$$P = \frac{1}{2}S_k + \frac{3}{4}P_k - \frac{V_Q}{2\sin 2\Theta_Q}. \tag{6}$$

Finally, one notes that V_Q is the scalar tilt order parameter. Both the absolute value and the direction of the tilt are specified by the pseudovector tilt order parameter

$$\mathbf{W}_Q = (\mathbf{k} \times \mathbf{Q} \cdot \mathbf{k}) = \tfrac{1}{2}V_Q(\mathbf{k} \times \mathbf{t}), \tag{7}$$

which is normal to the tilt plane.

2.2. Smectic C phase composed of simple biaxial molecules

Consider now molecules with lower symmetry, which orientation is described by three mutually orthogonal molecular axes $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. Introducing the third Euler angle of the molecule ψ, as that between the axis $\mathbf{b}$ and the direction of the tilt of the axis $\mathbf{a}$, one can write

$$\mathbf{b} = -\mathbf{k}\sin\gamma\cos\psi + \mathbf{t}(\cos\gamma\cos\varphi\cos\psi - \sin\varphi\sin\psi)$$
$$+ \mathbf{h}(\cos\gamma\sin\varphi\cos\psi + \cos\varphi\sin\psi), \tag{8}$$

and

$$\mathbf{c} = \mathbf{k}\sin\gamma\sin\psi - \mathbf{t}(\cos\gamma\cos\varphi\sin\psi + \sin\varphi\cos\psi)$$
$$+ \mathbf{h}(\cos\varphi\cos\psi - \cos\gamma\sin\varphi\sin\psi). \tag{9}$$

The simplest biaxial molecule is characterized by the D_{2h} symmetry, i.e., possesses three mutually orthogonal mirror planes and three C_2 symmetry axes (see figure 1(a)), and is, therefore, invariant under the transformations $\mathbf{a} \to -\mathbf{a}$, $\mathbf{b} \to -\mathbf{b}$ and $\mathbf{c} \to -\mathbf{c}$.

It is well known since the work of Straley [19] that such a biaxial molecule is characterized by two orthogonal second rank molecular tensors: the uniaxial tensor $a_\alpha a_\beta - (1/3)\delta_{\alpha\beta}$ and the symmetric biaxial tensor $b_\alpha b_\beta - c_\alpha c_\beta$. As a result, the SmC phase composed of biaxial molecules of the D_{2h} symmetry is characterized by two independent tensor order parameters $Q_{ij} = \langle a_i a_j - (1/3)\delta_{ij}\rangle$ and $B_{ij} = \langle b_i b_j - c_i c_j\rangle$. The uniaxial tensor order parameter $\mathbf{Q}$ is given by equations (1) and (2) of the previous subsection. In its own diagonal frame, the biaxial tensor order parameter $\mathbf{B}$ can be expressed in the form similar to equation (1):

$$B_{ij} = D\left(n_{1i}n_{1j} - \tfrac{1}{3}\delta_{ij}\right) + C(m_{1i}m_{1j} - h_i h_j), \tag{10}$$

where the order parameter $D = 3/2\langle(\mathbf{b}\cdot\mathbf{n}_1)^2 - (\mathbf{c}\cdot\mathbf{n}_1)^2\rangle$ describes the tendency of short molecular axes to order differently along the director $\mathbf{n}_1$ and the biaxial order parameter $C = 1/2\langle(\mathbf{b}\cdot\mathbf{m}_1)^2 - (\mathbf{c}\cdot\mathbf{m}_1)^2 - (\mathbf{b}\cdot\mathbf{h})^2 + (\mathbf{c}\cdot\mathbf{h})^2\rangle$ describes the nonpolar ordering of short molecular axes.

In equation (10) the 'director' $\mathbf{n}_1$ is defined as the primary axis of the macroscopic tensor $\mathbf{B}$ while the unit vector $\mathbf{m}_1$ is orthogonal to it. One notes that $\mathbf{n}_1$ has generally a different orientation in the tilt plane compared with the 'uniaxial' director $\mathbf{n}$ defined as the primary axis of the tensor $\mathbf{Q}$. Thus, in the SmC phase composed of biaxial molecules of D_{2h} symmetry it is possible to define two different tilt angles Θ_Q and Θ_B. Here Θ_Q is the angle between the 'uniaxial' $\mathbf{a}$-related director $\mathbf{n}$ and the layer normal $\mathbf{k}$, i.e. $\cos\Theta_Q = (\mathbf{n}\cdot\mathbf{k})$. At the same time,

Θ_B is the angle between the 'second' director $\mathbf{n}_1$ and $\mathbf{k}$, i.e. $\cos \Theta_B = (\mathbf{n}_1 \cdot \mathbf{k})$. The difference between the two tilt angles may be quite significant in some systems as shown later.

From the general symmetry point of view, the existence of two different 'directors' is related to the fact that in the SmC phase the orientation of the director in the tilt plane is not specified by any symmetry. It has been shown experimentally, for example, that the optical tilt angle noticeably depends on the wavelength of light [20]. Indeed, for any macroscopic second rank tensor in the smectic phase, the orientation of only one primary axis is fixed by the symmetry of the phase because one of the primary axis must be parallel to the C_2 symmetry axis of the phase which is normal to the tilt plane. The two remaining primary axes lie in the tilt plane, and their orientation may be different for different macroscopic tensors.

The biaxial tensor order parameter $\mathbf{B}$ can also be expressed in the nondiagonal $\mathbf{k}$, $\mathbf{t}$, $\mathbf{h}$-frame similar to equation (2):

$$B_{ij} = D_k \left(k_i k_j - \tfrac{1}{3} \delta_{ij} \right) + C_k (t_i t_j - h_i h_j) + \tfrac{1}{2} V_B (k_i t_j + t_i k_j), \tag{11}$$

where the explicit expressions for the order parameters are

$$D_k = \tfrac{3}{2} \langle \sin^2 \gamma \cos 2\psi \rangle, \tag{12}$$

$$C_k = \langle \cos 2\varphi \cos 2\psi (1 + \cos^2 \gamma)/2 - \cos \gamma \sin 2\varphi \sin 2\psi \rangle, \tag{13}$$

$$V_B = \langle 2 \sin \gamma \sin \varphi \sin 2\psi - \sin 2\gamma \cos \varphi \cos 2\psi \rangle, \tag{14}$$

and where V_B is the biaxial scalar tilt order parameter. The corresponding pseudovector tilt order parameter is expressed similar to equation (7):

$$\mathbf{W}_B = (\mathbf{k} \times \mathbf{B} \cdot \mathbf{k}) = \tfrac{1}{2} V_B (\mathbf{k} \times \mathbf{t}). \tag{15}$$

Similar to the previous case, the order parameters D, C, Θ_B can be expressed in terms of the order parameters D_k, C_k and V_B by diagonalizing the tensor B:

$$\tan 2\Theta_B = \frac{V_B}{D_k - C_k}, \tag{16}$$

$$D = \frac{1}{4} D_k + \frac{3}{4} C_k + \frac{3 V_B}{4 \sin 2\Theta_B}, \tag{17}$$

$$C = \frac{1}{4} D_k + \frac{3}{4} C_k - \frac{V_B}{4 \sin 2\Theta_B}. \tag{18}$$

It should be noted that the definition of the orientational biaxial order parameters given by equations (2) and (11) is the most natural and convenient one for a SmC phase composed of biaxial molecules. Indeed, the order parameters S_k, P_k, V_Q, D_k, C_k and V_B are explicitly expressed as statistical averages anchored to the smectic layer normal $\mathbf{k}$ which is usually well known in experiments. Thus these order parameters can, in principle, be measured using a number of experimental techniques including the infrared spectroscopy [13, 14, 15, 21]. In contrast, the order parameters S, P, D and C are defined in the director frame, and can be evaluated only if the director orientation is known. Moreover, the biaxial order parameters D and C are defined with respect to the 'biaxial' director $\mathbf{n}_1$ which is generally different from the director $\mathbf{n}$. Simultaneous experimental determination of the two different directors in the SmC phase is hardly possible at present because most macroscopic tensors, like the dielectric tensor, contain both uniaxial and the biaxial parts.
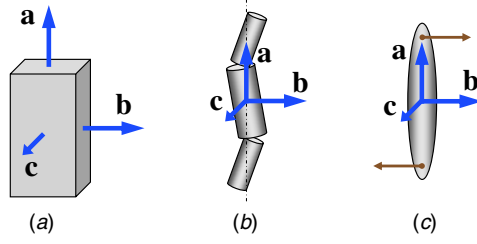
Figure 1. Simple models for biaxial molecules of different symmetry ($D_{2h}(a)$ and C_{2h} (b), (c)) and the corresponding molecular long and short axes.

2.3. Smectic C phase composed of biaxial molecules of low symmetry

One notes that the symmetry of real mesogenic molecules is lower than the D_{2h} group. Neglecting the weak effects of molecular chirality, we may assume that a molecule possesses a mirror plane, which is its only natural element of symmetry. In the nonchiral SmC phase there is no polar ordering of molecular axes, and thus the molecular orientations, which correspond to opposite directions of both long and short molecular axes, must have the same probability. Taking into consideration that a nonchiral molecule may be polar only in the mirror plane, the averaging over polar orientations results in a new effective symmetry element—the C_2 symmetry axis perpendicular to the molecular plane. As a result the molecule effectively acquires the C_{2h} symmetry.

Two examples of such molecules are pictured in figures 1(b) and (c). The one shown in figure 1(b) is quite often referred as being effectively 'zig-zag' shaped. The same symmetry corresponds also to a rod-like molecule with a transverse dipole. After accounting for no polar ordering of long axes, i.e., averaging over two equivalent opposite orientations of the axis **a**, the effective molecule acquires two antiparallel transverse dipoles (see figure 1(c)).

The molecules of the C_{2h} symmetry are characterized by the additional molecular tensor $a_i b_j$ which is invariant under all symmetry transformations of the molecule if the short axis **b** is parallel to the molecular plane. Naturally, the tensor can be expressed as a sum of the symmetric and antisymmetric parts: $a_i b_j = (1/2)(a_i b_j + b_i a_j) + (1/2)(a_i b_j - b_i a_j)$.

The average symmetric tensor $\Gamma_{ij} = \langle a_i b_j + b_i a_j \rangle$ can be written in its own diagonal frame $\mathbf{n}_2, \mathbf{m}_2, \mathbf{h}$,

$$\Gamma_{ij} = G(n_{2i} n_{2j} - \delta_{ij}/3) + H(m_{2i} m_{2j} - h_i h_j), \tag{19}$$

as well as in the nondiagonal **k**-frame:

$$\Gamma_{ij} = G_k(k_i k_j - \delta_{ij}/3) + H_k(t_i t_j - h_i h_j) + \tfrac{1}{2}V_\Gamma(k_i t_j + t_i k_j), \tag{20}$$

where the scalar order parameters entering the latter form are given by the explicit expressions:

$$G_k = -\tfrac{3}{2}\langle \sin 2\gamma \cos \psi \rangle, \tag{21}$$

$$H_k = \tfrac{1}{2}\langle \sin 2\gamma \cos 2\varphi \cos \psi - 2 \sin \gamma \sin 2\varphi \sin \psi \rangle, \tag{22}$$

$$V_\Gamma = 2\langle \cos 2\gamma \cos \varphi \cos \psi - \cos \gamma \sin \varphi \sin \psi \rangle, \tag{23}$$

and where V_Γ is the new biaxial scalar tilt order parameter. Similarly to equations (16)–(18) for the tensor **B**, one can use these parameters in the **k**-frame to calculate the parameters G and H in the diagonal frame of the tensor Γ as well as the tilt angle between those two frames Θ_Γ.

The corresponding pseudovector tilt order parameter is expressed as

$$\mathbf{W}_\Gamma = (\mathbf{k} \times \mathbf{B} \cdot \mathbf{k}) = \tfrac{1}{2} V_\Gamma (\mathbf{k} \times \mathbf{t}). \tag{24}$$

The average antisymmetric tensor $\langle a_i b_j - b_i a_j \rangle$ can be expressed in terms of a pseudovector $\boldsymbol{\Omega}$, i.e., $\langle a_i b_j - b_i a_j \rangle = \epsilon_{ijk} \Omega_k$ where ϵ_{ijk} is the antisymmetric Levi-Civita tensor, and where the pseudovector order parameter $\boldsymbol{\Omega}$ equals

$$\boldsymbol{\Omega} = \Omega (\mathbf{k} \times \mathbf{t}), \tag{25}$$

with the scalar order parameter

$$\Omega = \langle \cos \varphi \cos \psi - \cos \gamma \sin \varphi \sin \psi \rangle. \tag{26}$$

Thus the SmC phase composed of nonchiral biaxial molecules of low symmetry is characterized by ten independent order parameters. All of them are calculated numerically for particular models in the following. One notes, however, that not all of these parameters are important for the SmA–SmC transition. In particular, the order parameters S_k, D_k and G_k (or S, D, G) are nonzero already in the nematic phase and do not change much across the SmA–SmC transition. Here S_k is the nematic order parameter and the parameters D_k and G_k describe different types of uniaxial ordering of short molecular axes along the smectic layer normal. It has been shown before [12] that the type of the SmA–SmC transition strongly depends on the value of S at the transition point. In contrast, the parameters D_k and G_k are generally small and play only minor roles.

The biaxial order parameters P_k, C_k and H_k specify the biaxiality of the smectic phase. The parameters are nonzero in the rare nontilted biaxial SmA phase, where one of them is a primary order parameter which drives the transition from the uniaxial to the biaxial phase. In contrast, in the SmC phase P_k, C_k and H_k are the secondary order parameters induced by the tilt. The parameter P_k specifies the biaxial ordering of long molecular axes, and is generally rather small. One notes that the corresponding order parameter P, defined in the director frame, is close to zero both theoretically [12] and experimentally [15]. The parameters C_k and H_k specify the biaxial ordering of short molecular axes and can reach relatively large values in the SmC phase. These parameters are important for the correct description of the tilting transition.

The order parameters V_Q, V_B and V_Γ are the tilt order parameters which are nonzero only in a tilted smectic phase. One of them is the primary order parameter of the SmA–SmC phase transition depending on the corresponding molecular mechanism. In the previous papers [11, 12] we have considered the model of the tilting transition driven by uniaxial intermolecular interactions, i.e. by the tendency of long molecular axes to tilt. In this case, V_Q is the primary tilt order parameter and, as we demonstrate below, the other two parameters V_B and V_Γ play minor roles. In section 5 we consider a different mechanism of the SmA–SmC transition determined by biaxial interactions between molecules of C_{2h} symmetry or lower. The primary tilt order parameter of such a transition is V_Γ. One notes, however, that in realistic cases the order parameter V_B, which specifies the tendency of short molecular axes to tilt, is never a primary order parameter and is much smaller than V_Q or V_Γ.

Finally, the pseudovector order parameter $\boldsymbol{\Omega}$ has exactly the same symmetry as the tilt order parameters $\mathbf{W}_Q$, $\mathbf{W}_B$ and $\mathbf{W}_\Gamma$, and is also parallel to the C_2 axes of the SmC layer. Thus $\boldsymbol{\Omega} \| \mathbf{W}_a \| \mathbf{W}_B \| \mathbf{W}_\Gamma$. It is important to note that the order parameter $\boldsymbol{\Omega}$ is not the tilt order parameter because it is nonzero in the hypothetical biaxial *nontilted* SmA phase schematically presented in figure 2. This biaxial phase, however, is unstable with respect to the tilt because of the linear coupling between $\boldsymbol{\Omega}$ and the tilt order parameters $\mathbf{W}_a$, $\mathbf{W}_B$ and $\mathbf{W}_\Gamma$ which have the same symmetry. In other words, some tilt is always induced by any nonzero $\boldsymbol{\Omega}$. As shown in [28], the order parameter $\boldsymbol{\Omega}$ is directly related to the ferroelectricity of the chiral SmC* phase.
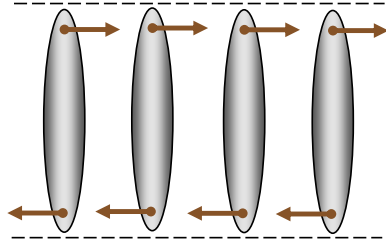
Figure 2. Unconventional biaxial SmA phase with nonzero biaxial order parameter Ω.

3. Influence of molecular biaxiality on the smectic A–smectic C phase transition

Statistical mean-field theory of the SmA–SmC phase transition in smectics consisting of uniaxial molecules has been developed recently by the authors [11, 12]. Below we generalize the approach taking into account the molecular biaxiality and the ordering of short molecular axes. In the approximation of perfect smectic ordering, the free energy of a smectic phase can be written in the form [12]:

$$F/V = \frac{1}{2}\rho^2 \int f_1(\mathbf{a}_1, \mathbf{b}_1) U(1, 2) f_1(\mathbf{a}_2, \mathbf{b}_2)\, \mathrm{d}^2\mathbf{R}\, \mathrm{d}\mathbf{a}_1\, \mathrm{d}\mathbf{b}_1\, \mathrm{d}\mathbf{a}_2\, \mathrm{d}\mathbf{b}_2$$

$$+ \rho k_B T \int f_1(\mathbf{a}_1, \mathbf{b}_1) \ln f_1(\mathbf{a}_1, \mathbf{b}_1)\, \mathrm{d}\mathbf{a}_1\, \mathrm{d}\mathbf{b}_1, \tag{27}$$

where ρ is the number density of molecules per unit area of the smectic layer, $\mathbf{R}$ is the intermolecular vector in the smectic plane, $U(1, 2)$ is effective pair interaction potential and $f_1(\mathbf{a}, \mathbf{b})$ is the orientational distribution function which describes the statistics of the molecular unit vectors $\mathbf{a}$ and $\mathbf{b}$.

Minimizing the free energy (27) one obtains

$$f_1(\mathbf{a}, \mathbf{b}) = \frac{1}{Z} \exp\left[-\frac{U_{MF}(\mathbf{a}, \mathbf{b})}{k_B T}\right], \tag{28}$$

where Z is the normalization constant

$$Z = \int \exp\left[-\frac{U_{MF}(\mathbf{a}, \mathbf{b})}{k_B T}\right] \mathrm{d}\mathbf{a}\, \mathrm{d}\mathbf{b}, \tag{29}$$

and U_{MF} is the mean-field potential expressed as

$$U_{MF}(\mathbf{a}, \mathbf{b}) = \rho \int f_1(\mathbf{a}_2, \mathbf{b}_2) U(1, 2)\, \mathrm{d}^2\mathbf{R}\, \mathrm{d}\mathbf{a}_2\, \mathrm{d}\mathbf{b}_2. \tag{30}$$

The total effective interaction potential of a pair of biaxial molecules can be presented as a sum of an effective interaction potential between uniaxial molecular cores, which depends only on the orientation of the long axis $\mathbf{a}_1, \mathbf{a}_2$, and the biaxial interaction potential which depends also on the orientation of short molecular axes $\mathbf{b}_1, \mathbf{b}_2$:

$$U(1, 2) = U^{\mathrm{aa}}(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2) + U^{\mathrm{ab}}(\mathbf{a}_1, \mathbf{b}_1, \mathbf{R}, \mathbf{a}_2, \mathbf{b}_2). \tag{31}$$

In recent papers we have developed the molecular theory of the SmA–SmC phase transition determined by uniaxial intermolecular interactions [11, 12]. As discussed in detail in [12], the essential form of the corresponding uniaxial interaction potential $U^{\mathrm{aa}}(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2)$ is given by the four terms containing the lowest powers of $\mathbf{a}_1$ and $\mathbf{a}_2$:

$$U^{\mathrm{aa}}(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2) \approx v_1(R)[(\mathbf{a}_1 \cdot \mathbf{u})^2 + (\mathbf{a}_2 \cdot \mathbf{u})^2] + v_2(R)(\mathbf{a}_1 \cdot \mathbf{a}_2)^2$$

$$+ v_3(R)(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{u})(\mathbf{a}_2 \cdot \mathbf{u}) + v_4(R)(\mathbf{a}_1 \cdot \mathbf{u})^2(\mathbf{a}_2 \cdot \mathbf{u})^2, \tag{32}$$
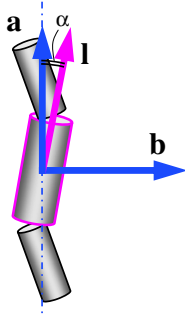
Figure 3. A model of a biaxial molecule with two pronounced 'principal' molecular axes **a** and **l**.

where the unit vector $\mathbf{u} = \mathbf{R}/R$. This form of the potential corresponds to the first few terms of a systematic expansion of an arbitrary uniaxial potential in spherical harmonics. The coupling constants v_{1-4} can be calculated numerically for particular model interactions including, for example, the Gay–Berne interaction of ellipsoidal cores, electrostatic interaction of longitudinal dipoles and induced dipole–dipole interaction [12].

Substituting equation (32) into equation (30) one obtains the following expression for the uniaxial mean-field potential [11, 12]:

$$U_{\mathrm{MF}}^{\mathrm{aa}}(\mathbf{a}) = w_1 P_2(\cos\gamma) + w_2 S_k P_2(\cos\gamma) + w_3 P_k \sin^2\gamma \cos 2\varphi + w_4 V_Q \sin 2\gamma \cos\varphi, \qquad (33)$$

which depends on the order parameters S_k, P_k and V_Q. The transition into the SmC phase occurs when the nematic order parameter exceeds the critical value

$$S_{AC} = \frac{3w_1}{4w_4 - 3w_2}, \qquad (34)$$

which means that the growth of the nematic order is the driving force of the tilting transition in this model based on the uniaxial potential.

The general structure of the biaxial part of the interaction potential is much more complicated because the biaxial potential depends on five different vectors. Even the low order terms in the expansion in spherical harmonics contain far too many coefficients. In this paper we show that the main features of the tilting transition, determined by biaxial interactions, can be described using simple but physically meaningful models which lead to reasonable expressions for the biaxial interaction potential.

The first model of the biaxial molecule, which will be used here, is obtained if one takes into account that biaxial molecules of the C_{2h} symmetry or lower often have at least two 'principal' axes which make some angle different from 90°. For example, in the case of 'zig-zag' molecules (see figure 3) the long molecular axes **a** may be associated with the overall molecular shape, while the main polarizability axis **l**, which is approximately parallel to the polarizable rigid core, is tilted from **a**:

$$\mathbf{l} = \mathbf{a}\cos\alpha + \mathbf{b}\sin\alpha. \qquad (35)$$

For biaxial molecules with two primary axes, one can introduce the molecular tensor $l_i l_j - \delta_{ij}/3$. The average of this tensor in the SmA and SmC phases can be written exactly in the same form as equations (2), (11) and (20):

$$L_{ij} = L_1(k_i k_j - \delta_{ij}/3) + L_2(t_i t_j - h_i h_j) + \tfrac{1}{2} V_l(k_i t_j + t_i k_j). \qquad (36)$$

Taking into account (35), the tensor **L** can be presented as a linear combination of the tensors **Q**, **B** and Γ:

$$\mathbf{L} = \mathbf{Q}P_2(\cos\alpha) + \tfrac{1}{2}\mathbf{B}\sin^2\alpha + \tfrac{1}{2}\Gamma\sin 2\alpha. \tag{37}$$

Accordingly, the order parameters L_1, L_2 and V_L can be expressed in terms of the independent order parameters discussed in section 2 :

$$L_1 = P_2(\cos\alpha)S_k + \tfrac{1}{2}\sin^2\alpha D_k + \tfrac{1}{2}\sin 2\alpha G_k, \tag{38}$$

$$L_2 = \tfrac{1}{2}P_2(\cos\alpha)P_k + \tfrac{1}{2}\sin^2\alpha C_k + \tfrac{1}{2}\sin 2\alpha H_k, \tag{39}$$

$$V_L = P_2(\cos\alpha)V_Q + \tfrac{1}{2}\sin^2\alpha V_B + \tfrac{1}{2}\sin 2\alpha V_\Gamma. \tag{40}$$

Now let us assume that the biaxial part of the interaction between such molecules can be expressed as a coupling between the molecular axes $\mathbf{l}_1$ and $\mathbf{l}_2$. If these axes are parallel to the molecular rigid cores, the corresponding coupling between $\mathbf{l}_1$ and $\mathbf{l}_2$ describes a dispersion interaction between the cores.

The general form of the biaxial potential which contains lowest order terms in $\mathbf{l}_1$ and $\mathbf{l}_2$ can be written similarly to (32):

$$U^{ab}(\mathbf{l}_1, \mathbf{R}, \mathbf{l}_2) = v_1^{(l)}(R)\left[(\mathbf{l}_1 \cdot \mathbf{u})^2 + (\mathbf{l}_2 \cdot \mathbf{u})^2\right] + v_2^{(l)}(R)(\mathbf{l}_1 \cdot \mathbf{l}_2)^2$$
$$+ v_3^{(l)}(R)(\mathbf{l}_1 \cdot \mathbf{l}_2)(\mathbf{l}_1 \cdot \mathbf{u})(\mathbf{l}_2 \cdot \mathbf{u}) + v_4^{(l)}(R)(\mathbf{l}_1 \cdot \mathbf{u})^2(\mathbf{l}_2 \cdot \mathbf{u})^2, \tag{41}$$

where all possible terms quadratic in $\mathbf{l}_{1,2}$ have been taken into account.

The mathematical similarity with the uniaxial interaction potential enables one to obtain directly the corresponding expression for the biaxial contribution to the mean field potential

$$U_{\text{MF}}^{ab}(\mathbf{l}) = w_1^{(l)}P_2(\cos\gamma_l) + w_2^{(l)}L_1 P_2(\cos\gamma_l)$$
$$+ w_3^{(l)}2L_2\sin^2\gamma_l\cos 2\varphi_l + w_4^{(l)}V_L\sin 2\gamma_l\cos\varphi_l, \tag{42}$$

where the polar angle γ_l and the azimuthal angle φ_l specify vector $\mathbf{l}$, and the parameters $w_\alpha^{(l)}$ are the following linear combinations of the coefficients $\bar{v}_\alpha^{(l)} = \rho \int d\mathbf{R}\, v_\alpha^{(l)}(R)$:

$$w_1^{(l)} = -\bar{v}_1^{(l)}/3 - \left(\bar{v}_3^{(l)} + \bar{v}_4^{(l)}\right)/9, \tag{43}$$

$$w_2^{(l)} = 2\bar{v}_2^{(l)}/3 + \left(\bar{v}_3^{(l)} + \bar{v}_4^{(l)}\right)/9, \tag{44}$$

$$w_3^{(l)} = \bar{v}_2^{(l)}/2 + \bar{v}_3^{(l)}/4 + \bar{v}_4^{(l)}/8, \tag{45}$$

$$w_4^{(l)} = \bar{v}_2^{(l)}/2 + \bar{v}_3^{(l)}/8. \tag{46}$$

Now the total mean-field potential of the system is the sum of the uniaxial contribution given by (33) and the biaxial contribution (42). Substituting (33) and (42) into equation (27), one obtains the following expression for the free energy of the SmC phase composed of biaxial molecules.

$$F/V = \tfrac{1}{2}\rho\left\{w_2 S_k^2 + w_3 P_k^2 + w_4 V_Q^2 + w_2^{(l)}L_1^2 + 4w_3^{(l)}L_2^2 + w_4^{(l)}V_L^2\right\} - \rho k_B T \ln Z, \tag{47}$$

where Z is given by equation (29).

The orientational order parameters of the SmC phase can now be calculated numerically by minimization of the free energy.

It is reasonable to assume that the biaxial intermolecular interaction energy is significantly weaker than the uniaxial one. Then the tilting transition remains determined by the uniaxial interactions, while the biaxial interactions are responsible for the biaxiality of the SmC phase, and may lead to a shift of the transition temperature and affect other parameters. To simplify
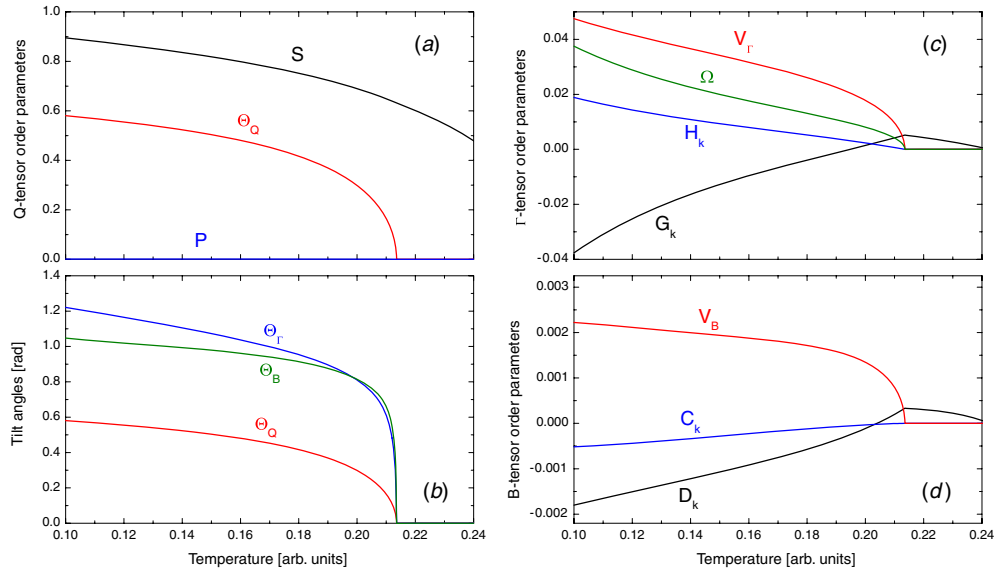
Figure 4. SmA–SmC phase transition modeled using the parameters $w_1 = -0.05$, $w_2 = -1$, $w_3 = -0.85$, $w_4 = -0.8$, $\bar{v}_2^{(l)} = -0.05$, $\bar{v}_3^{(l)} = -0.05$ and $\alpha = 30°$: (a) components of the **Q** tensor in its main axes and its tilt angle; (b) tilt angles of all four ordering tensors considered in this paper; (c) and (d) components of the biaxial tensor order parameters Γ and **B** respectively.

the analysis we present the results calculated for $v_1^{(l)} = v_4^{(l)} = 0$ and small nonzero $v_2^{(l)}$ and $v_3^{(l)}$. Typical temperature variation of all order parameters of the SmC phase with weak biaxial interactions is shown in figure 4.

One can readily see that the order parameters C_k, D_k and V_B, which specify the tensor order parameter **B**, are much smaller than the parameters G_k, H_k and V_Γ which determine the orientation of the tensor Γ. Thus, in this model, the purely biaxial tensor **B** existing for all biaxial molecules is much less important than the tensor order parameter Γ, which can be introduced only for biaxial molecules of sufficiently low symmetry. Remarkably, the tilt angle Θ_Q, which is the primary one here, is almost twice smaller than Θ_B and Θ_Γ of the induced biaxial tensor order parameters. One also notes that the tilt-induced biaxial order parameters C_k and D_k vary approximately linearly with decreasing temperature in the SmC phase in-line with the prediction of the phenomenological theory [22].

4. Dipolar model of the biaxial smectic C phase

Molecular biaxiality can be determined by different factors including shape, polarizability and charge distribution. Let us now consider a simple model where the biaxiality is determined by transverse dipoles. The corresponding molecule is schematically presented in figure 5 and is composed of a uniaxial core and a pair of off-center dipoles with large transverse components lying in orthogonal planes. One notes that this structure is chiral, and the model captures some key features of novel chiral dopants synthesized and investigated recently by Lemieux *et al* [23–26]. Introducing the orthogonal transverse unit vectors $\mathbf{e}^\pm$ one can express the two molecular dipoles as

$$\boldsymbol{\mu}^\pm = \mu(\mathbf{e}^\pm \sin \delta \pm \mathbf{a} \cos \delta). \tag{48}$$
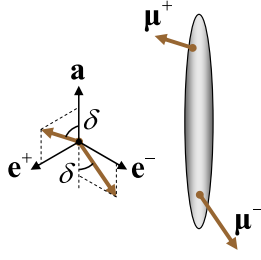
Figure 5. Model of a biaxial molecular with two transverse dipoles, and the molecular axes.

The total dipole moment of the molecule in figure 5 is purely transverse $\boldsymbol{\mu}_\perp = (\boldsymbol{\mu}^+ + \boldsymbol{\mu}^-)$ and is in the direction of the unit vector $\mathbf{c} = (\mathbf{e}^+ + \mathbf{e}^-)/\sqrt{2}$. Another short molecular axis is now defined as $\mathbf{b} = (\mathbf{e}^+ - \mathbf{e}^-)/\sqrt{2}$.

An interaction potential for a pair of such molecules is expressed as a sum of effective interaction potentials between rigid uniaxial cores and the sum of all electrostatic dipole–dipole interactions:

$$U(1, 2) = U^{\mathrm{aa}}(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2) + U^{\mu\mu}(1, 2), \tag{49}$$

where U_μ also depends on the orientation of short molecular axes:

$$U^{\mu\mu}(1, 2) = \boldsymbol{\mu}_1^+ \cdot \mathbf{D}_{\uparrow\uparrow} \cdot \boldsymbol{\mu}_2^+ + \boldsymbol{\mu}_1^- \cdot \mathbf{D}_{\downarrow\downarrow} \cdot \boldsymbol{\mu}_2^- + \boldsymbol{\mu}_1^+ \cdot \mathbf{D}_{\uparrow\downarrow} \cdot \boldsymbol{\mu}_2^- + \boldsymbol{\mu}_1^- \cdot \mathbf{D}_{\downarrow\uparrow} \cdot \boldsymbol{\mu}_2^+, \tag{50}$$

and where all the tensors $\mathbf{D}$ involved can be expressed in the following mathematical form

$$D_{ij}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{R}) = \frac{1}{r^5}(r^2 \delta_{ij} - 3 r_i r_j). \tag{51}$$

Here the distance between the interacting dipoles $\mathbf{r}$ is a function of molecular orientation and the intermolecular distance: $\mathbf{r} = \mathbf{r}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{R})$. In the expression for the tensor $\mathbf{D}_{\uparrow\uparrow}$ the distance $\mathbf{r} = \mathbf{R} + \nu\mathbf{a}_2 - \nu\mathbf{a}_1$ is the distance between upper dipoles, while in the expression for $\mathbf{D}_{\downarrow\downarrow}$ it is the distance between lower dipoles, and thus is expressed as $\mathbf{r} = \mathbf{R} - \nu\mathbf{a}_2 + \nu\mathbf{a}_1$. In the expression for the tensors $\mathbf{D}_{\uparrow\downarrow}$ and $\mathbf{D}_{\downarrow\uparrow}$ the distance between the dipoles equals $\mathbf{r} = \mathbf{R} + \nu\mathbf{a}_2 + \nu\mathbf{a}_1$ and $\mathbf{r} = \mathbf{R} - \nu\mathbf{a}_2 - \nu\mathbf{a}_1$, respectively.

Similarly to the previous model, we again assume that the tilting of the director in the SmC phase is determined by the uniaxial core–core interaction potential U^{aa} given by equation (32). The ordering of short molecular axes is then determined by relatively weak biaxial interaction (50). One notes, however, that the actual form of this interaction potential is too complicated to be used directly in the statistical theory. In particular, substituting the actual potential (50) into equation (30) one cannot obtain the mean-field potential as an explicit function of the orientational order parameters. Substantial simplification can be achieved if the actual dipole–dipole potential is expanded in spherical invariants neglecting the higher order terms. The statistical averages of higher order terms are expressed in terms of higher order orientational order parameters, which are normally not very important from the qualitative point of view [27] and are neglected in this paper.

As shown in [28], the actual interaction potential between the pairs of off-center dipoles can be approximated by the relatively simple expression:

$$U_{\mathrm{MF}}^{\mu\mu} = w_5[\cot \delta V_{\mathrm{Q}}(\mathbf{a} \cdot \mathbf{k})(\mathbf{b} \cdot \mathbf{t}) + \cot \delta \sin 2\gamma \cos \varphi (V_\Gamma + \Omega)/2 + (\mathbf{a} \cdot \mathbf{k})(\mathbf{b} \cdot \mathbf{t})(V_\Gamma + \Omega)/\sqrt{2}], \tag{52}$$

containing the biaxial order parameters in the combination $(V_\Gamma + \Omega)/2 = \langle (\mathbf{a} \cdot \mathbf{k})(\mathbf{b} \cdot \mathbf{t}) \rangle$.
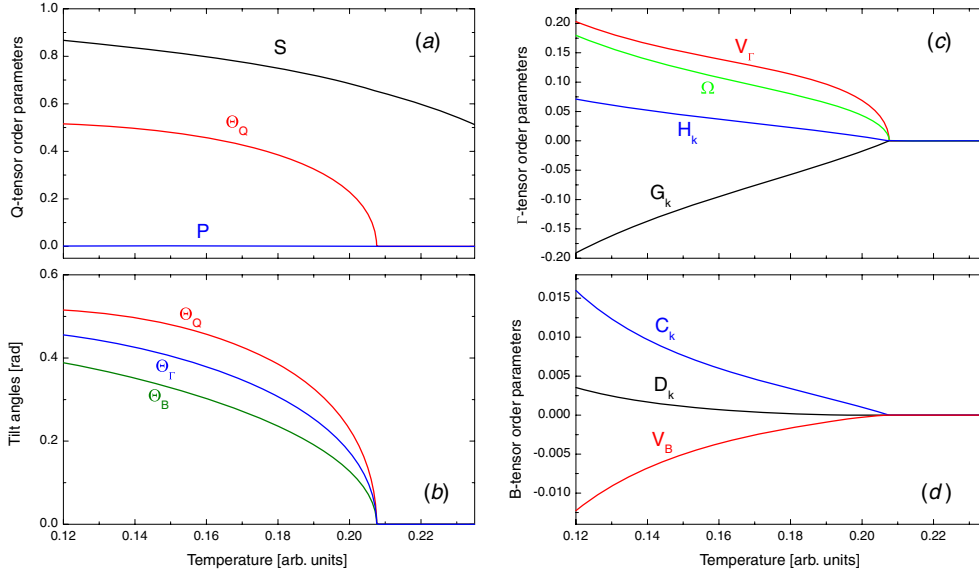
Figure 6. SmA–SmC phase transition obtained using the parameters $w_1 = -0.05$, $w_2 = -1$, $w_3 = -0.9$, $w_4 = -0.8$, $w_5 = -0.1$ and $\delta = 60^{\circ}$: (*a*) components of the **Q** tensor in its main axes and its tilt angle; (*b*) tilt angles of the **Q**, **B** and Γ tensor order parameters; (*c*) and (*d*) components of the biaxial tensor order parameters Γ and **B** respectively.

The total mean-field potential (30) is a sum of the uniaxial contribution (33) and the dipolar term (52). Then the free energy of the smectic phases (27) can be expressed as

$$F/V = \frac{1}{2}\rho\left\{w_2 S_k^2 + w_3 P_k^2 + w_4 V_Q^2 + w_5[\cot\delta\, V_Q(V_\Gamma + \Omega) + 2^{-3/2}(V_\Gamma + \Omega)^2]\right\}$$
$$- \rho k_B T \ln Z. \tag{53}$$

Now the orientational order parameters can be evaluated by numerical minimization of the free energy at a given temperature, and all the order parameters can be calculated according to their definitions as averages given in section 2 and the general expression for the orientational distribution function (28). Typical results of these calculations are presented in figure 6.

As seen from figure 6(*b*), the tilt angles, Θ_Q, Θ_B and Θ_Γ, are here also substantially different. In contrast to the case of biaxial molecules with two principal axes (see figure 4(*b*)), here the tilting of the main axis **a** is larger than those of the biaxial tensors Γ and **B**. Thus it is generally impossible to define a unique director in the SmC phase composed of biaxial molecules. One also notes that the order parameters specifying the tensor order parameter Γ, reach the values of the order of 0.1–0.2 at lower temperatures. At the same time, the typical values of the biaxial order parameters C_k, D_k and V_B are much smaller, i.e. the conventional biaxial tensor **B** is here also less significant.

4.1. Biaxial ordering and the de Vries type behavior

It is interesting to note that the biaxial interactions have a significant effect on the temperature variation of the smectic layer thickness. In particular, the interactions between transverse dipoles, considered above, may considerably suppresses the contraction of smectic layers in the SmC phase as shown in figure 7. This is an additional mechanism which leads to an anomalously weak layer contraction, and it is different from that considered in [11, 12].
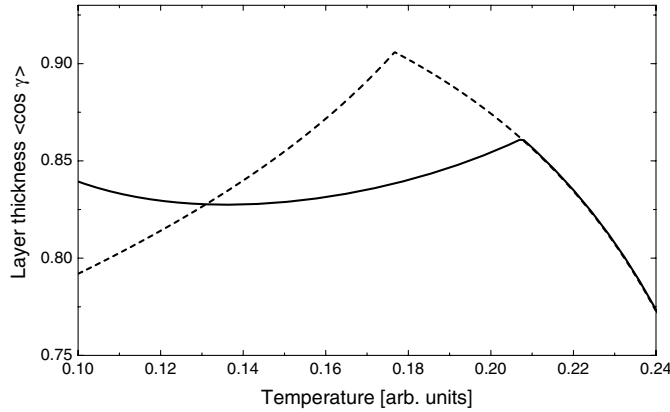
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Figure 7. Variation of the relative smectic layer thickness $\langle \cos \gamma \rangle$ near SmA–SmC phase transition obtained using the parameters $w_1 = -0.05$, $w_2 = -1$, $w_3 = -0.9$, $w_4 = -0.8$, with dipolar biaxial interaction $w_5 = -0.1$, $\delta = 60^\circ$ (solid) and without it (dashed).

5. Smectic A–smectic C phase transition determined by biaxial interactions

So far we have considered the case when the tilt in the SmC* phase is determined by the uniaxial interaction between molecular cores, i.e. by the effective uniaxial potential (32). On the other hand, the tilting transition may also be determined by sufficiently strong biaxial intermolecular interactions. From the thermodynamical point of view, this means that the free energy of the SmA phase may first lose its stability not with respect to the tilt angle, but with respect to the corresponding biaxial order parameter which then appears to be the primary order parameter of the SmA–SmC transition. This corresponds to a different scenario of the transition when the tilt is not a primary order parameter, but is induced by the biaxial ordering due to a linear coupling between biaxial order parameters and the uniaxial tilt. Such coupling is, for example, described by the term with $(\Omega + V_\Gamma)V_Q$ in the free energy equation (52).

The difference between the two scenarios of the SmA–SmC transition can be clarified using the simple Landau expansion of the free energy of the SmC phase in terms of a tilt angle Θ_Q and the biaxial order parameter V_Γ:

$$\Delta F(\Theta_Q, V_\Gamma) = A_1(T)\Theta_Q^2 + A_2(T)V_\Gamma^2 + \Lambda \Theta_Q V_\Gamma + \cdots. \tag{54}$$

Here the linear coupling term between the tilt angle Θ_Q and the biaxial tilt order parameter V_Γ stems from the linear coupling between the pseudovector order parameters $\mathbf{W}_Q$ and $\mathbf{W}_\Gamma$ which is allowed by symmetry (see also the potential (52) and the discussion at the end of section 2).

If the uniaxial intermolecular interactions are responsible for the tilt, the coefficient $A_1(T)$ in the Θ_Q^2 term changes sign first with decreasing temperature, and thus the tilt is a primary order parameter in this case. The biaxial order parameter V_Γ is then induced by the tilt in the SmC phase. However, if the biaxial interactions are sufficiently strong, the coefficient $A_2(T)$ in the V_Γ^2 term may change sign first, and then the biaxial parameter V_Γ appears to be the primary order parameter while the tilt angle Θ_Q appears to be the secondary order parameter induced by the biaxial ordering. We have also studied the latter scenario of the SmA–SmC phase transition in the framework of the present theory by using the uniaxial potential (32) which does not stabilize the tilted phase. The coefficients w_i in the uniaxial potential have been calculated using the expansion of the standard Gay–
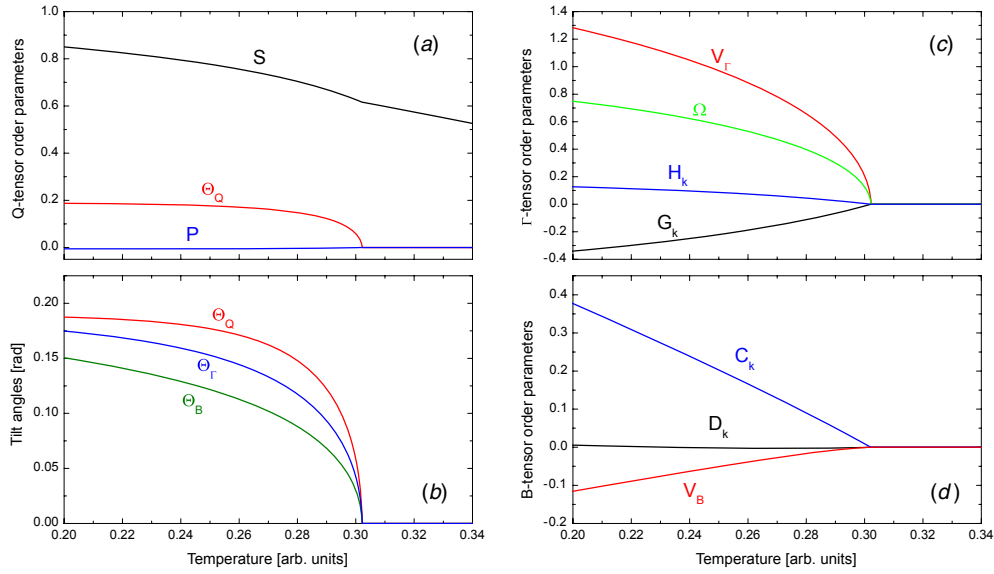
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Figure 8. SmA–SmC phase transition induced by the biaxial ordering. The angle $\delta = 60^{\circ}$, and the uniaxial interaction constants are obtained from the Gay–Berne potential (see [12]), $w_1 = -0.31, w_2 = -1, w_3 = -0.62, w_4 = -0.68$. Strong biaxial interaction is determined by the coupling constant $w_5 = -0.5$. (a) Components of the **Q** tensor order parameter in its own primary axes and the corresponding tilt angle; (b) tilt angles of the **Q**, **B** and **Γ** tensor order parameters; (c) and (d): components of the biaxial tensor order parameters **Γ** and **B** respectively.

Berne interaction potential which is known to promote no tilt (see [12]). Strong biaxial intermolecular interactions have been modeled by taking the large negative coupling constant $w_5 = -0.5$ which is of the same order as the coefficients in the uniaxial part of the total interaction potential.

Temperature variations of the order parameters for this type of the SmA–SmC transition are presented in figure 8. One can readily see that the temperature variation of the biaxial tilt order parameter V_Γ is typical of a classical primary order parameter, and is dramatically different from the variation presented in figures 4 and 6. In this case, the biaxial tilt order parameter V_Γ is also much larger than in the previous two cases when it has been induced by the tilt (see figures 4(c) and 6(c)). At the same time, the tilt angles are relatively small and, again, all different. The tilt angle of long molecular axes Θ_Q rapidly saturates with decreasing temperature, which is completely different from the two previous cases.

6. Conclusions

In this paper we have developed mean-field molecular model for the SmA–SmC phase transition in a liquid crystal material composed of biaxial molecules. The orientational order of biaxial molecules in the SmC phase is described by three tensor order parameters **Q**, **B** and **Γ**, which are discussed in detail in section 2. Here **Q** is the conventional uniaxial tensor order parameter which is widely used in the theory of nematic liquid crystals. The tensor **B** is the biaxial order parameter which specifies the nonpolar orientation of short molecular axes, and has originally been introduced by Straley [19] in the theory of biaxial nematics. Finally, the third tensor order parameter **Γ** can only be defined for biaxial molecules of the C_{2h} symmetry or lower. This ordering tensor has not been considered before neither in the theory of biaxial

nematics nor in the theory of smectics C. The tensor Γ specifies the simultaneous ordering of long and short molecular axes, and is expressed as the average of the novel molecular tensor $a_i b_j$ which is invariant with respect to all symmetry operations of the molecular C_{2h} symmetry group. As shown in section 2, all ordering tensors of the SmC phase contain ten independent scalar order parameters, which all have been calculated numerically as functions of temperature for two particular models.

It is important to note that in the general case one cannot define the unique tilt angle (or the unique director) in the SmC phase. This is because the three tensor order parameters, discussed above, are characterized by different tilt angles Θ_Q, Θ_B and Θ_Γ, respectively. The difference between these tilt angles may be very large as illustrated by both models of biaxial molecules used above. As a result, the 'directors' determined by various experimental techniques will differ from each other. This conclusion can be supported by the following example.

Most often, the director of the SmC liquid crystal is determined experimentally as the primary optical axis of the SmC material. In general, refractive indices of the SmC phase are complicated functions of the molecular polarizability, but for our illustrative purposes it is sufficient to take into account that the average dielectric tensor is approximately proportional to the average molecular polarizability tensor $\langle \alpha_{ij} \rangle$. For molecules of the C_{2h} symmetry, the molecular polarizability tensor α_{ij} can be presented as a linear combination of the three independent molecular tensors $(a_i a_j - \delta_{ij}/3)$, $(b_i b_j - c_i c_j)$ and $a_i b_j$:

$$\alpha_{ij} = \alpha_1(a_i a_j - \delta_{ij}/3) + \alpha_2(b_i b_j - c_i c_j) + \alpha_3 a_i b_j + \alpha_0 \delta_{ij} \tag{55}$$

where the coefficients $\alpha_0, \alpha_1, \alpha_2$ and α_3 have the meanings of the average molecular polarizability, polarizability anisotropy, biaxial part of the polarizability and the off-diagonal part of the polarizability, respectively. Accordingly, the average polarizability tensor can be expressed in terms of the three tensor order parameters of the SmC phase and the unit tensor **I**:

$$\langle \boldsymbol{\alpha} \rangle = \alpha_1 \mathbf{Q} + \alpha_2 \mathbf{B} + \alpha_3 \Gamma + \alpha_0 \mathbf{I}. \tag{56}$$

As discussed above, the tensors **Q**, **B** and Γ are generally diagonal in different frames. Only one principal axis, which is parallel to the C_2 symmetry axis of the SmC phase, is the same for all of them. Then the primary axis of the average polarizability tensor (56) will also differ from the primary axes of the three tensor order parameters, and its particular orientation will depend on the coefficients $\alpha_k, k = 1, 2, 3$. Thus one concludes that the 'director' determined by another experimental technique based on another macroscopic tensor (characterized by different coefficients analogous to α_k) will be different from the primary optical axis. Moreover, the orientation of optical axis itself is known to be frequency dependent [20] due to the frequency dispersion of the coefficients α_k. The situation becomes even more complicated if higher order tensors, like those describing the Raman scattering, are involved.

As a result, the values of the order parameters of the SmC phase calculated in the 'director frame', will be different for different techniques. This problem can be avoided by using the complete set of order parameters defined in the **k**-frame, as discussed in detail in section 2. The frame based on the layer normal **k** is unique, and thus the corresponding order parameters will also have unique values. Even the value of the conventional nematic order parameter S is to a certain extent not unique in the SmC phase as it can be evaluated with respect to different directors. In contrast, the order parameter S_k which specifies the ordering of long molecular axes along the smectic layer normal **k** does not depend on the definition of the director, and can be measured using different techniques.

Biaxial intermolecular interactions may also have a significant effect on the variation of the layer spacing with temperature in the SmC phase. It has been shown before [11, 12] that both conventional and anomalously weak layer contraction can be explained using only

uniaxial intermolecular interaction potential. In the present paper it has been suggested that relatively strong biaxial interaction may also be responsible for the low layer contraction.

We have also considered the role of biaxial interactions on the properties of SmA and SmC phases. It has been demonstrated that strong biaxial interactions may induce the SmA–SmC phase transition even when the uniaxial interactions promote no tilt. In this case, the system loses its stability with respect to the corresponding biaxial tilt order parameter, which appears then to be the primary order parameter of the phase transition, while the tilt of the long molecular axes is induced by the biaxial ordering. Such a phase transition is characterized by low values of the tilt angle, which saturates rapidly with decreasing temperature.

Finally, one notes that the biaxial pseudovector order parameter $\mathbf{\Omega}$, discussed in section 2, is directly proportional to the spontaneous polarization of the chiral SmC* phase [28]. According to [28], the spontaneous polarization can be expressed as $\mathbf{P}_s = \rho \Delta_\mu \mathbf{\Omega}$, where ρ is the molecular number density and Δ_μ is a pseudoscalar molecular parameter, which vanishes if the molecules are nonchiral and which depends on the orientation of dipoles in the molecular frame. Thus the temperature variation of the order parameter Ω corresponds to that of the spontaneous polarization in the chiral SmC*. In particular, the temperature dependences of Ω calculated in sections 4 and 5 using the model of dipolar biaxial molecules directly represent that of the polarization. The detailed theory of ferroelectric ordering in the SmC* phase is considered in [28] and [29].

Acknowledgments

References

[1] Goodby J W, Huang C C and Coates D 1998 *Handbook of Liquid Crystals* 2nd edn vol 2A ed D Demus, J Goodby, G W Gray, H-W Spies and V Vill (Weinheim: Wiley-VCH) (chapter 5)
[2] Lagerwall J P F and Giesselmann F 2006 *Chem. Phys. Chem.* **7** 20
[3] Stenull O and Lubensky T C 2005 *Phys. Rev. Lett.* **94** 018304
[4] Lehmann W, Skupin H, Tolksdorf C, Gebhard E, Zentel R, Krüger P, Lösche M and Kremer F 2001 *Nature* **410** 447
[5] Kaganer V M, Möwald H and Dutta P 1999 *Rev. Mod. Phys.* **71** 779
[6] Goossens W J A 1985 *J. de Phys. (Paris)* **46** 1411
[7] Goosens W J A 1987 *Mol. Cryst. Liq. Cryst.* **150B** 419
[8] van der Meer B W and Vertogen G 1979 *J. Phys. (Paris) Colloq.* **40** C3
[9] Poniwierski A and Sluckin T J 1991 *Mol. Phys.* **73** 199
[10] Govind A S and Madhusudana N V 2001 *Eur. Phys. Lett.* **55** 505
[11] Gorkunov M V, Giesselmann F, Lagerwall J P F, Sluckin T J and Osipov M A 2007 *Phys. Rev. E* **75** 060701
[12] Gorkunov M V, Osipov M A, Lagerwall J P F and Giesselmann F 2007 *Phys. Rev. E* **76** 051706
[13] Hayashi N, Kocot V, Linehan M J, Fukuda A, Vij J K, Heppke G, Naciri J, Kawada S and Kondoh S 2006 *Phys. Rev. E* **74** 051706
[14] Merkel K, Kocot A, Vij J K, Mehl G H and Meyer T 2004 *J. Chem. Phys.* **121** 5012
[15] Ossowska-Chrusciel M D, Korlacki R, Kocot A, Wrzalik R, Chrusciel J and Zalewski S 2004 *Phys. Rev. E* **70** 041705
[16] Wulf A 1975 *Phys. Rev. A* **11** 365
[17] Somoza A M and Tarazona P 1988 *Phys. Rev. Lett.* **61** 2566
[18] Photinos D J and Samulski E T 1995 *Science* **270** 783
[19] Straley J P 1974 *Phys. Rev. A* **10** 1881
[20] Giesselmann F, Langhof A and Zugenmaier P 1997 *Liq. Cryst.* **23** 927
[21] Korlacki R, Fukuda A and Vij J K 2007 *Europhys. Lett.* **77** 36004
[22] Osipov M A and Pikin S A 1995 *J. de Phys. II* **5** 1223

[23] Vizitiu D, Lazar C, Halden B J and Lemieux R P 1999 *J. Am. Chem. Soc.* **121** 8229
[24] Vizitiu D, Lazar C, Radke J P, Hartley C S, Glaser M A and Lemieux R P 2001 *Chem. Mater.* **13** 1692
[25] Lazar C, Yang K, Glaser M A, Wand M D and Lemieux R P 2002 *J. Mater. Chem.* **12** 586
[26] Boulton C J, Finden J G, Yuh E, Sutherland J J, Wand M D, Wu G and Lemieux R P 2005 *J. Am. Chem. Soc.* **127** 13656
[27] Osipov M A 1998 *Handbook of Liquid Crystals* 2nd edn vol 1 ed D Demus, J Goodby, G W Gray, H-W Spies and V Vill (Weinheim: Wiley-VCH)
[28] Osipov M A and Gorkunov M V 2008 *Phys. Rev.* E **77** 075106 (*Preprint* arXiv:0711.1607v1)
[29] Osipov M A, Gorkunov M V, Gleeson H and Jaradat S 2008 *Eur. Phys. J.* E at press