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Viscosity coefficients of smectics C*

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By extending the statistical theory of rheological properties of nematics, we derive elementary expressions for all phenomenological viscosity coefficients of ferroelectric smectics C* in terms of a small number of parameters. The results permit estimates of signs and ratios of viscosity coefficients and their tilt angle dependence. It is shown that a number of coefficients generally appear to be very small and can be neglected in practical calculations. We discuss also the influence of molecular biaxiality on the rotational viscosity of smectics C.

1. Introduction

Dynamical properties of smectic liquid crystals are more complicated than those of simple nematics because of the lowest symmetry of smectic phases. The detailed understanding of these properties is, however, extremely important in a technological context. In particular, there is a growing interest in the rheological properties of ferroelectric smectics C*, which are regarded as very promising materials for low voltage display devices [1]. In fact, ferroelectric liquid crystals can demonstrate the fastest response among all liquid crystal materials. This response is determined by the linear electro-optic effect in the chiral smectic C* phase. In the ferroelectric smectic C* phase the azimuthal molecular reorientation has no potential barrier and the corresponding switching time τ of the director $\mathbf{n}$ in an external electric field $\mathbf{E}$ is determined by the balance of electric and viscous torques. This time is, therefore, proportional to the rotational viscosity coefficient γ_ϕ and inversely proportional to the spontaneous polarization $\mathbf{P}_s$:

$$\tau \approx \gamma_\phi / P_s E. \qquad (1)$$

The rotational viscosity γ_ϕ is thus one of the most important parameters of ferroelectric liquid crystal materials.

In general, rheological properties of smectic C liquid crystals are described by a large number of independent viscosity coefficients [2] which characterize different couplings between the director orientation and a flow. Recent theoretical analysis [3, 4] has shown that the switching of the director in the smectic C* phase can be accompanied by the so-called backflow which is related to a number of other viscosity coefficients. To describe the complete switching process it is therefore necessary to have some information about all viscosity coefficients of ferroelectric smectics, not only the azimuthal rotational viscosity γ_ϕ. This information is important for the understanding of dynamics processes in real ferroelectrics, and can be used to estimate the influence of backflow. We note that, at present, only the rotational viscosity γ_ϕ has been measured for a few materials [5–7] and there is essentially no information about other viscosity coefficients of smectics C.

In this paper we develop a simple statistical theory of the rheological properties of smectics C by extending the general approach introduced by Kuzui and Doi [8] and Osipov and Terentjev [9]. This elementary theory will enable us to express all 20 viscosity coefficients of the smectic C phase in terms of a few parameters and to estimate the ratios and signs of these coefficients. In a previous paper [10], two of the authors have already attempted to calculate the rotational viscosity γ_ϕ. However, these calculations were based on an over-simplified kinetic equation, leading to an incorrect expression for the rotational viscosity. The present paper corrects these errors and uses a more consistent theory to estimate the rotational viscosity.

This paper is arranged as follows. In § 2, we discuss the phenomenological continuum expression for the viscous stress tensor and develop a statistical-mechanical theory of the viscosity of smectics C. In § 3 we derive expressions for the symmetric and antisymmetric parts of the stress tensor and present simple expressions for the Leslie coefficients of the smectic C phase. Finally in § 4 we discuss the results and present our conclusions.

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2. Viscous stress tensor of the smectic C phase

2.1. *Continuum theory*

The energy dissipation in a flowing smectic C is determined by the viscous stress tensor t_{ij} which generally depends on the orientational and translational order parameters and on the fluid velocity gradient tensor. A phenomenological expression for t_{ij} has been proposed recently by Leslie [2] with the framework of a continuum theory. In this theory the smectic layers are assumed to be of constant thickness and the tilt angle of the director with respect to the layer normal remains constant. These assumptions seem to be reasonable for a description of any real flow in a smectic C cell, provided that the system is not too close to a phase transition.

The macroscopic stress tensor t_{ij} can be written [2] as a sum of the symmetric part

$$\begin{aligned} t^{s}_{ij} = {} & \mu_0 D_{ij} + \mu_1 a_p a_q D_{pq} a_i a_j + \mu_2 (D_{ik} a_k a_j + D_{jk} a_k a_i) \\ & + \mu_3 c_p c_q D_{pq} c_i c_j + \mu_4 (D_{ik} c_k c_j + D_{jk} c_k c_i) \\ & + \mu_5 c_p a_q D_{pq} (a_i c_j + a_j c_i) + \lambda_1 (A_i a_j + A_j a_i) \\ & + \lambda_2 (C_i c_j + C_j c_i) + \lambda_3 c_p A_p (a_i c_j + a_j c_i) \\ & + \kappa_1 (D_{ik} a_k c_j + D_{jk} a_k c_i + D_{ik} c_k a_j + D_{jk} c_k a_i) \\ & + \kappa_2 [2 a_p c_q D_{pq} a_i a_j + a_p a_q D_{pq} (a_i c_j + a_j c_i)] \\ & + \kappa_3 [2 a_p c_q D_{pq} c_i c_j + c_p c_q D_{pq} (a_i c_j + a_j c_i)] \\ & + \tau_1 (C_i a_j + C_j a_i) + \tau_2 (A_i c_j + A_j c_i) \\ & + 2\tau_3 c_p A_p a_i a_j + 2\tau_4 c_p A_p c_i c_j, \end{aligned} \qquad (2)$$

and the antisymmetric part

$$\begin{aligned} t^{a}_{ij} = {} & \lambda_1 (D_{jk} a_k a_i - D_{ik} a_k a_j) + \lambda_2 (D_{jk} c_k c_i - D_{ik} c_k c_j) \\ & + \lambda_3 c_p a_q D_{pq} (a_i c_j - a_j c_i) + \lambda_4 (A_j a_i - A_i a_j) \\ & + \lambda_5 (C_j c_i - C_i c_j) + \lambda_6 c_p A_p (a_i c_j - a_i c_j) \\ & + \tau_1 (D_{jk} a_k c_i - D_{ik} a_k c_j) + \tau_2 (D_{jk} c_k a_i - D_{ik} c_k a_j) \\ & + \tau_3 a_p a_q D_{pq} (a_i c_j - a_j c_i) + \tau_4 c_p c_q D_{pq} (a_i c_j - a_j c_i) \\ & + \tau_5 (A_j c_i - A_i c_j + C_j a_i - C_i a_j). \end{aligned} \qquad (3)$$

Here the fluxes are represented by D_{ij}, the symmetric part of the velocity gradient tensor $v_{i,j} = \partial v_i / \partial r_j$:

$$2D_{ij} = v_{i,j} + v_{j,i}$$

and W_{ij}, the antisymmetric part of $v_{i,j}$, related to the local angular velocity of the fluid:

$$2W_{ij} = v_{i,j} - v_{j,i}.$$

Vectors A_i and C_i are covariant time derivatives of the smectic plane normal $\mathbf{a}$, and the unit vector $\mathbf{c}$, which is a projection of the director $\mathbf{n}$ onto the smectic plane:

$$A_i = \dot{a}_i - W_{ij} a_j; \quad C_i = \dot{c}_i - W_{ij} c_j.$$

2.2. *General statistical approach*

Now let us consider the viscous stress tensor in the framework of the general statistical theory. In this context, the stress tensor (2), (3) can be defined as an ensemble average of the corresponding microscopic stress tensor t^{M}_{ij}. The microscopic stress tensor depends only on the dynamical variables of a fluid and describes the evolution of the microscopic momentum density $\mathbf{p}(\mathbf{r})$ [11]

$$\dot{\mathbf{p}}(\mathbf{R}) = -\nabla \cdot \mathbf{t}^{M}(\mathbf{R}). \qquad (4)$$

The general expressin for the microscopic stress tensor $\mathbf{t}^{M}$ can be obtained with the help of the microscopic equations of motion for individual particles. The microscopic stress tensor is determined by interparticle forces and can be expressed in terms of the pair interaction potential. The detailed derivation of the tensor $\mathbf{t}^{M}$ for the fluid composed of spherical particles can be found, for example, in [11]. Recently an expression for the microscopic stress tensor t^{M}_{ij} has been derived also for a nematic fluid composed of rigid elongated particles [9]. In the case of prolate uniaxial molecules, which are characterized by a unit vector $\mathbf{e}$ in the direction of the long axis, the tensor $\mathbf{t}^{M}$ reads [9]:

$$\begin{aligned} t^{M}_{ij}(\mathbf{R}) \approx \sum_{\mu} \Bigg[& 3kT\left(e^{\mu}_i e^{\nu}_j - \frac{1}{3}\,\delta_{ij} \right) \\ & + \sum_{\nu \neq \mu} e^{\mu}_i \frac{\partial}{\partial e^{\nu}_j} U(\mathbf{e}^{\mu}, \mathbf{e}^{\nu}, \mathbf{r}_{\nu\mu}) \Bigg] \delta(\mathbf{R} - \mathbf{r}_{\mu}) + t^{\mathrm{iso}}_{ij} \end{aligned} \qquad (5)$$

where t^{iso}_{ij} is the part of the stress tensor which does not depend on the orientational variables. Equation (5) is valid for a system of sufficiently elongated particles with $I_{\parallel} \ll I_{\perp}$, where $I_{\parallel}$ and $I_{\perp}$ are the longitudinal and the transverse inertia moments, respectively.

The macroscopic (continuum) stress tensor t_{ij} can now be calculated by taking an ensemble average of (5), and can be written in the form

$$\begin{aligned} t_{ij}(\mathbf{R}) \equiv \langle t^{M}_{ij} \rangle = {} & 3\rho kT Q_{ij}(\mathbf{R}) \\ & + \frac{1}{2}\rho^2 \int d\mathbf{e}^{(1)} d\mathbf{e}^{(2)} d\mathbf{r}_{12} e^{(1)}_i \frac{\partial}{\partial e^{(2)}_j} \\ & \times U(\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \mathbf{r}_{12}) f_2(\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \mathbf{r}_{12}; \mathbf{R}) \end{aligned} \qquad (6)$$

where Q_{ij} is the nematic tensor order parameter and $f_2(1,2)$ is the pair distribution function of molecules '1' and '2'; ρ is the number density.

It is important to emphasize here that the averaging in equation (6) is performed with a non-equilibrium pair distribution function $f_2(1,2)$ which characterizes the flowing liquid crystal and which, therefore, depends on velocity gradients.

2.3. *Stress tensor of the smectic C phase in the mean-field approximation*

So far the expressions for the viscous stress tensor have been written in a very general form which can be used in the description of any liquid crystal phase of rod-like molecules. The application of these general results to nematics has already been carried out in [9, 12]. The description of the rheological properties of smectic phases is more complicated because it involves simultaneous averaging over the translational and orientational degrees of freedom. However, the theory can be dramatically simplified if one uses the approximation of perfect smectic order and takes into account that the intermolecular interaction is short-range. In this case the averaging over $\mathbf{r}_{12}$ in equation (6) can be performed separately for molecules which are in the same smectic plane, and for molecules which are in two neighbour planes [13, 14]:

$$t_{ij}(\mathbf{R}) = 3\rho kTQ_{ij}(\mathbf{R}) + \frac{1}{2}\rho^2\int d\mathbf{e}^{(1)}d\mathbf{e}^{(2)}e_i^{(1)}\frac{\partial}{\partial e_j^{(2)}}W(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{a}), \tag{7}$$

with

$$\begin{aligned}W(\mathbf{e}^{(1)},\mathbf{e}^{(1)},\mathbf{a}) = \sigma\int d\mathbf{r}_{12}\delta[(\mathbf{r}_{12}\cdot\mathbf{a})] & \\ \times U(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{r}_{12})f_2(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{r}_{12};\mathbf{R}) & \\ +(1-\sigma)\int dr_{12}r_{12}^2 & \\ \times U(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{a}r_{ij})f_2(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{a}r_{ij};\mathbf{R}), & \end{aligned} \tag{8}$$

where σ is the fraction of nearest neighbours which are in the same smectic plane as a given molecule. The first term in equation (8) is a contribution from the neighbouring molecules, which are in the same smectic plane. For such molecules, the intermolecular vector $\mathbf{r}_{ij}$ is approximately parallel to the plane, $(\mathbf{r}_{ij}\cdot\mathbf{a}) = 0$. The second term in equation (8) comes from the interaction of molecules which belong to the neighbour smectic planes. In this case $\mathbf{r}_{ij} \approx \mathbf{a}r_{ij}$.

In the mean field approximation, the pair distribution function is expressed in terms of the one-particle distribution, $f_2(1,2) = f_1(1)f_1(2)$. In this approximation, equation (7) can be rewritten as

$$t_{ij}(\mathbf{R}) = \rho\int d\mathbf{e}^{(1)}f_1(\mathbf{e}^{(1)},\mathbf{R})t_{ij}^{\mathrm{MF}}(\mathbf{e}^{(1)}) \tag{9}$$

with

$$t_{ij}^{\mathrm{MF}} = 3kT(e_ie_j - \tfrac{1}{3}\delta_{ij}) + e_i\frac{\partial}{\partial e_j}U^{\mathrm{MF}}(\mathbf{e},\mathbf{a}). \tag{10}$$

Here $U^{\mathrm{MF}}(\mathbf{e},\mathbf{a})$ is the effective mean field potential in the smectic C phase

$$U^{\mathrm{MF}}(\mathbf{e}^{(1)},\mathbf{a}) = \rho\int d\mathbf{e}^{(2)}\tilde{U}(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{a})f_1(\mathbf{e}^{(2)},\mathbf{R}), \tag{11}$$

where

$$\tilde{U}(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{a}) = \sigma\int d\mathbf{r}_{12}\delta[(\mathbf{r}_{12}\cdot\mathbf{a})]U(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{r}_{12}) + (1-\sigma)\int dr_{12}r_{12}^2U(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{a}r_{12}). \tag{12}$$

We note that the distribution function $f_1(1)$ in equations (9) and (11) corresponds to the flowing liquid crystal and differs from the equilibrium distribution function $f_1^{(0)}(1)$. The difference between the equilibrium and non-equilibrium distributions $f_1^{(0)}(1)$ and $f_1(1)$ is obviously proportional to the small perturbation, in this case the velocity gradient tensor $v_{i,j}$:

$$f_1(1) = f_1^{(0)}(1)[1 + h(1)] \tag{13}$$

with the correction

$$h(1) = h_{ij}(\mathbf{e}^{(1)},\mathbf{a})v_{i,j}. \tag{14}$$

Combining equations (9) and (13) yields the following expression for the viscous stress tensor in terms of the *equilibrium* distribution function $f^{(0)}(1)$ and the non-equilibrium correction $h(1)$:

$$t_{ij}(\mathbf{R}) = \rho\int d\mathbf{e}f^{(0)}(\mathbf{e},\mathbf{a})h(\mathbf{e},\mathbf{a};\mathbf{R})t_{ij}^{\mathrm{MF}} \tag{15}$$

where the mean-field microscopic stress tensor is given by equation (10) in which the effective mean-field potential $U^{\mathrm{MF}}(1)$ is determined by the equilibrium distribution function $f^{(0)}(1)$.

Thus the viscous contribution to the macroscopic stress tensor is expressed in terms of the stationary correction to the one-particle distribution function $h(1)$, where the quantity $h(1)$ characterizes the deviation from the thermodynamic equilibrium in the flowing smectic C. This correction can now be obtained as a stationary solution of an appropriate kinetic equation.

2.4. *Rotational diffusion equation for a molecule in the mean-field potential*

In the molecular field approximation, the dynamics of a liquid crystal are determined by a rotational Brownian motion of a molecule in the mean-field potential. This motion is described by the rotational diffusion equation, which has the same form as in the nematic phase and only the mean field potential is different. The corresponding equation has been discussed in detail by Kuzui and Doi [8], and has also been derived from Langevin equations of motion in [9]. The diffusion equation can be written in the following dimensionless form:

$$\dot{f}_1 + \epsilon\partial_k(\Omega_kf_1) = \epsilon^2\partial_k\left(\partial_kf_1 + \frac{\partial_kU^{\mathrm{MF}}}{kT}f_1\right) \tag{16}$$

where ∂_k is the differential operator of infinitesimal rotation of the molecular long axis **e**:

$$\partial_k = \epsilon_{kij} e_i \frac{\partial}{\partial e_j}$$

with ϵ_{ijk} the antisymmetric Levi-Civita tensor; $\mathbf{\Omega}_k$ is the local angular velocity of the long uniaxial particle in the flowing fluid [8, 9]

$$\mathbf{\Omega} = \tfrac{1}{2}[\nabla \times \mathbf{v}] - \tfrac{1}{2}(\mathbf{e} \cdot [\nabla \times \mathbf{v}])\mathbf{e} + \frac{p^2 - 1}{p^2 + 1}[\mathbf{e} \times \mathbf{D} \cdot \mathbf{e}]. \quad (17)$$

Here **D** is the symmetric part of the velocity gradient tensor, $2D_{ij} = v_{i,j} + v_{j,i}$, and $p = l/d$ is the ratio of principal molecular dimensions (we assume $p \gg 1$ in this paper). In equation (16) we have used a dimensionless time $\tau = t/\tau_\omega$, where $\tau_\omega = I_\perp/\lambda$ is the rotational velocity relaxation time [9] and λ is the 'molecular' friction coefficient. This coefficient will turn out to be the only model parameter of this theory. Kinetic equation (16) contains the small dimensionless parameter $\epsilon = (I_\perp kT)^{1/2}/\lambda \ll 1$.

The non-equilibrium correction $h(1)$ can now be determined from equation (16) using the stationary solution of (16) in the case of small velocity gradients $v_{i,j}$. We note that in the framework of this simple model, the only difference between the rotational dynamics in the nematic and in the smectic C phase lies in the mean-field potential, which exhibits the different symmetry of these phases. Thus, in the nematic phase the mean-field potential depends only on the angle between the director **n** and the molecular long axis **e** while in the biaxial smectic C phase it also depends on the local smectic plane normal **a**.

In the next section we obtain explicit expressions for the symmetric and antisymmetric parts of the macroscopic stress tensor and estimate all Leslie coefficients of the smectic C phase.

3. Leslie coefficients of the smectic C phase

3.1. *Symmetric part of the viscous stress tensor*

The simple statistical theory of viscosity employed in this paper is based on the general equation (9), (10) and (16), which have similar mathematical form for the nematic and smectic C phases. It is therefore possible to use directly some of the results already obtained in the theory of nematic viscosity [8, 9]. In particular, one can calculate the symmetric part of the macroscopic stress tensor directly from equation (16) (see [8] for a more detailed discussion). Multiplying both sides of the kinetic equation (16) by the factor $[e_i e_j - \frac{1}{3}\delta_{ij}]$ and integrating it over all orientations **e**, we arrive at the following result for the stationary case:

$$t^s_{ij} = \left\langle 3\rho kT(e_i e_j - \tfrac{1}{3}\delta_{ij}) + \tfrac{1}{2}\rho\left(e_i \frac{\partial U^{\mathrm{MF}}}{\partial e_j} + e_j \frac{\partial U^{\mathrm{MF}}}{\partial e_i}\right)\right\rangle$$

$$= \frac{\rho kT}{2\epsilon}\left[\frac{p^2 - 1}{p^2 + 1}(D_{i\alpha}\langle e_\alpha e_j\rangle + D_{j\alpha}\langle e_i e_\alpha\rangle - 2D_{\alpha\beta}\langle e_i e_j e_\alpha e_\beta\rangle) - W_{j\alpha}\langle e_i e_\alpha\rangle - W_{i\alpha}\langle e_j e_\alpha\rangle)\right] \quad (18)$$

where we have used the property [8] that

$$\int d\mathbf{e}\,\partial_k[f_1(1)\partial_k U^{\mathrm{MF}}](e_i e_j - \tfrac{1}{3}\delta_{ij}) = -\left\langle e_i \frac{\partial U^{\mathrm{MF}}}{\partial e_j} + e_j \frac{\partial U^{\mathrm{MF}}}{\partial e_i}\right\rangle$$

and the explicit form of perturbation $\mathbf{\Omega}$ has been substituted to the left hand side of the diffusion equation (16). Here the averages are taken with the equilibrium one-particle distribution function $f^{(0)}(\mathbf{e}, \mathbf{n}, \mathbf{a})$. We note here that the smectic C phase is macroscopically biaxial and thus the orientational distribution of molecules must also be biaxial even in the case when the molecules themselves are uniaxial. In this case, the one-particle distribution function $f^{(0)}(1)$ depends on two macroscopic parameters. These are the nematic ordering tensor $[n_i n_j - \frac{1}{3}\delta_{ij}]$ and the tensor $a_i a_j$, which determines the local orientation of the smectic planes.

As a result, the average tensor $\langle e_i e_j\rangle$ is not uniaxial (by contrast to the nematic phase) and can be written in the following general form:

$$\langle e_i e_j\rangle = \tfrac{1}{3}\delta_{ij} + S(n_i n_j - \tfrac{1}{3}\delta_{ij}) + P(m_i m_j - l_i l_j), \quad (19)$$

where S is the nematic order parameter, P is the biaxial order parameter and the unit vectors **m** and **l** are normal to the director **n**; $\mathbf{m} \perp \mathbf{l} \perp \mathbf{n}$. The order parameters S and P can be defined as

$$S = \langle \tfrac{3}{2}(\mathbf{e} \cdot \mathbf{n})^2 - \tfrac{1}{2}\rangle; \quad P = \langle [(\mathbf{e} \cdot \mathbf{m})^2 - (\mathbf{e} \cdot \mathbf{l})^2]\rangle. \quad (20)$$

The parameter P reflects the additional ordering, imposed on the molecular long axes by the constraint of oblique layers. It can be also rewritten in the form

$$P = \langle \sin^2\omega \cos 2\phi\rangle \quad (21)$$

where $\cos\omega = (\mathbf{e} \cdot \mathbf{n})$ and ϕ is the azimuthal angle in the plane perpendicular to **n**. The biaxial order parameter P characterizes the asymmetry of molecular long axes fluctuations around the director in the biaxial smectic C phase. Indeed, the parameter P must vanish when $S = 1$, because in the case of perfect orientational order $\omega = 0$ and $P_2(\cos\omega) = 1$. It then follows necessarily from equation (21) that $P = 0$. More detailed estimates of the biaxial order parameter are performed in the Appendix, in which we show that the parameter P appears to be very small when the nematic order parameter is close to unity:

$$P \sim (1 - S)^2 \sin^2\Theta, \quad (22)$$

when $(1 - S)^2 \ll 1$, where Θ is the tilt angle of the director with respect to the smectic plane normal, $\cos\Theta = (\mathbf{n}\cdot\mathbf{a})$.

In the smectic C phase, the nematic order parameter is rather large ($S \approx 0{\cdot}8$–$0{\cdot}9$ [15]) and hence the biaxial order parameter can be estimated as $P \sim 10^{-2}$. This estimate shows that one can in fact neglect biaxiality of the distribution function in the evaluation of the averages $\langle e_k e_j\rangle$ and $\langle e_i e_j e_\alpha e_\beta\rangle$ in equation (18). In the case of the unixial distribution the relevant averages are

$$\langle e_i e_j\rangle = \tfrac{1}{3}\delta_{ij} + S(n_i n_j - \tfrac{1}{3}\delta_{ij}),$$

$$\begin{aligned}\langle e_i e_j e_p e_q\rangle = {}& m_1 n_i n_j n_p n_q + m_2(n_i n_j \delta_{pq} + n_i n_p \delta_{jq}\\ &+ n_i n_q \delta_{jp} + n_j n_p \delta_{iq} + n_j n_q \delta_{ip} + n_p n_q \delta_{ij})\\ &+ m_3(\delta_{ij}\delta_{pq} + \delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}),\end{aligned}$$

where

$$m_1 = \langle P_4(\cos\omega)\rangle, m_2 = \tfrac{1}{7}(S - \langle P_4(\cos\omega)\rangle)$$

and

$$m_3 = \tfrac{1}{15}(1 - \tfrac{10}{7}S + \tfrac{3}{7}\langle P_4(\cos\omega)\rangle).$$

Here $\langle P_4(\cos\omega)\rangle$ is the equilibrium average of the Legendre polynomial of the fourth order. Inserting these expressions into equation (18) and returning to dimensional variables, we arrive at

$$\begin{aligned}t^s_{ij} = \frac{\rho\lambda}{2}\bigg[& -2\frac{p^2-1}{p^2+1}\langle P_4\rangle n_i n_j n_\alpha n_\beta D_{\alpha\beta}\\ &+ \frac{2}{35}\frac{p^2-1}{p^2+1}(7 - \ + 5S - 2\langle P_4\rangle)D_{ij}\\ &+ \frac{1}{7}\frac{p^2-1}{p^2+1}(3S + 4\langle P_4\rangle)(n_i n_\alpha D_{\alpha j} + n_j n_\alpha D_{\alpha i})\\ &- S(n_i N_j + n_j N_i\bigg],\end{aligned} \tag{23}$$

where $N_i = \dot{n} - W_{ij}n_j$.

We can now transform equation (23) into the form (2) proposed by Leslie, using the substitution $\mathbf{n} = \mathbf{a}\cos\Theta + \mathbf{c}\sin\Theta$. This yields, after some algebra, the following simple expressions for the Leslie coefficients involved in equation (2):

$$\mu_0 = \tfrac{1}{35}\rho\lambda\frac{p^2-1}{p^2+1}(7 - 5S - 2\langle P_4\rangle), \tag{24}$$

$$\mu_1 = \alpha_1\frac{p^2-1}{p^2+1}\cos^3\Theta, \tag{25}$$

$$\mu_2 = \alpha_0\frac{p^2-1}{p^2+1}\cos^2\Theta, \tag{26}$$

$$\mu_3 = \alpha_1\frac{p^2-1}{p^2+1}\sin^4\Theta, \tag{27}$$

$$\mu_4 = \alpha_0\frac{p^2-1}{p^2+1}\sin^2\Theta, \tag{28}$$

$$\mu_5 = \tfrac{1}{2}\alpha_1\frac{p^2-1}{p^2+1}\sin^2 2\Theta, \tag{29}$$

$$\kappa_1 = \alpha_0\frac{p^2-1}{p^2+1}\sin\Theta\cos\Theta, \tag{30}$$

$$\kappa_2 = \alpha_1\frac{p^2-1}{p^2+1}\sin\Theta\cos^3\Theta, \tag{31}$$

$$\kappa_3 = \alpha_1\frac{p^2-1}{p^2+1}\sin^3\Theta\cos\Theta, \tag{32}$$

$$\lambda_1 = \tfrac{1}{2}\gamma_0\cos^2\Theta, \tag{33}$$

$$\lambda_2 = \tfrac{1}{2}\gamma_0\sin^2\Theta, \tag{34}$$

$$\tau_1 = \tau_2 = \tfrac{1}{4}\gamma_0\sin 2\Theta, \tag{35}$$

$$\lambda_3 = \tau_3 = \tau_4 = 0, \tag{36}$$

where the common factors α_0, α_1 and γ_0 are defined by

$$\begin{aligned}\alpha_0 &= \tfrac{1}{14}\rho\lambda(3S + 4\langle P_4\rangle),\\ \alpha_1 &= -\rho\lambda\langle P_4\rangle, \quad \gamma_0 = -\rho\lambda S.\end{aligned} \tag{37}$$

The 15 viscosity coefficients have now been expressed in terms of a small number of parameters and the tilt angle Θ. In equation (37), the only the microscopic friction constant λ is a parameter, introduced by the model, while the number density ρ and orientational order parameters are typically known for any practical system. It is interesting to note that in this simple approach the viscosity coefficients λ_3, τ_3 and τ_4 vanish. This follows directly from the neglect of the biaxiality of the orientational distribution function. These coefficients are proportional to the biaxial order parameter P which is very small, and we conclude that these viscosity coefficients are much smaller than the others, and can usually be neglected in the hydrodynamics of smectics C.

One concludes also that at small tilt angles, the coefficients μ_0, μ_1, μ_2 and λ_1 are expected to be larger than the coefficients μ_3, μ_4, μ_5, κ_1, κ_2, κ_3, λ_2, τ_1 and τ_2. In particular, the coefficients $\mu_3 \sim \sin^4\Theta$ and $\kappa_3 \sim \sin^3\Theta$ are expected to be the smallest.

It is interesting to note that equation (2) for the symmetric part of the stress tensor with the coefficients (24)–(36) is dramatically simplified when one formally puts $\Theta = \pi/2$. According to equations (24)–(36), in this case $\mu = \mu_2 = \mu_5 = \kappa_1 = \kappa_2 = \kappa_3 = \lambda_1 = \tau_1 = \tau_2 = 0$, and the symmetric part of the viscous stress tensor t^s_{ij} can be written exactly in the same form as the corresponding expression for the nematic phase:

$$\begin{aligned}t^s_{ij} = {}& \alpha_4 D_{ij} + \alpha_1 c_i c_j c_p c_q D_{pq}\\ &+ \tfrac{1}{2}(\alpha_5 + \alpha_6)(D_{ik}c_k c_j + D_{jk}c_k c_i)\\ &+ \tfrac{1}{2}(\alpha_2 + \alpha_3)(N_i c_j + N_j c_i),\end{aligned} \tag{38}$$

where $\alpha_4 \equiv \mu_0$, $(\alpha_5 + \alpha_6)/2 \equiv \alpha_0$ and $(\alpha_2 + \alpha_3)/2 \equiv \gamma_0/2$.

The strong analogy between equation (38) and the corresponding expression for the nematic stress tensor (see, for example, [16]) is not surprising taking into account that we have neglected the biaxiality of the distribution function. At $\Theta = \pi/2$, the director **n** is parallel to the smectic plane and is equivalent to the **c**-director, forming a 2-dimensional nematic. Then the coupling between the director **n** and the smectic plane normal **a** is determined only by the biaxiality which has been neglected in the present theory.

Thus we conclude that the coefficient α_1 is expected to be close to the nematic Leslie coefficient α_1 (at the same temperature). The coefficient α_0 must be close to the sum of Leslie coefficients $(\alpha_6 + \alpha_5)/2$ and the coefficient γ_0 is similar to the sum $(\alpha_2 + \alpha_3)$.

One can now deduce several practical conclusions from these approximate results. In particular, one can use the present simple approach to estimate the viscosity coefficients of the smectic C phase using some experimental data obtained for the nematic phase. Indeed, it is, in principle, possible to estimate the absolute values of the viscosities μ_0, μ_4 and λ_2 by extrapolation from the nematic phase, using equations (28) and (34), the Arrhenius law, the value of the tilt angle in the smectic C phase and the experimental values of the corresponding Leslie coefficients in the nematic phase.

3.2. *Antisymmetric part of the viscous stress tensor*

The general continuum expression for the antisymmetric part of the stress tensor is given by equation (3). It contains only four independent viscosity coefficients λ_4, λ_5, λ_6 and τ_5 which do not also enter the expression for the symmetric part of the stress tensor. These viscosity coefficients determine the dissipation related to the rotation of the director and of the local smectic plane normal.

In the mean-field approximation, the viscous stress tensor is given by equations (10) and (15). The antisymmetric part of the tensor t_{ij} can be written as

$$t_{ij}^{\mathrm{a}} = \tfrac{1}{2}\rho \int d\mathbf{e}\, f_0(\mathbf{e}) h(\mathbf{e}) \left(e_i \frac{\partial U^{\mathrm{MF}}}{\partial e_j} - e_j \frac{\partial U^{\mathrm{MF}}}{\partial e_i} \right) \tag{39}$$

where the non-equilibrium correction $h(\mathbf{e})$ can be determined from the stationary solution of the rotational diffusion equation (16).

What remains is only the calculation of the rotational viscosity coefficients λ_4, λ_5, λ_6 and τ_5; we thus need only to evaluate the corresponding part of the stress tensor. In order to do this, we consider formally a system without any flow, and put $\Omega = 0$ in the main equation (16). The only sources of dissipation are now the rotation of the director **n** and the smectic plane normal **a** which determine the time derivative of the distribution function on the left hand side of equation (16). Taking into account only the linear terms in the correction $h(\mathbf{e})$ we can rewrite equation (16) in the simplified form:

$$\dot{f}_0 = \epsilon^2 \partial_k [f_0 \partial_k h], \tag{40}$$

where we have taken into account that

$$f_0 = C \exp[-U^{\mathrm{MF}}/kT].$$

Neglecting the biaxiality, we can write the mean field potential in the Maier–Saupe form,

$$U^{\mathrm{MF}}(\mathbf{e}) = -J_0 S P_2[(\mathbf{e}\cdot\mathbf{n})]$$

and obtain

$$\dot{f}_0 = \frac{3J_0 S}{kT} (\mathbf{e}\cdot\mathbf{n})(\mathbf{e}\cdot\dot{\mathbf{n}}) f_0[(\mathbf{e}\cdot\mathbf{n})]. \tag{41}$$

The correction $h(\mathbf{e})$ can now be estimated by expanding $h(\mathbf{e})$ in terms of the irreducible tensors composed of the components of the unit vector **e**. In the lowest order approximation one obtains

$$h(\mathbf{e}) \approx h_0 (\mathbf{e}\cdot\mathbf{n})(\mathbf{e}\cdot\dot{\mathbf{n}}), \tag{42}$$

where h_0 is a constant coefficient.

Substituting equations (41) and (42) into (40) we obtain the following estimate for h_0:

$$h_0 \approx -\frac{\lambda}{kT} \frac{J_0 S}{2kT + J_0 S}. \tag{43}$$

Finally, substituting equation (43) into equation (39), we obtain the following simple expression for the rotational contribution to the viscous stress tensor:

$$t_{ij}^{\mathrm{a}} \approx \lambda_0 (n_i \dot{n}_j - n_j \dot{n}_i),$$

with

$$\lambda_0 = \frac{1}{70} \rho \lambda S^2 (7 + 5S - 12\langle P_4 \rangle) \frac{(J_0/kT)^2}{2 + J_0 S/\mathrm{k}T}. \tag{44}$$

Similarly to the previous section, we again represent the director **n** in terms of the local smectic plane normal **a** and the in-plane director **n** and obtain a part of the antisymmetric stress tensor (3) involving the coefficients λ_4, λ_5, λ_6 and τ_5. These rotational viscosity coefficients of the smectic C can now be written as

$$\lambda_4 = \lambda_0 \cos^2 \Theta, \tag{45}$$

$$\lambda_5 = \lambda_0 \sin^2 \Theta, \tag{46}$$

$$\tau_5 = \tfrac{1}{2} \lambda_0 \sin 2\Theta, \tag{47}$$

and

$$\lambda_6 = 0. \tag{48}$$

We would like to note again that the coefficient λ_6 vanishes in this simple theory. We conclude by analogy with the previous section that in the general case λ_6 is proportional to the biaxial order parameter and hence much smaller than other coefficients. These simple expressions for the rotational viscosity coefficients have been obtained neglecting the biaxial part of the mean field potential. In the smectic C phase, the mean field potential is generally biaxial even when the molecules are uniaxial (see the Appendix, for more detail). However, the biaxial part of the potential gives a contribution to the rotational viscosities which is proportional to higher powers of the tilt angle Θ.

From the practical point of view, the most important rotational viscosity coefficient is λ_5. It controls the azimuthal rotation of the direction around the smectic plane normal. In smectic C with fixed layers and fixed tilt angle the rotation of the director is associated with the following contribution to the entropy production:

$$kT\dot{S} = t^{a}_{ij} n_i \dot{n}_j = \gamma_\phi (\dot{\phi})^2. \tag{49}$$

where ϕ is the azimuthal angle and $\gamma_\phi \equiv \lambda_5$ is the familiar rotational viscosity of the smectic C phase.

This rotational viscosity γ_ϕ has been measured for a few ferroelectric smectic materials using several different techniques [5–7]. All measurements confirm that γ_ϕ is indeed proportional to $\sin^2\Theta$ at small Θ. At large tilt angles (typically when $T_{AC} - T > 20\,K$)), the ratio $\gamma_\phi/\sin^2\Theta$ is not a constant, but grows rapidly as a function of the tilt angle. This behaviour may be related to large biaxiality contributions (mainly from molecular biaxiality) which can become important at large Θ.

4. Discussion

In this paper we have developed an elementary statistical-mechanical theory for the viscosity of smectics C using the molecular field approximation and neglecting the molecular biaxiality. This theory enables one to express all twenty phenomenological viscosity coefficients in terms of a few parameters and therefore to reduce dramatically the number of independent coefficents. From the theory, it is possible to determine the signs of the coefficients and to estimate their ratios. The results do not, however, permit the calculation of the absolute values of the viscosity coefficients, because all expressions are proportional to the unknown molecular friction coefficient λ. On the other hand, since all other constants entering the expressions for viscous coefficients are known, a single measurement of one such coefficient will allow one to estimate λ and, therefore, to predict values of all other coefficients. One may also expect that the microscopic friction constant λ is not very sensitive to the macroscopic structure of the phase and its value is close to that in the nematic phase of the same material.

The strong analogy between the statistical theory of viscosity in the nematic and in the smectic C phases can be used directly to estimate parameters of the theory. As discussed in § 3.1, the parameters α_0, α_1 and γ_0 in equations (24)–(36) can be approximately considered as 'continuations' of certain combinations of Leslie coefficients from the nematic phase. Thus the absolute values of these coefficients can, in principle, be estimated by extrapolation to a given temperature using the Arrhenius law, provided that the liquid crystal material forms both the smectic C and the nematic phases.

The viscosity coefficients λ_3. λ_6, τ_3 and τ_4 are equal to zero within the present simple model. In a more complete calculation they would be proportional to the biaxial order parameter. This quantity has been estimated in the Appendix and appears to be very small. Thus these particular coefficients, although not identically zero, are expected to be much smaller than the others and can be neglected in most contexts.

At small tilt angles Θ, different viscosity coefficients are proportional to different powers of Θ and thus some of them can also be neglected in particular expressions. In particular, the coefficients $\mu_3 \sim \Theta^4$ and $\kappa_3 \sim \Theta^3$ will be very small close to the phase transition. By contrast, the coefficients μ_0, μ_1, μ_2 and λ_1 do not vanish at the smectic A to smectic C transition point; these terms also determine a dissipation in the smectic A phase.

In this paper we have essentially neglected biaxiality in the smectic C phase. It is interesting to note that this biaxiality is determined by two different factors. First, the orientational distribution of uniaxial molecules in the tilted smectic phase is already biaxial. However, because the nematic order parameter is close to unity, this type of biaxiality is extremely weak. We show in the Appendix that the biaxial order parameter $P \sim (1 - S)^2 \sin^2\Theta \sim 10^{-2}$ and thus can generally be neglected in the first approximation. On the other hand, there also exists a molecular biaxiality which is determined primarily by a flattened molecular shape. The interaction between biaxial molecules results in the ordering of the short molecular short axes. This contribution is non-zero even when $S = 1$. The molecular biaxiality has not been considered in the present paper because the existing theory of rheological properties of liquid crystals [8, 9, 17] is confined to systems of uniaxial particles. In the general case, the orientational distribution of biaxial molecules in a biaxial phase is determined by two tensor order parameters which have different relaxation times. One of the them is the usual nematic order parameter, which characterizes the ordering of molecular long axes. The second order parameter charcterizes the ordering of molecular planes and must be an independent dynamical variable in the Landau–De Gennes theory of the dynamical properties of smectics C.

Since the spontaneous polarization is determined by the ordering of short axes, the molecular biaxiality can be particularly important in ferroelectric smectics C*. Usually the rheological properties of chiral smectics C* are expected to be practically the same as those of non-chiral smectics due to the weakness of the chirality effects. Indeed, one can readily accept that the dynamics of the molecular long axes in the smectic C phase can hardly be affected by the appearance of spontaneous polarization. On the other hand, in smectics with very high polarization, the contribution from the molecular biaxiality could be very large. This effect may be responsible for the strongly non-linear dependence of the rotational viscosity of ferroelectric liquid crystals at temperatures and tilt angles far from the phase transition point. We plan to consider this problem in more detail in a future publication.

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Appendix: Estimates of the biaxial order parameter in the smectic C phase composed of uniaxial molecules

In the smectic C phase the biaxial order parameter P is given by

$$P = \langle ((\mathbf{e}\cdot\mathbf{m})^2 - (\mathbf{e}\cdot\mathbf{l})^2) \rangle. \qquad (\mathrm{A}\,1)$$

where the unit vector **e** is in the direction of the molecular long axis and the unit vectors **m** and **l** are orthogonal to the smectic plane normal **a**; $\mathbf{m}\perp\mathbf{l}\perp\mathbf{a}$. The vector **m** is also normal to the plane of the tilt. The averaging in (A 1) is performed with the one-particle distribution function

$$f_1(1) = Z^{-1}\exp[-\beta U^{\mathrm{MF}}(\mathbf{e}^{(1)}, \mathbf{a}, \mathbf{n})], \qquad (\mathrm{A}\,2)$$

where $U^{\mathrm{MF}}(1)$ is the effective field potential.

The quantity P is the phase biaxial order parameter which characterizes the biaxiality of the one-particle distribution function in the smectic C phase. The mean-field potential is given by equation (11):

$$U^{\mathrm{MF}}(\mathbf{e}^{(1)}, \mathbf{a}, \mathbf{n}) = \rho\int d\mathbf{e}^{(2)}\tilde{U}(\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \mathbf{a}) f_1(\mathbf{e}^{(2)}, \mathbf{a}, \mathbf{n}), \qquad (\mathrm{A}\,3)$$

where $\tilde{U}(\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \mathbf{a})$ is the effective pair interaction averaged over the distribution of molecular centres in the smectic C phase.

In the general case, the effective interaction potential $\tilde{U}(1,2)$ contains various couplings between the tensors $Q_{ij}^{(1)} = e_i^{(1)}e_j^{(1)} - (1/3)\delta_{ij}$; $Q_{ij}^{(2)} = e_i^{(2)}e_j^{(2)} - (1/3)\delta_{ij}$ and the tensor $a_i a_j$. In the first approximation one can write

$$\begin{aligned}\tilde{U}(\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \mathbf{a}) = J_0(\mathbf{Q}^{(1)}:\mathbf{Q}^{(2)}) + J_2[(\mathbf{a}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{a}) \\ + (\mathbf{a}\cdot\mathbf{Q}^{(2)}\cdot\mathbf{a})] + J_3(\mathbf{a}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{Q}^{(2)}\cdot\mathbf{a}) \\ + J_4(\mathbf{a}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{a})(\mathbf{a}\cdot\mathbf{Q}^{(2)}\cdot\mathbf{a}),\end{aligned} \qquad (\mathrm{A}\,4)$$

where we have taken into account all invariants which are linear in $Q_{ij}^{(1)}$ and $Q_{ij}^{(2)}$. Substitution of equation (A 4) into equation (A 3) yields the following expression for the mean-field potential:

$$\begin{aligned}U^{\mathrm{MF}}(\mathbf{e}^{(1)}, \mathbf{a}, \mathbf{n}) = I_0(\mathbf{n}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{n}) \\ + I_1\sin 2\Theta(\mathbf{m}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{n}) \\ + I_2\sin^2\Theta(\mathbf{m}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{m}),\end{aligned} \qquad (\mathrm{A}\,5)$$

with

$$\left.\begin{aligned}I_0 &= \rho J_0 S + \rho G\cos^2\Theta + \tfrac{3}{2}\rho J_2 S\cos^2\Theta, \\ I_1 &= \rho G + \tfrac{1}{2}\rho J_2(\tfrac{1}{3}S + P), \\ I_2 &= \rho G - \rho J_2(\tfrac{1}{3}S - P), \\ G &= J_1 S + J_4(\tfrac{2}{3}SP_2(\cos\Theta) + P\sin^2\Theta),\end{aligned}\right\} \qquad (\mathrm{A}\,6)$$

where the unit vector $\mathbf{m}\perp\mathbf{n}$ and $(\mathbf{m}\cdot\mathbf{a}) = \sin\Theta$.

The first term in equation (A 5) is simply the nematic-like mean-field potential

$$I_0(\mathbf{n}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{n}) = \tfrac{2}{3}I_0 P_2(\cos\omega), \qquad (\mathrm{A}\,7)$$

where $\cos\omega = (\mathbf{n}\cdot\mathbf{e}_1)$.

The last two terms in equation (A 5) represent the biaxial part of the mean-field potential and can be written as

$$\begin{aligned}I_1\sin 2\Theta(\mathbf{m}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{n}) &\approx I_1\sin 2\Theta(\mathbf{m}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_1) \\ &= \tfrac{1}{2}I_1\sin 2\Theta\sin 2\omega\cos\phi,\end{aligned} \qquad (\mathrm{A}\,8)$$

and

$$\begin{aligned}I_2\sin^2\Theta(\mathbf{m}\cdot\mathbf{Q}^{(1)}\cdot\mathbf{m}) &\equiv I_2\sin^2\Theta\tfrac{2}{3}P_2((\mathbf{m}\cdot\mathbf{e}_1)) \\ &= \tfrac{2}{3}I_2\sin^2\Theta\sin^2\omega\cos^2\phi,\end{aligned} \qquad (\mathrm{A}\,9)$$

where ϕ is the azimuthal angle in the plane perpendicular to the director **n**.

One can now estimate the biaxial order parameter P, substituting equations (A 8) and (A 9) into equation (A 5) and then the mean-field potential (A 5) into equations (A 1) and (A 2). Expanding the one-particle distribution function powers of the biaxial part of the potential, we obtain the estimate

$$P \sim \frac{I_2}{kT}\sin^2\Theta\int d(\cos\omega)\sin^4\omega\, f_0(\cos\omega). \qquad (\mathrm{A}\,10)$$

Here the maximal distribution function takes the form

$$f_0(\cos\omega) = Z_0^{-1}\exp[-\beta I_0\sin^2\omega] \qquad (\mathrm{A}\,11)$$

with

$$Z_0 = \int d(\cos\omega)\exp[-\beta I_0\sin^2\omega].$$

Let us now estimate the integral in equation (A 10) in the case of high nematic order. Indeed, in the smectic C phase the nematic order parameter S is close to unity and thus the distribution function $f_0(\cos\omega)$ must have a sharp maximum at $\omega = 0$. Then the main contribution to the integral (A 10) comes from the region of small ω where $\sin\omega \ll 1$. In this case it is possible to make the following approximate change of variables:

$$d(\cos\omega) \approx -\tfrac{1}{2}dx$$

where $x = \sin^2\omega$. Now the integral in equation (A 10) can be readily estimated as

$$Z_0^{-1}\int d(\cos\omega)\sin^4\omega\exp\left[-\alpha\sin^2\omega\right]$$

$$\approx -Z_0^{-1}\int_0^1 dx\,x^4e^{-\alpha x} \sim 2\alpha^{-2}, \qquad \text{(A 12)}$$

where $\alpha = I_0/kT$. One can also establish a relation between the constant α and the nematic order parameter S when $S - 1 \ll 1$:

$$S - 1 = \tfrac{3}{2}Z_0^{-1}\int d(\cos\omega)\sin^2\omega\exp\left[-\alpha\sin^2\omega\right]$$

$$\sim \tfrac{3}{2}Z_0^{-1}\int_0^1 dx\,xe^{-\alpha x} \sim \tfrac{3}{2}\alpha^{-1}. \qquad \text{(A 13)}$$

Combining equation (A 12) and (A 13), we obtain the final estimate

$$P \sim \frac{8I_2}{9kT}\sin^2\Theta(1-S)^2 = K\sin^2\Theta(1-S)^2, \qquad \text{(A 14)}$$

where the constant K is of the order of unity. In the smectic C phase, the nematic order parameter is typically of the order of 0·8–0·9. Therefore the biaxial order parameter P is expected to be very small even at large tilt angles Θ.

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